THEORY OF CONDENSED MATTER

LECTURES PRESENTED AT AN INTERNATIONAL COURSE. TRIESTE, 3 OCTOBER - 16 DECEMBER 1967.

> ORGANIZED BY THE INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS. TRIESTE

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INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1968

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SECTION FRANÇAISE

THEORY OF CONDENSED MATTER

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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS, TRIESTE

THEORY OF CONDENSED MATTER

Lectures presented at an international course organized by and held at the International Centre for Theoretical Physics, Trieste from 3 October to 16 December 1967

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> INTERNATIONAL ATOMIC ENERGY AGENCY VIENNA, 1968

THEORY OF CONDENSED MATTER (Proceedings Series)

ABSTRACT. Proceedings of an international Course organized by, and held at the IAEA's International Centre for Theoretical Physics in Trieste, 3 October - 16 December 1967. The Course was attended by 148 lecturers, participants and observers representing 34 countries and also by the staff and fellows of the Centre.

The publication is divided into four parts containing 29 papers. Part I – General Courses, Part II – Dynamical lattice properties; Part III – Liquids and molecules; Part IV – Electronic properties. Most of these papers have been compiled from series of lectures given during the Course and each paper is preceded by a list of its contents. Contributors are: E. Antončík, F. Aymerich, A. Blandin, R. Blinć, V.L. Bonch – Bruevich, B. Buras, G. Caglioti, W. Cochran, J. des Cloizeaux, C.P. Enz, S. Franchetti, F. Garcia-Moliner, C.J. Gorter, P.K. Iyengar, B. Jacrot, J.A. Janik, G. Leibfried, P. Lloyd, G.G. Low, S. Lundqvist, A.R. Mackintosh, N. Majlis, C.K. Majumdar, N.H. March, W. Marshall, A. Paoletti, R.P. Singh, K.S. Singwi, H. Thomas, J. Ziman. Entirely in English

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FOREWORD

The International Centre for Theoretical Physics, since its inception, has striven to maintain an interdisciplinary character in its research and training programme as far as different branches of theoretical physics are concerned. In pursuance of this aim the Centre has followed a policy of organizing extended research seminars with a comprehensive and synoptic coverage on varying disciplines. The first of these — lasting over a month — was held in 1964 on fluids of ionized particles and plasma physics; the second, lasting for two months, was concerned with physics of elementary particles and high-energy physics; the third, of three months' duration, October — December 1966, covered nuclear theory; the fourth, bringing the series through a complete cycle, was a course on condensed matter held from 3 October to 16 December 1967.

The present volume records the proceedings of this research seminar. The long duration of these seminars combines the completeness of presentation characteristic of a conference with the relaxed atmosphere necessary for discussion and review. The programme of lectures and seminars was organized by Professors J. Ziman (United Kingdom), F. Bassani (Italy) and G. Caglioti (Italy). They were assisted by Prof. F. Garcia-Moliner (Spain) who acted as Monitor for nearly the whole duration of the Course.

It is a pleasure to thank the United Nations Educational, Scientific and Cultural Organization and the Italian National Committee for Nuclear Energy for their financia' support.

Abdus Salam

EDITORIAL NOTE

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PART I

GENERAL COURSES

ON THE BAND STRUCTURE PROBLEM

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Abstract

1. Introduction. 2. Pseudo-atoms. 3. Model potentials. 4. The APW method. 5. Green function method. 6. Transition metals.

1. INTRODUCTION

The following notes do not constitute a self-contained account of this basic topic, but are intended to supplement Chapter 3 of Principles of the Theory of Solids [1], where such topics as the nearly free electron model, the LCAO method, the OPW method, etc., are dealt with at an elementary level. Since this chapter was written in the spring of 1963, there has been considerable development in our understanding of the basic mathematics of the problem, along lines that will be sketched out here. Unfortunately this material has been published only in primary papers, so that no general reference can yet be given to it.

2. PSEUDO-ATOMS

The problem of calculating electronic band structures really falls into two parts: we must first set up a periodic one-electron potential in the crystal and then solve the Schrödinger equation for Bloch states in that potential. These procedures cannot, of course, be independent of one another; the form of the Bloch functions must, in its turn, determine the electrostatic field within the crystal and hence the potential of which these functions are eigenstates. In other words, we must allow for the electron-electron interaction within the valence electron states.

In principle, this ought to be soluble by a self-consistent iterative procedure of the Hartree, Hartree-Slater or Hartree-Fock type; but such a computation is extremely laborious and nobody seems to have carried it through to a convergent answer. It is necessary, in practice, to make a number of approximations in the definition of $\mathscr{V}(\mathbf{r})$ that we use in the Bloch problem.

A relatively simple procedure is used within the framework of the pseudopotential method. First, let us take the potential of an array of bare ions, and transform it to a pseudopotential in reciprocal space, e.g.,

$$\mathscr{Y}_{\mathbf{b}}(\vec{\mathbf{r}}) \rightarrow W_{\mathbf{b}}(\vec{\mathbf{g}}) = \mathscr{Y}_{\mathbf{b}}(\vec{\mathbf{g}}) - \sum_{t} (\mathscr{E} - \mathscr{E}_{t}) \langle e^{i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}}, \mathbf{b}_{t} \rangle \langle e^{i(\vec{\mathbf{k}}-\vec{\mathbf{g}})\cdot\vec{\mathbf{r}}}, \mathbf{b}_{t} \rangle$$
(1)

Now this is a relatively weak potential and may therefore be treated as a small perturbing potential acting on the electron gas. As shown, for example, in Chapter 5 of the Principles of the Theory of Solids [1], the effect is to screen the bare potential by an amount governed by the <u>dielectric function</u> $\epsilon(\vec{q})$ of the electron gas. The matrix elements to be used in the NFE equations must be of the form

$$\Gamma_{\vec{g},\vec{g}'} = \frac{W_b(\vec{g} - \vec{g}')}{\epsilon(\vec{g} - \vec{g}')}$$
(2)

To use this formula, we need a theory of the dielectric function, which is not necessarily very easy to define, but since, in practice, we only use values of $\Gamma_{\overrightarrow{gg}}$ at a relatively few values of $\overrightarrow{g} - \overrightarrow{g}^{\dagger}$, it is generally held to be adequate to use the simple free electron formula for $\epsilon(\overrightarrow{q})$ which is not very far from unity anyway, except near q = 0.

The above argument is the basis of the procedures discussed at length by Harrison in his book on the pseudopotential method (1966) [2]. It is instructive, however, to go a little further. Suppose we construct our periodic "bare" potential by the superposition of bare ion potentials, i.e.,

$$\mathscr{Y}_{b}(\vec{r}) = \sum_{\vec{\ell}} v_{b}(\vec{r} - \vec{\ell})$$
(3)

Then by elementary algebra ([1], section 2.7) the Fourier transform must be of the form

$$\mathscr{Y}_{b}(\vec{g}) \equiv \int \mathscr{Y}_{b}(\vec{r}) e^{i\vec{g}\cdot\vec{r}} d^{3}\vec{r}$$
$$= \left(\frac{1}{N}\sum_{\vec{l}} e^{i\vec{g}\cdot\vec{l}}\right) v_{b}(\vec{g})$$
$$= F(\vec{g}) v_{b}(\vec{g}) \qquad (4)$$

where

$$\mathbf{v}_{\mathbf{b}}(\vec{\mathbf{g}}) = \mathbf{N} \int \mathbf{e}^{i\vec{\mathbf{g}}\cdot\vec{\mathbf{r}}} \mathbf{v}_{\mathbf{b}}(\vec{\mathbf{r}}) d^{3}\vec{\mathbf{r}}$$
(5)

In other words, each Fourier component of the potential can be represented as the product of a <u>structure factor</u>, $F(\vec{g})$ and an <u>atomic form</u> <u>factor</u> $v_b(\vec{g})$, just as in the theory of X-ray or neutron diffraction. For the valence electrons, however, the full bare potential (5) is much too strong; the correct atomic form factor must be something like the pseudopotential for a single atom, which we might call $w_b(\vec{g})$. Thus, our expression (1) must also be a product like (4):

$$W_{\rm b}(\vec{g}) = F(\vec{g}) W_{\rm b}(\vec{g}) \tag{6}$$

Now when this is screened, according to the formula (2), we get for our screened pseudopotential

$$\Gamma_{\vec{g}\vec{g}} = F(\vec{g} - \vec{g}') \frac{w_b(\vec{g} - \vec{g}')}{\epsilon(\vec{g} - \vec{g}')}$$
$$= F(\vec{g} - \vec{g}') w_{scr}(\vec{g} - \vec{g}')$$
(7)

where we introduce a screened pseudopotential for a <u>single</u> atom by simply dividing the bare pseudopotential by the appropriate dielectric function.

Eq. (7) is, in fact, the form used by Harrison. But to understand it physically, let us go back into real space. The Fourier analysis of (3) and (4) may be inverted, so that we may write, in place of (7),

$$\Gamma(\vec{r}) = \sum_{\vec{\ell}} w_{scr}(\vec{r} - \vec{\ell})$$
(8)

In other words, the effective periodic potential acting on an electron may be constructed by superposing the corresponding screened pseudopotentials of the separate ions of the crystal.

What is the function w_{scr} (\vec{r}) like? At large distances we recall that the bare ion potential must be of the form

$$v_{b}(\vec{r}) \rightarrow \frac{-Z e^{2}}{r}$$
, (9)

whose Fourier transform, near q = 0 is given by

$$v_{\rm b}(\vec{q}) \rightarrow \frac{-4\pi \,\rm NZ \,e^2}{q^2} \tag{10}$$

The pseudopotential transformation acts only within the range of the atomic core states, so we may assume the same behaviour for $w_b(q)$. Using the standard theory of the dielectric function ([1], section 5.3) we get, as $q \rightarrow 0$

$$w_{scr}(\vec{q}) \rightarrow \frac{-\frac{2}{3}E_{F}}{1+q^{2}/\lambda^{2}}$$
 (11)

which is the Fourier transform of

$$W_{sct}(r) \rightarrow \frac{-Ze^2}{r} \exp(-\lambda r) \text{ as } r \rightarrow \infty$$
 (12)

Thus, each ion carries a screened Coulomb potential, just as it might if it were treated as a simple point charge immersed in the electron gas.

On the other hand, for large values of q, the dielectric function is not very different from 1, so the screened pseudopotential is much the same as the pseudopotential of the bare ion, and depends sensitively on the "chemistry" of the element in question. In practice, the smallest reciprocal lattice vector \vec{g} is already in this region, so that for band structure calculations the screening procedure is not very important. We find (see Fig.1), for example, that the pseudopotential is often just changing sign, from the large negative value $-\frac{2}{3} \mathscr{E}_F$ at q=0, to some small positive value, in the neighbourhood of the first reciprocal lattice vector, so that the magnitude and sign of the NFE matrix element may depend very sensitively on details of the atomic potential or on the procedure used for defining the pseudopotential. This is one of the reasons why it is so difficult to calculate band structures and Fermi surfaces very accurately from first principles — a difficulty that is only indirectly related to the electron-electron interaction.



FIG.1. Pseudo-potential curve

In the band structure problem the real space representation of $w_{scr}(\mathbf{r})$ is not of much importance, but it has great conceptual power when we come to deal with thermally disturbed crystals or even with disordered systems such as liquid metals. Within the approximation of linear screening, as defined by any formula such as (2), we may imagine that each ion carries about with it a screening cloud which changes its external field from (9) to (12), and which contains, indeed, exactly enough charge to neutralize the positive valence charge $Z |\mathbf{e}|$ of the ion when seen from a large distance. In moderation, these charges may be superposed (for they must, eventually, add up to the total charge of the gas of valence electrons) and treated as if independent of one another; we say that the metal behaves like an assembly of "neutral pseudo-atoms". The applications of this concept to the electrical and dynamical properties of solid and liquid metals are reviewed at length elsewhere (Ziman [3]).

3. MODEL POTENTIALS

Nevertheless, in spite of its power as a conceptual tool, the pseudopotential method has serious limitations. For example, the linear screening procedure that we have used is quite unjustified by any rigorous argument; it is surely much too naive to replace the deep potential of the ion core, where linear dielectric screening would certainly not be valid, by a "weak" pseudopotential, and then treat the latter as if it were an ordinary small potential. We know indeed that the pseudopotential is "nonlocal", and that it is energy and momentum dependent, so that great care is needed in any application of perturbation theory involving matrix elements between states of different energy. Even in the calculation of the pseudopotential according to the standard Phillips-Kleinman prescription we often have great difficulty in estimating the energy difference $\mathscr{E} - \mathscr{E}_t$ between the state being studied and a core state, so that band structure computations by different authors differ by quite large amounts depending upon the <u>core shifts</u> that they have assumed as the separate atoms are brought together into a crystal (Lin and Phillips [4]).

But the most serious limitation of the pseudopotential method is its arbitrarities. As we have already seen, \mathscr{Y}_R is not unique. The spectrum of the original Schrödinger equation is reproduced by any pseudopotential operator of the form

$$\mathscr{Y}_{\mathsf{R}}\phi = \sum_{\mathsf{t}} \langle \mathsf{F}_{\mathsf{t}}, \phi \rangle \mathsf{b}_{\mathsf{t}}(\vec{\mathsf{r}})$$
(13)

where the functions $F_t(\vec{r})$ are completely arbitrary functions of \vec{r} . Thus, innumerable different pseudopotentials could be constructed at will.

This may seem surprising, but there is nothing mysterious about it. Think of the analogous problem of scattering by a spherical potential. Having chosen the energy of our electron, all we have to do is to find a potential that will reproduce the correct wave function outside some particular radius r_c . It is obvious that this can be done in any number of ways: we can modify (Fig. 2) our pseudopotential w(r) endlessly, without altering the equivalence of $\phi(r)$ and $\psi(r)$ outside the core.



The reason why the pseudopotential is usually dependent on energy and angular momentum is obvious from this figure. A potential that reproduces the correct phase shift for a given angular momentum will not necessarily do the same job for another angular momentum, where the equation for the radial part of the wave function contains a different value of the centrifugal term $\ell(\ell+1)/r^2$. Again, a pseudopotential that works at one energy will not be able to produce a wave function to match the true solution at another energy. What we have gained by making w(r) relatively "weak" we lose in its applicability to a very limited range of circumstances. These limitations are fundamental. Although the pseudopotential is arbitrary, it can never be defined so as to be completely independent of energy and momentum. All that we can do is to try to find the "best possible" representation in some approximate sense.

At the heart of our difficulties is the lack of a formal mathematical prescription for "the" pseudopotential. What does it all mean? This is a subtle question, recently answered by Rubio and Garcia-Moliner [5].

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Basically it is a question of the convergence of the Born series (i.e., perturbation series) for the T-matrix (i.e., scattering amplitude) of the potential v(r). This is a subject discussed in detail by certain authors. in particular by Weinberg [6]. The critical question is the existence of bound states in the potential; roughly speaking, the Born series only converges when the energy of the scattered electron is greater, in magnitude. than the distance in energy down to the lowest bound state of the potential well. Since our atomic potential v(r) has many bound states (i.e., the core states) at energies of tens or hundred of volts below the bottom of the valence bond, an electron at the Fermi level, perhaps only 5 volts up, certainly does not satisfy these conditions. It is essential to transform to a perturbation series in a pseudopotential, w(r), to achieve the necessary convergence. Using Weinberg's method. Rubio and Garcia-Moliner have been able to show that the best convergence (within the general framework of pseudopotentials constructed from core functions in the manner of Phillips and Kleinman), is achieved by putting

$$\mathbf{F}_{\star} = -\mathscr{Y}(\mathbf{r}) \mathbf{b}_{\star}(\mathbf{r}) \tag{14}$$

in (13). This is the so-called Austin pseudopotential, with repulsive part

$$\mathscr{Y}_{R}^{A}\phi = -\sum_{t} \langle b_{t}, \mathscr{Y}\phi \rangle b_{t}, \qquad (15)$$

i.e., giving rise to matrix elements between pseudo-wave functions of the form

$$\langle \phi, (\mathscr{Y} + \mathscr{Y}_{R}^{A})\phi \rangle = \langle \phi, \mathscr{Y}\phi \rangle - \sum_{t} |\langle b_{t}, \mathscr{Y}\phi \rangle|^{2}$$
 (16)

In other words, we subtract from the true potential $\mathscr{V}(r)$ as much as can be expanded as a sum of core functions, as if

$$\mathscr{Y} + \mathscr{Y}_{R}^{A} = \mathscr{Y}(\vec{r}) - \sum_{t} \langle b_{t}, \mathscr{Y} \rangle b_{t}(\vec{r})$$
(17)

This function, originally suggested as the "smoothest" pseudopotential, is actually the best in this special sense.

Experience has shown, however, that even the best pseudopotential that one can calculate directly from the atomic potential does not usually reproduce the experimental band structure with any great accuracy. Heine and Abarenkov [7] suggested one might do just as well with a model potential -i.e., one that has been simplified in analytical form but which reproduces the scattering properties of the metallic ion. For example, consider the function

$$v_{M}(\mathbf{r}) = \frac{-Z e^{2}}{\mathbf{r}} \qquad \mathbf{r} > \mathbf{r}_{c}$$

$$-A_{\ell}(\mathscr{C}) \qquad \mathbf{r} < \mathbf{r}_{c} .$$
(18)

It is easy to find the bound states of energy \mathscr{E} and angular momentum ℓ , in such a potential and to adjust the value of the parameter $A_{\ell}(\mathscr{E})$ so as to reproduce the atomic terms of the observed optical spectrum of the atom or ion. Now we can screen the outer coulombic field, as in the metal, and calculate the corresponding atomic form factors for a band structure calculation.

This method is obviously very similar in spirit to the <u>quantum</u> <u>defect method</u> of Kuhn and van Vleck, which is a rather elaborate mathematical device for deriving values of the radial derivative of the wave function, on, say, the Wigner-Seitz sphere, from the atomic term values, without having actually to construct a full atomic potential. In principle, it is very attractive to try to link two quite different "experimental" quantities – atomic spectral levels and the shape of the Fermi surface – without the intermediary of an unobservable potential; but there are assumptions about screening and about the superposition of potentials which are probably not valid and which considerably reduce the reliability of the argument in both these methods.

4. THE APW METHOD

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This is independent of the OPW and pseudopotential methods, being essentially a development of the cellular method. The basic problem of matching wave functions is greatly simplified by choosing spherical surfaces rather than complicated polyhedral unit cells. There is some error introduced in defining a <u>muffin-tin potential</u> of atomic spheres in empty space, but this does not seem to be serious except perhaps, in a diamond lattice.

We divide the wave function into two parts, each separately satisfying a wave equation in the two regions. Thus, in each unit cell

$$e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \mathbf{r} > \mathbf{R}_{s}$$

$$\phi_{\vec{k}}(\vec{r}) = \sum_{\ell m} \mathbf{a}_{\ell m} \mathscr{R}_{\ell}(\mathbf{r}, \mathscr{E}) Y_{\ell m}(\theta, \phi), \qquad \mathbf{r} < \mathbf{R}_{s}$$
(19)

where $\mathscr{R}_{\ell}(r,\mathscr{E})$ is a solution of the ordinary radial equation of angular momentum ℓ inside the potential well of radius R_s . This solution is at the energy \mathscr{E} of the state being studied; note that the exterior solution is not chosen to be a wave of the same energy, but only to satisfy the Bloch condition; we shall eventually use a combination of such <u>augmented plane</u> waves in our Bloch function.

The two parts of $\phi_{\vec{k}}(\vec{r})$ can be matched in amplitude by the proper choice of the coefficients $a_{\ell m}$. We may use the standard expansion in spherical harmonics $Y_{\ell m}$ and spherical Bessel functions j_{ℓ}

$$\mathbf{e}^{\mathbf{i}\vec{\mathbf{k}\cdot\mathbf{r}}} = 4\pi \sum_{\ell m} \mathbf{i}^{\ell} \mathbf{j}_{\ell}(\mathbf{k}\mathbf{r}) \ \mathbf{Y}_{\ell m}(\boldsymbol{\theta}_{\vec{\mathbf{r}}}, \boldsymbol{\phi}_{\vec{\mathbf{r}}}) \mathbf{Y}_{\ell m}^{*}(\boldsymbol{\theta}_{\vec{\mathbf{k}}}, \boldsymbol{\phi}_{\vec{\mathbf{k}}})$$
(20)

(which we write = $4\pi \sum_{L} i^{\ell} j_{\ell}(kr) Y_{L}(\hat{\vec{r}}) Y_{L}^{*}(\hat{\vec{k}})$ for short)

Thus if
$$a_{\ell m} = \frac{j_{\ell}(kR_s)}{\mathscr{R}_{\ell}(R_s,\mathscr{E})} Y_L^*(\hat{\vec{k}}).$$
 (

Then $\phi_{\vec{k}}(r)$ is continuous at $r = R_s$.

Now suppose the Bloch function is just a sum of these:

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{g}} \alpha_{\vec{k}-\vec{g}} \phi_{\vec{k}-\vec{g}}(\vec{r})$$
(22)

21)

We can substitute this into Schrödinger equation to find the correct values of the coefficients $\alpha_{k-g}^{\rightarrow \rightarrow}$ and the corresponding energy eigenvalue \mathscr{E} as a function of the chosen value of \vec{k} .

Unfortunately, this is not quite simple. Slater's original procedure was to use (22) as variational trial function (and hence to get linear equations for $\alpha_{\vec{k}} \cdot \vec{g}$) for the expectation value of the Hamiltonian. The algebra is rather messy, but one can see the sort of thing that happens by looking at the diagonal element

$$\int \phi_{\vec{k}}^{*} (-\nabla^{2} + \mathscr{V}) \phi_{\vec{k}} d^{3} \vec{r} = k^{2} \omega + \mathscr{O} \sum_{L} a_{L}^{2} + \text{ surface term.}$$
(23)

The first term is just the energy of the plane wave part outside the atomic sphere, in the fraction ω of the unit cell. The second term, again, comes from the fact that the radial functions exactly satisfy the Schrödinger equation inside the sphere. But the surface term, where $\phi_{\vec{k}}$ has a discontinuity of slope, is by no means negligible. From Green's theorem this gives rise to an expression containing the derivative of $\mathscr{R}_{\ell}(\mathbf{r}, \mathscr{E})$ at R_s : with a little juggling we find the condition

$$\mathscr{E} = k^{2} + \sum_{\ell} (2\ell+1) j_{\ell}^{2} (k R_{s}) \left[\frac{d}{dr} \ln \mathscr{R}_{\ell}(r, \mathscr{E}) \right]_{r=R_{s}}$$
(24)

for the expectation value of the energy of a single APW.

The expression for cross products between APW's of different wave vectors are more complicated, but again all the properties of the atomic potentials are expressed via the derivatives of the radial functions. Thus, eventually, we get a rather elaborate set of equations for the coefficients $\alpha_{k-\vec{g}}$, similar in form to the standard NFE/OPW equations, but with matrix elements of the form

$$\Gamma_{gg'} = \frac{4\pi R_s^2}{v_c} \left\{ -\left[(\vec{k} - \vec{g'}) \cdot (\vec{k} - \vec{g}) - \mathscr{O} \right] \frac{j_1(|\vec{g} - \vec{g'}|R_s)}{|\vec{g} - \vec{g'}|} + \sum_{\ell=0}^{\infty} (2\ell+1) P_\ell \left(\cos \theta_{\vec{g'}} \vec{g'} \right) j_\ell(|\vec{k} - \vec{g}|R_s) j_\ell(|\vec{k} - \vec{g'}|R_s) \frac{\mathscr{Q}^{\dagger}(R_s, \mathscr{O})}{\mathscr{Q}_{\ell}(R_s, \mathscr{O})} \right\}$$
(25)

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These are fairly easily computed by machine, and the secular determinant can be solved for the function $\mathscr{E}(\vec{k})$. The method obviously exploits to the full the spherical symmetry of the atomic potential and the translational symmetry of the crystal lattice. Unlike the OPW and pseudopotential methods, it can deal perfectly well with d-bands in transition metals, etc.

Nevertheless, in this formulation, the technique is very laborious for a very simple reason. Let us try the empty lattice test. The best way to do this is to suppose that all the scattering phase shifts of the muffin-tin wells are zero. By the standard theory of phase shifts – i.e., by matching each radial solution to the corresponding free-space waves outside R_s – we have the following relation:

$$\frac{\mathscr{R}_{\ell}^{t}(\mathbf{R}_{s},\mathscr{B})}{\mathscr{R}_{\ell}(\mathbf{R}_{s},\mathscr{B})} = \left[\frac{\mathbf{j}_{\ell}(\kappa\mathbf{r}) - \tan\eta_{\ell}(\epsilon)\mathbf{n}_{\ell}^{t}(\kappa\mathbf{r})}{\mathbf{j}_{\ell}(\kappa\mathbf{r}) - \tan\eta_{\ell}(\epsilon)\mathbf{n}_{\ell}(\kappa\mathbf{r})}\right]_{\mathbf{r}=\mathbf{R}_{s}}$$
(26)

where $\kappa^2 = \mathscr{E}$. Putting each $\eta_{\ell}(\mathscr{E}) = 0$ does not make all the coefficients $\Gamma_{\overrightarrow{g},\overrightarrow{g}} = 0$ — nor do we find, for example, in (24), that the free-electron solution is the limiting case of a single APW. Thus, to reproduce the simple solution $\mathscr{E} = \kappa^2$ requires detailed computation, involving, in principle, all values of ℓ and of \overrightarrow{g} and $\overrightarrow{g'}$. In the end, of course, the correct result is obtained, but only by virtue of some complicated hidden identities within the algebraic formalism. It is not surprising, therefore, that the relative simplicity of the band structure of metals such as Na or Al, which are very close to free-electron systems, was not obvious to those who calculated by the APW method.

It is interesting to note (Lloyd [8]) that the APW matrix elements can be generated from a model potential, with matrix elements (in real space, for given angular momenta L, L')

$$\langle L, \vec{r} | \Gamma | L', \vec{r}' \rangle = \delta_{LL'} \left[-H(R_s - r)(-\nabla_{\ell}^2 - \kappa^2) \frac{\delta(\vec{r} - \vec{r}')}{r'^2} - \delta(R_s - r) \left\{ \frac{\partial}{\partial r} - \frac{\mathscr{R}_{\ell}'(R_s)}{\mathscr{R}_{\ell}(R_s)} \right\} \frac{\delta(\vec{r} - \vec{r}')}{r'^2} \right]$$
(27)

where H is a step function, etc. This is obviously a rather complicated operator, and not what one would have chosen in the first instance as an expression capable of representing the scattering action of our given atomic potential.

5. GREEN FUNCTION METHOD

The most subtle, but also most enlightening, method of calculating band structure is the procedure of Korringa and of Kohn and Rostoker -

the KKR method. The basic idea is as follows: - The Schrödinger equation may be rewritten as an integral equation

$$\psi(\vec{\mathbf{r}}) = \int \mathscr{G}_{0}(\vec{\mathbf{r}} - \vec{\mathbf{r}}) V(\vec{\mathbf{r}}) \psi(\vec{\mathbf{r}}) d^{3}\vec{\mathbf{r}}$$
(28)

where

$$\mathscr{G}_{0}(\vec{\mathbf{r}} - \vec{\mathbf{r}}') = -\frac{1}{4\pi} \quad \frac{\exp i\kappa |\vec{\mathbf{r}} - \vec{\mathbf{r}}'|}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|}$$
(29)

is the free-particle propagator, or Green function, for the energy $\mathscr{E} = \kappa^2$.

In a muffin-tin potential, we may express the integral as the sum of contributions from the separate cells, i.e.,

$$\psi(\vec{\mathbf{r}}) = \sum_{\ell'} \int \mathscr{G}_{0}(\vec{\mathbf{r}} - \vec{\mathbf{r}'}) \, v(\vec{\mathbf{r}'} - \vec{\ell}') \, \psi(\vec{\mathbf{r}'}) \, d^{3}\vec{\mathbf{r}'}, \qquad (30)$$

where v(r) = 0 for $r > R_s$. Since the spheres do not overlap, this is really a sum of separate integrals, as may be shown by introducing a variable $\vec{\rho}$ such that $\vec{r} = \vec{l} + \vec{\rho}$ in the \vec{l} th cell of the crystal. Thus

$$\psi(\vec{\ell} + \vec{\rho}) = \sum_{\vec{\ell}'} \int \mathcal{G}_0(\vec{\rho} - \vec{\rho}' + \vec{\ell} - \vec{\ell}') \, v(\vec{\rho}') \, \psi(\vec{\ell}' + \vec{\rho}') d^3 \vec{\rho}' \tag{31}$$

Now recall that ψ is a Bloch function, so that

$$\psi_{\vec{k}}(\vec{\ell}^{\,\prime} + \vec{\rho}^{\,\prime}) = e^{i\vec{k}\cdot\vec{\ell}^{\,\prime}} \psi_{\vec{k}}(\vec{\rho}^{\,\prime})$$
(32)

Substituting into (31), we get the following integral equation: -

$$\psi_{k}(\vec{\rho}) = \int G_{\vec{k},\kappa}(\vec{\rho},\vec{\rho'}) v(\vec{\rho'}) \psi_{k}(\vec{\rho'}) d^{3}\vec{\rho'}, \qquad (33)$$

where

$$G_{\vec{k},\kappa}(\vec{\rho},\vec{\rho'}) \equiv \sum_{\vec{\ell'}} \mathscr{G}_{0}(\vec{\rho}-\vec{\rho'}+\vec{\ell}-\vec{\ell'}) e^{i\vec{k}\cdot(\vec{\ell}-\vec{\ell'})}$$
(34)

This function – which depends on the momentum \vec{k} and the energy κ^2 of the state being studied, as well as the matrix labels $\vec{\rho}, \vec{\rho'}$ – we call the <u>complete Greenian</u> of the lattice. It measures the effect of the lattice as a whole in transforming the wave function into itself – not merely the

effect of the atom in the central cell as in ordinary scattering problems, but the effects of waves re-radiated from all other spheres. It is obvious, from the translational symmetry of the lattice, that (34) is in fact independent of the choice of \overline{l} .

The fact that $\psi(\rho)$ satisfies the Schrödinger equation within the potential $v(\rho)$, which vanishes for $\rho > R_s$, allows us to transform the integral Eq.(33) into a simple surface condition. Applying Green's theorem we get

$$\begin{split} \psi(\vec{\rho}) &= \int G(\vec{\rho}, \vec{\rho}') \, v(\vec{\rho}') \, \psi(\vec{\rho}') \, d^{3} \vec{\rho}' \\ &= \int G(\rho, \rho') \left\{ \nabla^{2} + \kappa^{2} \right\} \, \psi(\vec{\rho}') \, d^{3} \vec{\rho}' \\ &= \int \delta(\vec{\rho} - \vec{\rho}') \, \psi(\vec{\rho}') \, d^{3} \vec{\rho}' \\ &+ \int \left\{ G(\rho, \rho') \, \frac{\partial \psi(\vec{\rho}')}{\partial \rho'} - \psi(\vec{\rho}') \, \frac{\partial G(\rho, \rho')}{\partial \rho'} \right\} \, dS' \end{split}$$
(35)

because of the singularity in G at the origin $\vec{\rho} = \vec{\rho}'$. Only the surface integral survives as a condition

$$\int \left[G(\vec{\rho},\vec{\rho'}) \frac{\partial \psi(\vec{\rho})}{\partial \rho'} - \psi(\rho') \frac{\partial G(\vec{\rho},\vec{\rho'})}{\partial \rho'} \right]_{\vec{\rho'} = R_s - \epsilon} d\Omega(\vec{\rho'}) = 0$$
(36)

involving integration over all directions of $\vec{\rho}'$, on the surface of a sphere "just within" R_s . This condition must hold for all values of $\rho < R_s - 2\epsilon$.

What we now have to do is to find a wave function $\psi(\rho)$ satisfying the Schrödinger equation in the potential well and also satisfying this boundary condition. For a given value of \vec{k} , this can only be done for certain values of κ ; hence we discover the function $\mathscr{E}(\vec{k})$ in each band. It is natural to expand in solutions of the radial equation inside the well

$$\psi(\vec{\rho}) = \sum_{L} i^{\ell} \alpha_{L} \mathscr{R}_{L}(\rho, \mathscr{E}) Y_{L}(\vec{\rho}), \qquad (37)$$

with coefficients α_L to be determined.

But then we need an expansion of $G(\vec{\rho}, \vec{\rho}')$ in spherical harmonics a rather more complicated problem. Thus for $\rho < \rho'$

$$\mathscr{G}_{0}(\vec{\rho} - \vec{\rho'}) = \kappa \sum_{L} j_{\ell}(\kappa \rho) \left\{ n_{\ell}(\kappa \rho') - i j_{\ell}(\kappa \rho') \right\} Y_{L}(\vec{\rho}) Y_{L}(\vec{\rho'}), \qquad (38)$$

by a standard theorem for the expansion of $\exp(i\kappa r)/r$. This takes care of the term with $\ell = \ell^{1}$ in (34). For the remainder we suppose that we can write the <u>incomplete Greenian</u> in the form

$$G^{\dagger}(\vec{\rho} - \vec{\rho}^{\dagger}) \equiv G(\vec{\rho}, \vec{\rho}^{\dagger}) - \mathscr{G}_{0}(\vec{\rho} - \vec{\rho}^{\dagger})$$
$$= \sum_{LL'} i^{\ell} - \mathscr{G}_{LL'} j_{\ell}(\kappa \rho) j_{\ell}(\kappa \rho^{\dagger}) Y_{L}(\vec{\rho}) Y_{L'}(\vec{\rho}^{\dagger}), \qquad (39)$$

and try to construct formulae for the coefficients $\mathscr{B}_{LL'}$. This is where the real work lies in the papers of Kohn and Rostoker and their successors. For example, we find the following formulae

$$\mathscr{B}_{LL'} = 4 \pi \sum_{L''} C_{L'' LL'} \mathscr{D}_{L''}, \qquad (40)$$

where

$$C_{L''LL'} \equiv \int Y_{L}(\vec{r}) Y_{L'}(\vec{r}) Y_{L''}(\vec{r}) d\Omega(\vec{r})$$
(41)

is essentially a "Clebsch-Gordan" coefficient, whilst

$$\mathscr{D}_{L} = \kappa \sum_{\ell \neq 0} e^{i\vec{k} \cdot \vec{\ell}} \left[n_{L}(\kappa \ell) - ij_{L}(\kappa \ell) \right] Y_{L}(\vec{\ell}) - \frac{i\kappa}{\sqrt{4\pi}} \delta_{L0}$$
(42)

requires an actual summation over the real crystal lattice. But this is only one of many different alternative expressions, containing sums over the reciprocal lattice, or mixed sums over both real and reciprocal space with Ewald convergence factors, etc. I have only quoted these formulae to show that they are explicit and that they involve only the lattice structure, not the atomic potentials.

Now put all those equations -(37)-(42) – into the surface condition (36); we get, after an obvious integration,

$$\sum_{\mathbf{L}'} \left\{ \left(\mathscr{B}_{\mathbf{L}\mathbf{L}'} - i\kappa \, \delta_{\mathbf{L}\mathbf{L}'} \right) \left[\mathbf{j}_{\ell}, \, \mathscr{R}_{\ell'} \right] + \kappa \left[\mathbf{n}_{\ell'}, \, \mathscr{R}_{\ell'} \right] \delta_{\mathbf{L}\mathbf{L}'} \right\} \alpha_{\mathbf{L}'} = 0 \tag{43}$$

where

$$[\mathbf{j}_{\ell}, \mathcal{R}_{\ell}] \equiv \left[\mathbf{j}_{\ell}(\kappa \rho) \frac{\partial \mathcal{R}_{\ell}(\rho)}{\partial \rho} - \mathcal{R}_{\ell}(\rho) \frac{\partial \mathbf{j}_{\ell}(\kappa \rho)}{\partial \rho}\right]_{\rho = R_{s}}$$
(44)

Just as in the APW method (cf.(25)) only the radial derivative of \mathscr{R}_{ℓ} finally appears as a witness to the behaviour of the atomic potential. In terms of phase shifts – i.e., as in (26), we have

$$\cot \eta_{\ell} = \frac{[\eta_{\ell}, \mathcal{R}_{\ell}]}{[j_{\ell}, \mathcal{R}_{\ell}]}$$
(45)

The condition, therefore, for the self-consistency of the linear Eqs.(43) for the unknown coefficients $\alpha_{\rm L}$ becomes simply

$$\det \left| \left| \mathscr{B}_{LU}(\vec{k},\kappa) + \kappa \left\{ \cot \eta_{\ell}(\kappa) - i \right\} \delta_{LU} \right| \right| = 0.$$
(46)

The band structure calculation proceeds as follows. Construct tables of the coefficients $\mathscr{B}_{1,1}(\vec{k},\kappa)$ for our given crystal structure, as functions

of the wave vector \vec{k} and energy κ^2 . Then calculate radial derivatives (i.e., phase shifts) for solutions of the radial equation in our chosen potential v(r) as functions of energy. Put these into the determinant, and find values of \vec{k} for a given κ making the determinant vanish.

The KKR method works all right and has been used to get band structures for the noble metals and for A1. It is valid under the same circumstances as the APW method and exploits the same symmetry properties of the potentials. In its original formulation by Kohn and Rostoker, Eqs (43) for the coefficients in (37) were derived from a variational expression constructed to generate the integral Eq. (33), but this is not essential to the argument; it merely demonstrates that the choice of a finite number of these coefficients as variational parameters produces a "best" fit in some analytic sense.

Although the above argument is exact only for a perfect lattice, the method can be made the basis for an approximate procedure for calculating the band structure of a disordered system such as a liquid metal (Phariseau and Ziman [9], Ziman [10]). We merely assume that the "Bloch condition" (32) is still valid for the translation from a point in an atomic sphere to an equivalent point in another sphere of the assembly. We find then that \vec{k} has to be made complex, to allow for scattering and dissipation of the electron wave as it progresses through the medium. But the structure factors \mathscr{D}_L , defined in (42) retain exactly the same form, i.e.,

$$\mathscr{D}_{i} = N\kappa (2\ell+1)^{\frac{1}{2}} (4\pi)^{\frac{1}{2}} \int_{0}^{\infty} \{n_{\ell}(\kappa x) - ij_{\ell}(\kappa x)\} j_{\ell}(kx) g(x) x^{2} dx \qquad (47)$$

where g(x) is the radial distribution function of the atoms of the liquid.

Nevertheless, for actual calculation, the KKR method has the grave disadvantage of requiring very heavy computing. To understand this, let us apply, as usual, the empty lattice test. We see at once that in the limit as $\eta_{\ell} \rightarrow 0$ the term containing cot η_{ℓ} becomes infinite. In order to make the determinant vanish, we have to find a corresponding singularity

in the coefficients $\mathscr{B}_{LL'}$; in the neighbourhood of the free-electron system the determinant is very unstable mathematically and great care is required in locating the roots.

That these roots do indeed correspond to NFE solutions for small values of η_{ℓ} can be checked by looking at another formula for the set of coefficients $\mathscr{B}_{LL'}$. As a sum in reciprocal space this reads

$$\mathscr{B}_{LL'} = -(4\pi)^2 \operatorname{N} \sum_{\overrightarrow{g}} \frac{\mathbf{j}_{\ell}(|\vec{\mathbf{k}} - \vec{g}|\mathbf{R}_{s}) \mathbf{j}_{\ell'}(|\vec{\mathbf{k}} - \vec{g}|\mathbf{R}_{s})}{\mathbf{j}_{\ell'}(\kappa \mathbf{R}_{s}) \mathbf{j}_{\ell'}(\kappa \mathbf{R}_{s})} \frac{\mathbf{Y}_{L}(\vec{\mathbf{k}} - \vec{g}) \mathbf{Y}_{L'}(\vec{\mathbf{k}} - \vec{g})}{|\vec{\mathbf{k}} - \vec{g}|^{2} - \mathscr{O}}$$
$$-\kappa \left(\frac{n_{\ell}(\kappa \mathbf{R}_{s})}{\mathbf{j}_{\ell}(\kappa \mathbf{R}_{s})} - \mathbf{i}\right) \delta_{LL'}$$
(48)

This is singular if $\mathscr{E} = |\vec{k} - \vec{g}|^2$ for some value of \vec{g} , so if all $\eta_{\ell} = 0$ we get the free-electron solutions.

What is immediately evident is that the whole theory is upside down; it would be much happier if the determinant could be made to vanish trivially in the empty lattice case. The following abstract algebraic analysis (Ziman [11]) shows how this can be done.

First let us give a new label to the coefficients $\mathscr{B}_{LL'}$. As we see from (39) these should be called, $G'_{LL'}$ since they are matrix elements of the incomplete Greenian, G' in an angular momentum representations. On the other hand, the factor derived from the atomic potential in (46) is also quite familiar; we may write

$$\kappa (\cot \eta_{\ell} - i) = \left(\frac{1}{\kappa} \sin \eta_{\ell} \exp i\eta_{\ell}\right)^{-1}$$
$$= -T_{\ell}^{-1}$$
(49)

since we recognize the usual contribution of the lth phase shift to the scattering amplitude in the standard partial-wave formula. In the formal language of scattering theory, this is just the corresponding diagonal element of the so-called <u>T-matrix</u> of the atomic sphere; because v(r) is spherically symmetric, the T-matrix is diagonal in this angular momentum representation. Thus, our KKR determinant is abstractly of the form

$$\det \left\| \left[G' - T^{-1} \right]_{LL'} \right\| = 0.$$
 (50)

No wonder the vanishing of the T-matrix, in the empty lattice case, picks out the singularities of G'.

What we must do is construct a matrix with T in it, rather than T^{-1} . But notice a very simple result. The <u>complete</u> Greenian can be expanded in plane waves as follows

$$G(\vec{\rho},\vec{\rho}') = \sum_{\vec{g}} \frac{e^{i(\vec{k}-\vec{g})\cdot(\vec{\rho}-\vec{\rho}')}}{|\vec{k}-\vec{g}|^2 - \mathscr{G}}$$
(51)

as may readily be shown from the familiar Fourier transform of the ordinary free-space propagator (29), i.e.,

$$\mathscr{G}_{0}(\vec{r}) = \int \frac{e^{i\vec{K}\cdot\vec{r}} d^{3}\vec{K}}{K^{2}-\mathscr{O}}$$
(52)

In other words the matrix G is diagonal in a "reciprocal lattice representation", and may therefore be inverted at once

$$[G^{-1}]_{\overrightarrow{gg'}} = -\frac{1}{N} \left\{ \left| \vec{k} - \vec{g} \right|^2 - \mathscr{O} \right\} \delta_{\overrightarrow{gg'}}$$
(53)

which looks very familiar. So now we write

$$T^{-1} - G' = T^{-1} + \mathscr{G}_0 - G$$

= N^{-1}G { NG^{-1} - N(T^{-1} + \mathscr{G}_0)^{-1} } (T^{-1} + \mathscr{G}_0) (54)

and provided that neither ||G|| nor $||T^{-1} + \mathscr{G}_0||$ vanishes our condition (50) requires the vanishing of the determinant (in any representation) of the matrix NG⁻¹ - Γ where

$$\Gamma \equiv N(T^{-1} + \mathscr{G}_{0})^{-1} \tag{55}$$

From (53) we want this in a "reciprocal lattice representation", so that our determinant reads

 $\det \left| \left| \left\{ \left| \vec{k} - \vec{g} \right|^2 - \mathscr{E} \right\} \right| \delta_{\overrightarrow{gg'}} + \Gamma_{\overrightarrow{gg'}} \right| = 0$ (56)

That is to say, the operator Γ defined by (55) plays the role of a pseudopotential in a typical NFE type of expression. The reduction of Γ to this representation is not quite trivial, nor unambiguous, but the following formula may be derived:

$$\Gamma_{\vec{g}\vec{g'}} = -\frac{4\pi N}{\kappa} \sum_{\ell} (2\ell+1) \tan \eta'_{\ell} \frac{j_{\ell}(|\vec{k}-\vec{g}|R_s)j_{\ell}(|\vec{k}-\vec{g'}|R_s)}{[j_{\ell}(\kappa R_s)]^2} P_{\ell}(\cos \theta_{\vec{g}\vec{g'}})$$
(57)

where

$$\cot \eta'_{\ell} = \cot \eta_{\ell} - \frac{n_{\ell}(\kappa R_s)}{j_{\ell}(\kappa R_s)}$$
(58)

defines a modified phase shift η'_{ℓ} , and where $\theta_{\overrightarrow{g}\overrightarrow{g}}$ is just the angle between the vectors $\vec{k} - \vec{g}$ and $\vec{k} - \vec{g'}$.

The above derivation of (57) is rather abstract, and some steps have only been sketched. It is possible to arrive at the same result by more

direct algebraic manipulations of the KKR determinant, using the formula (48) for the coefficients \mathscr{B}_{LL} as a series in \vec{g} . But this does not demonstrate the inwardness of the theorem, which goes to the very heart of the band structure problem.

We see at once, from (57) and (58), that the empty lattice test is satisfied automatically; all Γ_{gg} go to zero with the phase shifts η_{ℓ} . It is also obvious that in situations where the electrons are nearly free – 1.e., where the phase shifts are small – the matrix elements also are small, and the determinantal equations converge rapidly. In such circumstances, this representation of the KKR method is much better for computation than either the original angular momentum representation or the APW method.

It is interesting to note (Lloyd 1965) that this form of $\Gamma_{\rightarrow \rightarrow}$ can be deduced from the model potential, in real space,

$$\langle L, \vec{r} | \Gamma | L^{\dagger}, \vec{r^{\dagger}} \rangle = \delta_{LL} A_{\ell} \delta (r - R_{s}) \frac{\delta (\vec{r} - \vec{r^{\dagger}})}{r^{1/2}}$$
(59)

- i.e., a delta function of strength A_ℓ (for the ℓ th partial wave) on the surface of the sphere R_s . This will match the true scattering of the actual atomic potential if

$$A_{\ell} = \frac{\mathscr{R}'_{\ell}(R_{s},\mathscr{C})}{\mathscr{R}_{\ell}(R_{s},\mathscr{C})} - \kappa \frac{j'_{\ell}(\kappa R_{s})}{j_{\ell}(\kappa R_{s})}$$
$$= -\frac{1}{\kappa} \tan \eta'_{\ell} \{R_{s}j_{\ell}(\kappa R_{s})\}^{-2}$$
(60)

Putting the potential into the Schrödinger equation instead of v(r) gives exactly the NFE equations with matrix elements (57).

It can also be derived from the APW method (Morgan 1966). Let us express ψ_k as a sum of APW's, as in (19)-(22), and substitute in the surface matching condition (36). Then we get exactly the Eqs.(56) and (57) as conditions for the existence of the coefficients $\alpha_{\overrightarrow{k}, \overrightarrow{g}}$. In fact, one can prove the following algebraic relation

$$\Gamma_{\overrightarrow{gg}}^{APW} = \Gamma_{\overrightarrow{gg}}^{KRR} + \Gamma_{\overrightarrow{gg}}^{0} \tag{61}$$

where Γ_{gg}^{APW} are the APW matrix elements (25), Γ_{gg}^{KKR} are the matrix elements (57), whilst Γ_{gg}^{0} . are the values of the APW matrix elements in the empty lattice case, as discussed in connection with (26). This shows explicitly that the KKR matrix elements automatically vanish in this limiting case. It may seem strange that there should apparently exist two quite distinct expansions of the exact wave function in APW's, with quite different sets of coefficients α_{k-g}^{-} . The reason is that we

only have to produce a suitable wave function outside the atomic spheres, and are therefore looking for a Fourier series representation of a periodic function that is defined only over part of the range within each unit cell. Such a series is not unique, for we may give the function any arbitrary form in the remaining range of its variables and look for the special series that defines this complete function; but changing the arbitrary function will change the series.

The connection of (57) with the conventional types of pseudopotential formulae is not so direct, although one can go some way by noticing that for small η_{ℓ} the matrix elements $\Gamma_{\rightarrow\rightarrow}$ approximate to the ordinary

scattering amplitudes for plane waves

$$\Gamma_{\overrightarrow{gg'}} \longrightarrow -\frac{4\pi N}{\kappa} \sum_{\ell} (2\ell+1)\eta_{\ell} P_{\ell} (\cos \theta).$$
 (62)

In other words, the pseudopotential is very much the same thing as the atomic form factor of each atomic potential (or muffin-tin well) as we might attempt to calculate it by direct phase shift analysis, and would be a suitable choice for the matrix element in a Born approximation calculation of this quantity.

We can also connect the KKR method with the Wigner-Seitz method. Let us look at the equations near $\vec{k} = 0$, and assume that only one plane wave is needed — so that only the term with $\vec{g} = \vec{g}' = 0$ appears in the determinant. Let us also assume that only s-wave scattering is important. Then we have

$$\mathscr{B} \approx k^2 - \frac{4\pi N}{\kappa} \tan \eta'_0 \tag{63}$$

i.e., $\mathscr{E}_0 \approx (-4\pi N/\kappa) \tan \eta_0$

since n_0 and n_0^* are approximately equal. It is well known in scattering theory that for small energies the s-wave shift is proportional to κ , i.e.,

$$\tan \eta_0(\kappa) \approx -\kappa a$$
 (65)

where a is a quantity called the <u>scattering length</u> of the potential well. Thus, if we introduce the radius of the Wigner-Seitz cell, so that $(4\pi/3) r_s^3 = 1/N$, we have

$$\mathcal{B}_0 \approx \frac{3a}{r_s^3} \tag{66}$$

Now, on the other hand, the wave function outside the atomic sphere \mathbf{R}_{s} is of the form

$$\frac{\psi(\mathbf{r})}{\mathbf{r}} = u(\mathbf{r}) = j_0(\kappa \mathbf{r}) - \tan \eta_0(\kappa) n_0(\kappa \mathbf{r})$$
(67)

because it is shifted in phase by $n_0(\kappa)$ relative to a free-wave solution. The Wigner-Seitz condition is that the derivative of this function should vanish on the boundary of the Wigner-Seitz sphere, when $r = r_s$, i.e.,

$$\tan \eta_0(\kappa) = j_0'(\kappa r_s)/n_0'(\kappa r_s)$$
(68)

(64)

Using the asymptotic form of the spherical Bessel functions for small values of κr_s and also using (65), we get again the same condition (66) for the value of $\mathscr{E}_0 = \kappa^2$ at which (68) is satisfied.

For an attractive potential, the scattering length a, by convention, is negative, so \mathscr{E}_0 lies below zero; this means that we have really used an analytic continuation of scattering theory into the region of imaginary κ , but this is perfectly proper. Thus, the bottom of the band lies a little below the assumed zero of our scattering problem — below the assumed zero of the empty space between muffin-tin wells. In other words, the effect of making a lattice of such wells is to allow a certain amount of tunnelling of electrons between neighbouring wells, even in the "free-electron" band, hence lowering the energy.

The crude result of perturbation theory would be

$$\mathscr{E}_{0} = \mathscr{V}_{0} = \int \vec{V(\mathbf{r})} d^{3}\vec{\mathbf{r}}, \qquad (69)$$

- the average potential in the lattice, or in a unit cell. This would be negative, but much larger in magnitude than (66). Here is another obvious case of the failure of the Born approximation; at such low energies we may <u>not</u> use (69), say, to calculate the scattering length and phase shifts. On the other hand, it is worth remarking that if we put the Phillips-Kleinman pseudopotential for $\mathscr{V}(r)$ in (69) we get a formula which is equivalent to a variational estimate of the scattering length of a potential containing bound states, i.e.,

$$\mathbf{a} \leq \int_{0}^{\infty} \phi_0 \mathbf{v}(\mathbf{r}) \phi_0 \mathbf{r}^2 d\mathbf{r} - \sum_{\mathbf{t}} (\mathscr{B}_0 - \mathscr{B}_{\mathbf{t}}) \left| \langle \phi_0, \mathbf{b}_{\mathbf{t}} \rangle \right|^2$$
(70)

quoted, for example, by Mott and Massey ([12], p.128).

It is worth noting further that the value of \mathscr{E}_0 depends only on the atomic volume, not on the crystal lattice or reciprocal lattice. Thus, it is essentially independent of structure and holds equally well for liquid metals. Since this is one of the most important factors in fixing the position of the band on the energy scale and hence determines the cohesive energy of the metal, this is a valuable argument in support of the general principle that metallic binding is a volume effect and not very sensitive to the detailed arrangement of the ions.

6. TRANSITION METALS

An interesting feature of the KKR formula in its reciprocal lattice representation (57) is that the matrix elements are real (i.e. hermitian), and contain tan η'_{ℓ} instead of sin $\eta_{\ell} \exp i\eta_{\ell}$ which occurs in the t-matrix. What is the significance of this? It seems to be connected with the socalled reaction matrix or <u>K-matrix</u> of the scattering centre which is defined by

$$K = \frac{T}{1 - i\kappa T}$$
(71)

with diagonal angular momentum representation

$$K_{\ell} = -\frac{1}{\kappa} \tan \eta_{\ell} \tag{72}$$

This signifies that we are interested, in our band structure problem, in states which are, so to speak, stationary and self-consistently diffracted by the lattice, and not with waves that appear from one direction, are scattered and then disappear again into the distance. It is, in fact, possible to set up the band-structure problem in ordered and disordered systems solely in terms of the K-matrices of the scattering spheres (de Dycker and Pharisea [13].

But if η_{ℓ} were to go through $\pi/2$, then tan η_{ℓ} would become infinite. According to the conventional theory of the K-matrix, this must occur when there is a resonance, or virtual level, of the muffin-tin potential. Consider, for example, the construction of such potentials for a metal such as Cu. The ordinary s and p levels disappear by the overlapping of neighbouring potentials, and hence give rise to a NFE band. But the radial equation for the d-level contains a centrifugal term

$$v_{\ell}(\mathbf{r}) = \frac{\ell(\ell+1)}{r^2}$$
(73)

which looks like a potential barrier. Even when the position of the original bound state is above the "muffin-tin zero", this barrier prevents free exit of the electron from the core; it must tunnel slowly through the barrier, and hence still preserves some characteristic properties of the original bound state from which it was derived.

In general, the phase shift in the neighbourhood of such a resonance behaves like

$$\tan \eta_{\ell} = \frac{\frac{1}{2}W}{\vartheta_{r} - \vartheta}, \qquad (74)$$

where \mathscr{E}_r is the energy of the resonance and W is its width (in fact, the reciprocal of the typical decay lifetime of the state). Such behaviour of the phase shifts in (57) (it is easy to show that $\tan \eta_l$ behaves in a parallel manner) has a profound effect on the band structure. Consider the sort of simple expression used in (64), i.e., a single plane wave affected by only the d-wave phase shift. We have

$$k^{2} \approx \mathscr{B} + \frac{2\pi N}{\kappa} \frac{W}{\mathscr{B}_{r} - \mathscr{B}}$$
(75)

for the wave vector of the state of energy \mathscr{E} .

Since k must be real - and not infinite - we find that the free electron curve is split, just as if it were crossed by a very narrow d-band with which it could "hybridize". This is only schematic, and ignores the

crystal structure, etc., but in fact the band structure of Cu is rather like this, with much more detail (Fig. 3).

Note an important elementary point (Ziman [14]). The position of the d-band relative to the s-p band depends essentially on the position of \mathscr{E}_r relative to \mathscr{E}_0 . But, as we have seen, \mathscr{E}_0 must lie a certain distance (defined, for example, by the Wigner-Seitz method) below the zero assumed for the muffin-tin potentials, which depends in its turn, on the details of the overlap of the external parts of the atomic potentials, and more especially on the approximation used to deal with electron-electron screening effects. On the other hand, \mathscr{O} , depends upon the potential deep in the core of the ion where such screening effects are not very important. Thus, the distance $\mathscr{C}_r - \mathscr{C}_0$, which determines the position of the whole d-band relative to the conduction band - a most important parameter in. say, the optical properties of the metal - is not naturally a stable quantity independent of the type of atomic potential used in the calculation: various authors have reported quite different calculated values of this feature of the band structure, without apparently having realized its origin.



The resonance scattering approach can be connected algebraically with the tight-binding and pseudopotential theories in a paper by Heine [15] to which reference should be made for the details. One finds that the secular determinant can be transformed into a mixed representation of the following form:

 $\det \begin{vmatrix} \mathbf{M}_{\vec{G}\vec{G}}^{*} & \gamma_{\vec{G}m}^{*} \\ \gamma_{\vec{G}m}^{*} & D_{mm} \end{vmatrix} = 0$

where $M_{\vec{G}\vec{G}'}^{i}$ is a NFE matrix in a finite set of reciprocal lattice vectors \vec{G} , \vec{G}' (e.g., 4×4).

 D_{mm} is a tight binding matrix involving mixing and overlap of various d-orbitals with various magnetic quantum numbers m (so this is 5×5 matrix).

 $\gamma !_{Gm}$, etc., is a matrix of hybridization coefficients mixing the d-states with the NFE type states.

This sort of expression was originally suggested as a parametrized model for the band structure of transition metals – but Heine's analysis gives it a solid basis as yet another algebraic representation of the "Greenian" formalism. But work is proceeding on such formulae and we have not yet had the latest word on the subject.

BAND STRUCTURE PROBLEM

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MANY-BODY THEORY

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Abstract

1. Introduction. 2. Elementary excitations or quasiparticles. 3. The modern theory of electrons in metals: the Landau theory of the Fermi liquid. 4. The many-body wave function and operators in second quantization. 5. Some useful results from general quantum mechanics. 6. How "Green" is my valley. 7. Some examples of Green's functions and their use. 8. Perturbation series expansions. The use of diagrams. 9. Green's functions and experiments: the driven response of a system. 11. Double-time Green functions and their equations of motion. 12. The dielectric function. 13. The one-electron Green function for an interacting Fermi gas.

1. INTRODUCTION

Solid state physics is a branch of science dealing with the properties of systems containing an enormous number of elementary particles organized in a coherent whole. In this way it is one of the fundamental branches of physics. The many-body aspects of the material world pose problems which are quite different in kind from those of, e.g., elementary particle physics. It may very well turn out to be the case that progress in the understanding of many-body systems will be of even greater significance to our knowledge of the world than further progress in elementary particle physics.

Obviously the complete solution of the many-body problem in the sense that the motion of all the particles in the system is determined is completely out of question. Fortunately, the observable macroscopic characteristics of a solid are determined by certain average properties of the system. Forming such averages implies that practically all of the enormous number of co-ordinates are eliminated from the description of the system. The physical properties related to observations thus depend on a small number of co-ordinates, and the primary task of any many-body theory is to find exact or approximate ways of reducing the full many-body problem to a problem of manageable size.

The main cause of the difficulties is that the many-particle Schrödinger equation is, from the mathematical standpoint, nonseparable and extremely complicated. This, in turn, is a reflection of the physical situation: the particles in the systems interact all the time and single-particle properties like wave function, energy etc. for an individual particle have no simple meaning; indeed only the states of the system as a whole have a precise meaning.

It must be clear from what has been said that the many-body problem can only be solved approximately. A number of approximate methods have been developed since the early days of quantum theory, such as the Thomas-Fermi method, the Hartree and Hartree-Fock approximation, the valence-band and molecular orbital approach for

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molecules etc. The key method used during the first few decades of quantum mechanics was the <u>independent-particle approximation</u>. This approximation implies the reduction of the N-body problem to N onebody problems. Each particle is considered as moving in the <u>average</u> field created by the other particles. This average field is of course itself determined by the motion of the particles, i.e. by the solution of the equations and therefore there is usually a self-consistency condition involved. Depending on the choice of self-consistent potential one obtains the Hartree theory, the Hartree-Fock theory or some more refined single-particle theory.

It should be remarked that the independent particle model has been and still is an enormously successful tool in describing many key properties of atoms, molecules, metals, semiconductors, insulators and even nuclei. In fact, most of our present understanding of electronic properties of solids has been almost exclusively based upon the oneelectron approximation. Indeed, e.g., for metals, it has been working almost too well and one of the important achievements of many-body theory of more recent date has been to explain why the one-electron theory works so well.

From the quantitative point of view the success of the older methods has been less tangible. This has been particularly true of the conventional perturbation methods. Such methods have been very unwieldy. One has run into severe technical difficulties, the region of applicability of the approximation has been difficult or impossible to assess and one has even run into divergence problems making the perturbation theory approach seemingly rather meaningless. Indeed, perturbations methods usually give divergent results unless infinite-order perturbation theory is used.

The remarkable progress in many-body theory over the past decade has been strongly dependent on the developments in field theory and particularly quantum electrodynamics in the late forties and early fifties. Relativistic quantum field theory was from the beginning facing severe convergence difficulties. Because of the extremely strong challenge to understand the fundamental properties of radiation and matter it is not surprising that the breakthrough in handling infiniteorder perturbation theory problems occurred in the field of elementary particles, notable through work by Dyson, Feynman, Schwinger, Tomonaga and others. The methods they developed are very general and their usefulness in the study of many-body problems was soon recognized. The first applications to solid state theory appeared by the middle of the fifties. (To my knowledge the very first one was a paper on the theory of superconductivity published in 1953 by the Director of this Institute, Professor A. Salam.)

Within the last decade a large number of formulations of the manybody problem have been published using a huge arsenal of different mathematical formulations: equation of motion methods, (canonical) transformation methods, e.g., to collective co-ordinates, density matrix formulations, time-independent and time-dependent perturbation methods often systematized by means of diagrammatic methods of which the Feynman diagrams, originally devised for quantum electrodynamics, are by far the most usual ones. The main role, however, is played by the so called Green's functions or propagators. They are essentially

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generalizations of the ordinary Green functions in the elementary treatments of differential and integral equations. They form the basic element of the field theoretical description and contain considerable information about the system, which can be calculated from it in a rather straightforward way. There is a variety of Green's functions: advanced, retarded, causal, zero-temperature, finite-temperature, real-time, imaginary-time; there are Green's functions for 1 particle. 2 particles, n particles. This enormous assortment will together match every possible situation and need (but with no promise that you can actually solve the equations). The key part in any contemporary formulation of many-body theory is the method of second quantization. This method, which today seems to be the superior method to study many-body problems, was developed in the very early days of quantum theory, when the conventional configuration space description to manyparticle problems was still in its infancy. In the method of second quantization the concept of a particle is less prominent and is taken over by the concept of a complex quantized field $\psi(x)$, $\psi^*(x)$ (the particle creation and annihilation operators); the particles themselves appear as field quanta. The method is particularly well adapted to discuss the probably most important many-body concept - elementary excitations or quasiparticles, which will be introduced in the next section.

I have no intention to try to explain all the different formulations currently in use in my lectures. They have, however, a common central core of very useful concepts which I shall try to explain in as simple terms as I can and show how they work in some applications to solids. The discussion will be largely intuitive and on an elementary level. They are in fact just meant as an appetizer preceding a study of the more technical and mathematical aspects of the theory. The mathematics of most realistic many-body situations is by and large "experimental", which I take as a further excuse for sacrificing mathematical details and completeness.

2. ELEMENTARY EXCITATIONS OR QUASI-PARTICLES

Many important aspects of solids can be conveniently discussed in terms of particularly simple kinds of motion in which the system behaves approximately as a collection of independent, or more or less collectively acting entities, - the <u>quasi-particle or elementary excitations</u>. They have a direct experimental significance and can be observed, e.g., by scattering experiments and they are also of great importance in discussing the thermodynamic properties. The language of many-body theory is particularly well adapted to investigate the properties of elementary excitations. However, already before going into the many-body theory I would like to start with a purely descriptive discussion of elementary excitations in order to introduce the key objects with which the theory has currently been concerned.

To be explicit, let us consider the thermodynamic properties of a solid. As is familiar, from statistical physics, the thermodynamic quantities can be calculated if the <u>energy levels</u> of the system are known, by calculating the partition function in e.g., the canonical distribution

$$Z = \sum_{n} e^{-E_{n}/k_{B}T}$$
(2.1)
In the case of an ideal gas the energy of the system is just the sum of the energies of the separate particles, and the problem then reduces to find the energies of a single particle. In general, however, it is impossible to determine the energy levels of a system consisting of a large number of interacting particles. There are a few exceptions, and an important one is the case of low temperatures. In this region only the weakly excited states are important, i.e., the states whose energies differ only very little from energy of the ground state. The excited states in a solid have the form of waves (propagating or standing). They have a definite excitation energy which depends on the wavelength of the wave. For weakly excited states these waves will interact only little, and so the excitation energy will just be the sum of the energies of the waves which are excited. This means that energy levels have the same form as for an ideal gas, only with the important difference that the energy of the wave may often refer to a motion of a large number of particles, i.e., the wave describes a collective type of motion, rather than the motion of a simple particle. A sound wave is a good example of such a wave motion. These waves of excitations are what we call the elementary excitations of the solids and some types deserve the popular name quasi-particles. Some people reserve the name quasiparticle for excitations which behave like particles (often so-called dressed particles), whereas other people use the term even for excitations which are predominantly collective in nature, i.e., motions of macroscopic groups of particles in the system.

We shall list the common types of elementary excitations below and describe their properties. Later on in this lecture we shall discuss how the reality of these concepts can be demonstrated directly from experiments.

a) Phonons

Consider for example the well-known case of a one-dimensional chain of atoms coupled by nearest-neighbour elastic forces (see, e.g., Kittel [1]). One starts from the coupled equations for the individual atoms:

$$M \ddot{u}_{n} = \beta (u_{n+1} + u_{n-1} - 2u_{n})$$
(2.2)

where β is the force constant and M the atomic mass. Then one passes from a <u>particle picture</u> to a wave picture by looking for solutions in the form of a wave number k and frequency ω :

$$u_n = u_0 e^{i (kna - \omega t)}$$
(2.3)

The solution gives the eigenfrequencies as a function of k, that is the dispersion relation for the lattice waves

$$\omega = \sqrt{\frac{4\beta}{M}} \sin \frac{ka}{2}$$
 (2.4)

Introducing boundary conditions one translates the whole description of N individual particles into a description involving N independent waves each characterized by its energy $\omega = \omega(k)$. Each such wave behaves like a harmonic oscillator and its energy levels are given by elementary quantum mechanics.

The same arguments apply to a three-dimensional crystal. We obtain a system of 3N linear wave oscillators with characteristic frequencies ω_i and the energy spectrum is given by the formula

$$\mathbf{E} = \mathbf{E}_0 + \sum_i \hbar \omega_i \left(n_i + \frac{1}{2} \right)$$
(2.5)

where n_i are the quantum numbers of the oscillator i and various sets of n_i correspond to various energy levels of the system. The vibrations of the lattice are here described as a superposition of monochromatic waves propagating in the crystal. Each wave is characterized by a wave vector \vec{k} and a frequency ω and also by an index s specifying the type (polarization) of the wave.

We now recall that <u>light</u> waves can be regarded either as electromagnetic waves or as consisting of "particles" (quanta), called <u>photons</u>, each of them having energy $\hbar\omega$. We apply the same type of reasoning to the lattice waves: We consider the lattice wave i.

In a state with energy

$$\mathbf{E}_{i} = \hbar\omega_{i} \left(n_{i} + \frac{1}{2} \right) \tag{2.6}$$

we can, in analogy with photons, consider it as $\underline{n_i}$ quanta each having energy $\hbar\omega_i$. These quanta of the lattice waves are the phonons, and we say that we have $\underline{n_i}$ phonons of frequency ω_i present in the state given above.

Thus the elementary excitations of the lattice motion are the <u>phonons</u>. We emphasize that the phonons are a good example of a <u>collective</u> motion. It follows from the standard treatment of the thermodynamics of lattice vibrations that the phonons obey <u>Bose statistics</u> (see, e.g. [1]). In the limit of long wave-lengths the phonons correspond to sound waves in an anisotropic continuum, i.e., they have a classical counterpart in this limit.

Typical phonon energies are of the order $k_B \theta_D (k_B = Boltzmann's constant, \theta_D = Debye temperature \approx room temperature for most materials). Thus the energies are of the order 0.025 eV and the corresponding frequencies are of the order of <math>10^{13} \text{ s}^{-1}$ or less.

b) Magnons

They are the quanta of <u>spin waves</u>. In a solid with atoms having unfilled inner shells the electrons may have a resulting magnetic moment, which is approximately localized on the atom. In the ground state of a ferromagnetic crystal all the spins are pointing in the same direction. The lowest excited states correspond to deviating just one spin from the preferred direction. However, the spin interacts with the spins on

neighbouring atoms and so the deviating spin may jump to a neighbouring site. This coupling to the neighbouring spins is the analog to the elastic force in lattice vibrations. The coupling between spins means that the deviating spin cannot stay localized on the atom, but has a tendency to move, and by arguments in complete analogy with lattice vibrations one finds that the elementary motions have the form of waves. Thus the low-lying excited states of coupled spins are spin waves.

The quanta of the spin waves are called <u>magnons</u>, and they act like bosons. Obviously, the spin waves are examples of collective modes involving a macroscopic number of atoms. In the long-wave length limit the magnons correspond to classical waves of the magnetization in the solid.

There are spin waves of similar characteristics also in the itinerant electron theory of ferromagnetism as well as in anti-ferromagnets and in ferrites. Typically magnons have frequencies in the microwave range ($\sim 10^{10} \text{ s}^{-1}$) and thus their energies are of order of $5 \times 10^{-5} \text{ eV}$.

c) Plasmons

Let us consider wave-like fluctuations of the electron density of the electron gas in a metal (similar to sound waves, but with the positive ions not participating). Because of the long-range Coulomb force any deviation from charge neutrality gives rise to an unbalanced electric field, which gives strong restoring forces and so the frequency of the motion will be finite (and high) even for very long wavelengths. These oscillations are known as <u>plasma oscillations</u> and the corresponding quanta are the plasmons and behave like bosons.

Plasmons were first discussed in the classical case, e.g., in the case of ionized gases. By suitable doping of a pure semiconductor one can produce solid-state plasmas within a wide range of densities from the low-density limit where the plasma is described by classical Boltzmann statistics to the high-density case where the electrons are completely or almost completely degenerate. Solid state physics has in this way offered the best possibilities of studying under varying conditions the many interesting properties of plasmas.

In semiconductors the plasma frequency is in the range from microwaves to infra-red depending on the degree of doping. In good metals the plasma frequency is of the order $10^{15} - 10^{16}$ s⁻¹, corresponding to energies of order of 20 eV. This high energy means that plasmons are not excited at ordinary temperatures and therefore play no direct role in the thermodynamics of electrons in metals.

d) Electrons (quasi-electrons)

They are the elementary excitations, which behave very much like free electrons. However, they also include the interaction with the electrons in the neighbourhood as well as with the phonons. An electron in an electron gas repels the other electrons and thus surrounds itself with a positive screening cloud. The bare electron plus its screening cloud constitutes the quasi-electron. The effective interaction between two quasi-electrons is a screened interaction which is of much shorter

range than the bare Coulomb interaction. What are usually treated as the quasi-electrons are the weakly excited states of the conduction electrons. When electrons are in the ground state (T = 0) they fill the Fermi sea, this state is often referred to as the "vacuum". When an electron is taken out of the Fermi sea, one speaks of creating a quasi-electron. Thermal excitation corresponds to increasing the energies of the electrons near the Fermi surface by an amount of order $k_{\rm B}T$, which is indeed a weak excitation relative to the total energy of the electron ($\Delta E/E \approx 10^{-2}$ at room temperature in good metals).

The average energy of conduction electrons in metals is of the order of several electron volts. This corresponds to very high velocities of the order of 10^8 cm/s. Quasi-electrons are fermions.

e) Holes

Holes can be characterized as the absence of a quasi-electron in a state which is normally occupied by an electron. Thus if we create an electron by raising it out of the Fermi sea, we leave behind a hole. Electrons and holes are of equal importance when discussing electronic excitations, e.g., in connection with optical properties or thermodynamics of the solid.

f) Polaron

is an electron moving through a polar insulating crystal and interacting with the ions of the host lattice. This interaction causes a polarization around the electron, which is formally described by means of a local excitation of phonons. The polaron is thus a bare electron surrounded by a cloud of phonons.

g) Exciton

is a bound electron-hole pair which moves as an entity in a wave-like manner through the crystal. If the distance between the electron and hole is small (so that they are essentially on the same atom) we talk about a <u>Frenkel exciton</u>, if it is loosely bound (=large distance of separation) we talk about a Wannier exciton. Excitons behave like bosons.

h) Bogolon or Bogolyubov quasi-particle

is the elementary excitation in a superconductor. It consists of a linear combination of one electron in state ($+\vec{k}$, spin up) and another in state ($-\vec{k}$, spin down).

Localized excitations

In a lattice with imperfections the elementary excitations will be scattered by the imperfection. If the interaction is strong enough we may have new states appearing in which the motion is essentially localized to a finite region of space surrounding the impurity. Such states can appear either as strictly bound states falling outside the usual continuous band of excitations, or, they can appear as strong resonances or virtual

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states within the band. All the elementary excitations just mentioned may, in principle, occur as localized excitations. Localized phonons, magnons and excitons are, at present, of much interest both experimentally and theoretically, whereas varieties like localized plasmons and polarons seem somewhat controversial.

This brief discussion of the most common types of elementary excitations shows that it is often possible to perform a transformation (here unspecified) from a system of strongly interacting particles to a set of approximately non-interacting modes of motion which we call elementary excitations or quasi-particles. These elementary excitations do not correspond to exact states of the system but do instead represent wave packets, i.e., superpositions of eigenstates with a reasonable spread in energy. As a result we have a non-vanishing probability for transition out of such wave packet states and this leads to an attenuation or damping of the elementary excitation. This implies that the description in terms of elementary excitations requires the width of the wave packet to be small compared with its energy. The spread of the wave packet can be considered as the result of interaction processes between the quasi-particles during which the laws of energy and momentum conservation are satisfied. Such processes can be divided into processes in which excitations are scattered by each other and processes in which an excitation decays into several others. If we consider low temperatures, only low-lying excitations are present and there are few of them. The mechanism for damping is then ineffective for scattering as well as decay. The interaction between excitations is accordingly weak, so that we can regard them as an almost ideal gas of quasi-particles. At higher temperatures there are more excitations present, their average interaction will be stronger, the width will increase and raising the temperature further will imply that the picture of a gas of independent elementary excitations will gradually lose its meaning. The concept of elementary excitation is indeed a useful one only when we have a reasonably small number of elementary excitations present at a time.

The concept of elementary excitation is particularly useful when considering the interaction between a solid and external field and their quanta. The most striking evidence for the existence of elementary excitation is obtained from experiments involving external probes such as electromagnetic waves, thermal neutrons, beams of charged particles, etc. The experiment can be, e.g., an inelastic scattering event in which an elementary excitation is created or annihilated and the characteristics of the elementary excitation are determined from an analysis of the energy and momentum of the outgoing external wave or particle.

Neutron scattering and interaction with electromagnetic waves (Brillouin and Raman scattering) are of this type. Another type occurs when a quantum of the incident radiation is absorbed, such as in the infrared absorption of light in polar crystals.

The fundamentals of the interaction between a solid and an external field are best understood if we take a specific example such as non-magnetic inelastic neutron scattering. Let \vec{q} be the wave vector and $\omega_i(\vec{q})$ the frequency of a phonon in the branch i. Let \vec{k}_0 be the momentum of the incoming neutron and \vec{k} its momentum after the scattering has taken place. In the scattering process involving a single phonon the

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energy is conserved so that

$$\frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 k^2}{2m} \pm \hbar \omega_i(\vec{q})$$
(2.7)

(plus if a phonon is emitted and minus if a phonon has been absorbed). In addition to energy conservation we have a condition imposed on the momenta involved. Because of the periodic structure of the medium in which the elementary process occurs (which implies periodicity properties also in momentum space, e.g., that $\omega(\vec{q}) = \omega(\vec{q} + \vec{\tau})$) momentum is conserved only up to an arbitrary reciprocal lattice vector $\vec{\tau}$. Thus, the momentum law in a lattice takes the form

$$\vec{k}_0 = \vec{k} \pm \vec{q} + \vec{\tau}$$

The energy and momentum relations imply that for a given direction of the scattering neutrons, they will only appear with discrete energies corresponding to the possible values of $\omega_i(\vec{q})$. By varying the direction and increasing the energies at which neutrons appear, one obtains a mapping of the dispersion relation $\omega_i(\vec{q})$, i.e., one determines the energy versus momentum for the phonons. In the simple picture described here, one would obtain infinitely sharp lines. In reality the phonons are damped and in several good recent experiments one has indeed determined the width of the phonon lines and its temperature dependence. Many-body theory indicates that even the phonon lines may show some interesting structure.

Considerations as those indicated here will also hold for other types of elementary excitations. The elementary excitations, thus, are objects of good physical significance, and experimental investigations of their energies, widths and structure of the lines are most valuable for the understanding of the microscopic dynamics in solids.

3. THE MODERN THEORY OF ELECTRONS IN METALS: THE LANDAU THEORY OF THE FERMI LIQUID

We mentioned in passing that the independent particle model has been extremely successful in describing the properties of conduction electrons in metals. In the one-electron theory each electron has an energy versus wave-number relation $\epsilon = \epsilon(\vec{k})$ (we do not consider the spin explicitly in this discussion). In the ground state the single particle states are filled with two electrons per level (if no magnetic field is present) up to a highest level, the Fermi level ϵ_F . The relation $\epsilon_F = \epsilon(\vec{k})$ defines a surface in k-space - the Fermi surface. At finite temperature the distribution over single-particle states is described by the Fermi distribution function and for good metals we are always in the region of almost complete degeneracy, i.e., $k_B T \ll \epsilon_F$. From this follows a number of properties, e.g., that the specific heat of the conduction electrons is proportional to the temperature and that the spin susceptibility is to leading order independent of the temperature and that both of these properties are related to the density of states at the Fermi level. Furthermore, the one-electron theory is used as starting point for non-

equilibrium properties, in particular transport properties. The motion in the presence of external fields or thermal forces is described by a perturbed distribution function for the electrons, which satisfies a Boltzmann transport equation, from which the transport coefficient then can be calculated.

From the experimental side most of the qualitative features of the one-electron theory are extremely well verified. The existence of a sharp Fermi surface in metals has been demonstrated with several different experimental methods and the determination of shape and size of Fermi surfaces has developed into the noble art of "fermiology". The linear law of the specific heat, the temperature independence of the spin susceptibility as well as the gross features of transport phenomena in metals are in good accordance with experimental facts. Therefore, these key results of one-electron theory are indeed facts of life, and are with us to stay.

From a theoretical point of view it is indeed puzzling that the oneelectron theory works at all for metals. Already Wigner and Seitz in their pioneering work on metallic cohesion observed that there must be an appreciable correlation in the motion of the electrons because of the repulsive Coulomb interaction, Wigner made an approximate calculation of the effect, showing that the correlation energy gives a considerable contribution to the cohesive energy, that can by no means be neglected. We would like to comment here that ordinary perturbation theory cannot at all be used to calculate the contribution to the energy from the Coulomb interaction: The first order perturbation gives a finite result but from then on each individual order in perturbation theory simply diverges, representing a complete breakdown in the straightforward approach.

In the one-electron picture the conduction electrons are described as an ideal gas of fermions. Because of the ever-present interaction this picture represents a tremendous oversimplification and one uses the term <u>Fermi liquid</u> for such a system, the best known examples being He³ and metals. Around ten years ago Landau developed, with remarkable intuition and insight, the theory of the Fermi liquid. His first papers assumed a short-range interaction between the particles, but with appropriate modifications the theory is equally valid for conduction electrons in metals, including also, e.g., effects due to electron-phonon interaction. In this section we shall present those aspects of the theory, which are particularly relevant for these lectures. Landau's theory is phenomenological in the sense that the theory contains certain parameters. The parameters can only be calculated using the full machinery of manybody theory, which also has to provide the formal justification for the basic assumptions in the theory.

We shall present the theory in the simplest form, where we assume full translational invariance of the system. In a real metal, of course, the electrons move in a periodic potential. The main differences between the uniform model and a periodic lattice are the following: (a) the plane waves describing particles moving in a uniform system have to be replaced by Bloch wave functions, (b) the energy of a free electron $\epsilon = \hbar^2 k^2/2m$ has to be replaced by a general dispersion curve $\epsilon = \epsilon(k)$ or, if only effects close to the Fermi surface are being discussed, the mass m of a free electron has to be replaced by the band mass m_{band} . The discussion is restricted to what we call a <u>normal Fermi</u> system, which we shall a bit loosely define as a system that behaves somewhat like a system of non-interacting fermions. To be only slightly more explicit: Let us imagine that we start from the non-interacting system and slowly turn on the interaction. If there is a mapping of the states of the non-interacting system onto the states of the interacting system so that, e.g., the ground state of the non-interacting system is transformed into the ground state of the interacting system, then the system is said to be normal. We can visualize this process as one in which we start from the bare electrons in the metal and by switching on the interaction slowly we gradually "dress" the electrons so that finally we have fully dressed electrons or quasi-particles of the system.

Next we formulate the key postulates of the Landau theory:

- i) The single particle labels for wave number and spin $(\vec{k}, \sigma) = k$ are still good quantum numbers.
- ii) There exists a single particle dispersion curve $\epsilon = \epsilon(k)$.
- iii) The state of the system can be characterized by a single particle distribution function n_k , giving the average occupation of the single particle state k.
- iv) There are as many quasi-particles as there are bare particles, which implies the normalization $N = \sum_{k} n_{k}$, N being the total number

of electrons in the system.

v) The total energy E of the system is a functional of the distribution of quasi-particles, i.e., $E = E(\{n_k\})$.

It is important to note that the total internal energy E of the liquid does not reduce to the sum of the energies of the quasi-particles. In fact E represents a general functional as indicated inv). However, for weak excitations, the difference in energy when we consider an infinitesimal change of the distribution

$$\delta n_k = n_k - n_k^0 \tag{3.1}$$

 n_k^0 being the unperturbed distribution, can be written in the form

$$\delta \mathbf{E} = \sum_{k} \epsilon(\mathbf{k}) \, \delta \mathbf{n}_{\mathbf{k}} \tag{3.2}$$

This relation defines the quasi-particle energy as the derivative of the energy with respect to the distribution function, i.e.,

$$\epsilon(\mathbf{k}) = \frac{\partial \mathbf{E}}{\partial n_{\mathbf{k}}} \tag{3.3}$$

Thus the quasi-particle energy $\epsilon(k)$ is the change in the total energy E when we add one quasi-particle with wave number and spin \vec{k} , σ to the system. It is important to observe, however, that $\epsilon(k)$ is itself a functional of the distribution,

$$\epsilon(\mathbf{k}) = \epsilon(\mathbf{k}, \{\mathbf{n}_{\mathbf{k}'}\})$$

so that $\epsilon(k)$ is only known when the distribution of all the quasi-particles in the system is given.

In most cases of interest we must go one step further in expanding the change in energy because we must know the change in the quasiparticle energy $\epsilon(k)$ when we change the distribution of quasi-particles. We therefore write

$$\delta \mathbf{E} = \mathbf{E}(\{\mathbf{n}_{k}\}) - \mathbf{E}(\{\mathbf{n}_{k}^{0}\}) = \sum_{k} \left(\frac{\partial \mathbf{E}}{\partial \mathbf{n}_{k}}\right) \delta \mathbf{n}_{k}$$

$$+ \frac{1}{2} \sum_{kk'} \left(\frac{\partial^{2} \mathbf{E}}{\partial \mathbf{n}_{k} \partial \mathbf{n}_{k'}}\right)_{0} \delta \mathbf{n}_{k} \delta \mathbf{n}_{k'} + \dots \qquad (3.4)$$

$$= \sum_{k} \epsilon_{0}(\mathbf{k}) \delta \mathbf{n}_{k} + \frac{1}{2} \sum_{k} \sum_{k'} f(\mathbf{k}, \mathbf{k'}) \delta \mathbf{n}_{k} \delta \mathbf{n}_{k'} + \dots$$

This formula defines a new quantity

$$f(k, k') = \left(\frac{\partial^2 E}{\partial n_k \partial n_{k'}}\right)_0$$
(3.5)

with the property

$$f(k, k') = f(k', k)$$

f(k, k') has obviously the meaning of an interaction energy between quasi-particles of wave-number spin k. It is referred to as the <u>quasi-particle interaction</u> and plays a fundamental role in the Landau theory.

According to $(3.4) \epsilon_0(k)$ is the energy of the quasi-particle when it is present alone; to be precise, if we have added just one particle to the system, all the rest being in the ground state configuration described by n_k^0 . If we have other excitations present, i.e., adding more particles and considering excited states of the system, we must calculate the energy for a quasi-particle imbedded in a gas of other excitations described by δn_k . According to Eq.(3.4) its energy becomes

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + \sum_{\mathbf{k}'} f(\mathbf{k}, \mathbf{k}') \delta n_{\mathbf{k}'}$$
(3.6)

The quantities $\epsilon_0(k)$ and f(k, k') are the basic parameters of the Landau theory and they are assumed to be known in the phenomenological theory. The quantity $\epsilon_0(k)$ is what we should identify with the dispersion curve from an energy band calculation. The quasi-particle interaction is a screened short-range interaction that can, at least in principle, be calculated by using the methods of many-body theory.

We shall first discuss the <u>equilibrium distribution</u> of the quasiparticles which can be obtained in a straightforward way. We just recall one of the basic assumptions: that there is a one-to-one correspondence between the states of the interacting system and the states of the ideal Fermi gas. Thus, the classification and enumeration of states are identically the same. Since the entropy depends only on the counting of quantum levels (a purely combinatorial problem), it will then have the same form as the entropy of an ideal gas of fermions, namely:

$$S = -k_{B_{k}} \left\{ n_{k} \ln n_{k} + (1 - n_{k}) \ln (1 - n_{k}) \right\}$$
(3.7)

The equilibrium distribution is determined from the condition that the entropy should be a maximum with the constraints that the number of particles and the energy is conserved, i.e., when the following three relations hold:

$$\delta S = \delta E = \delta N = 0 \tag{3.8}$$

These three relations are identical in form with those for an ideal Fermi gas, and so the solution is formally the same:

$$n_{k} = \frac{1}{\frac{\epsilon(k) - \mu}{e^{\frac{k}{B}T} + 1}}$$
(3.9)

Although of the same form as the Fermi distribution, (3.9) is strictly speaking a very complicated implicit relation because the quasiparticle energies themselves depend on the distribution.

Let us consider the case corresponding to complete or almost complete degeneracy in the Fermi gas, $k_BT \ll \mu$. Assuming that there is no violent dependence on distributions in the single-particle energies $\epsilon(k)$, we notice that in the limit when T goes to zero, we shall approach the step-function distribution as in an ideal Fermi gas.

This defines a Fermi surface S_F in momentum space also for the interacting system, which is given by the relation $\epsilon(k) = \mu$. Since the ground state for the N+1 particle system is obtained by adding a quasiparticle at the Fermi surface, μ will be equal to the chemical potential. We refer to μ as the Fermi energy also in the interacting case and shall often use the alternative symbol ϵ_F for it.

Most of the successful applications to metals are concerned with the study of quasi-particles close to the Fermi surface. If no magnetic field is present the quasi-particle energy will only depend upon momentum \vec{p} and in our isotropic model only on its magnitude $|\vec{p}|$. The velocity (group velocity) of the quasi-particle is given by

$$\vec{\nabla} = \nabla_{\vec{p}} \epsilon(\vec{p})$$

For isotropic systems \vec{V} and \vec{p} are collinear and therefore we can write on the Fermi surface

$$\vec{v}_{\rm F} = \frac{{\rm p}_{\rm F}}{{\rm m}^*} \tag{3.10}$$

where m* is the effective mass of the quasi-particle.

A considerable simplification is also possible for the quasi-particle interaction f(k, k') if we restrict ourselves to the region very near the Fermi surface. Both \vec{k} and k' will then have the absolute magnitude k_f and for an isotropic system f(k, k') will only be a function of the angle θ between \vec{k} and $\vec{k'}$ so that $f(k, k') = f(\theta)$.

To summarize the last few paragraphs: For Fermi surface phenomena the parameters $\epsilon_0(k)$ and f(k, k') are replaced by the effective mass m^{*} and $f(\theta)$ – of the latter, essentially only the first few coefficients in a Legendre polynomial expansion will be needed.

As shown by Landau, there is a definite connection between the effective mass m^* and the quasi-particle interaction f, that follows from the Galilean invariance of a uniform system: The momentum of a unit volume must be equal to the flow of mass. The momentum of the liquid equals the total momentum of the quasi-particles, i.e.,

 $2\sum_{\vec{p}} \vec{p} n(\vec{p})$. The mass flow, on the other hand, must be determined by

the current of quasi-particles, which is given by

$$2\sum_{\overrightarrow{p}} \vec{V}_{\overrightarrow{p}} n(\overrightarrow{p}) = 2\sum_{\overrightarrow{p}} \nabla_{\overrightarrow{p}} \epsilon(\overrightarrow{p}) n(\overrightarrow{p})$$

Galilean invariance requires that

$$\sum_{\vec{p}} \vec{p} n(\vec{p}) = \sum_{\vec{p}} m \nabla_{\vec{p}} \epsilon(\vec{p}) n(\vec{p})$$
(3.11)

Let us now consider an infinitesimal change in the distribution function, remembering that the quasi-particle energies change according to

$$\delta \in (\vec{p}) = \sum_{p'} f(\vec{p}, \vec{p}') \delta n(\vec{p}')$$

From (3.11) we obtain that

$$\sum_{\vec{p}} \frac{\vec{p}}{m} \delta n(\vec{p}) = \sum_{p} \nabla_{\vec{p}} \epsilon(\vec{p}) \delta n(\vec{p}) + \sum_{p} \sum_{p'} \nabla_{\vec{p}} f(\vec{p}, \vec{p'}) \delta \vec{n}(p') n(\vec{p})$$
$$= \sum_{p} \nabla_{\vec{p}} \epsilon(\vec{p}) \delta n(\vec{p}) - \sum_{p} \sum_{p'} f(\vec{p}, \vec{p'}) \nabla_{\vec{p}} n(\vec{p}) \delta n(\vec{p'}) \qquad (3.12)$$
$$= \sum_{p} \nabla_{\vec{p'}} \epsilon(\vec{p}) \delta n(\vec{p}) - \sum_{p} \sum_{p'} f(\vec{p}, \vec{p'}) \nabla_{\vec{p}} n(\vec{p'}) \delta n(\vec{p'})$$

Since δn is arbitrary the result is that

$$\frac{\vec{p}}{m} = \nabla_{\vec{p}} \epsilon(\vec{p}) - \sum_{\vec{p}'} f(\vec{p}, \vec{p}') \nabla_{\vec{p}} n(\vec{p}')$$
(3.13)

As already mentioned we are mainly interested in quasi-particles at or near the Fermi surface and temperatures low compared with the Fermi temperature. We then have that

$$\nabla_{\vec{p}} \epsilon(\vec{p}) = \vec{V} = \frac{\vec{p}}{m^*}$$

and

$$\nabla_{\vec{p}} n(\vec{p}) \cong - \frac{\vec{p}}{|\vec{p}|} \delta(|\vec{p}| - p_F)$$

Passing from summation to integration by using $\sum_{\vec{p}\sigma} = 2V \int \frac{d^3p}{(2\pi\hbar)^3}$ we obtain

$$\sum_{\mathbf{p'}} \mathbf{f}(\vec{\mathbf{p}}, \vec{\mathbf{p'}}) \nabla_{\vec{\mathbf{p}}} \mathbf{n}(\vec{\mathbf{p'}}) = \mathbf{V} \int \frac{2\mathbf{p'}^2 \, d\mathbf{p'} \, \mathrm{d}\, \Omega'}{(2\pi\hbar)^3} \mathbf{f}(\vec{\mathbf{p}}, \vec{\mathbf{p'}}) \nabla_{\vec{\mathbf{p}}} \mathbf{n}(\vec{\mathbf{p'}}) = \frac{-2\mathbf{p}_F}{(2\pi\hbar)^3} \mathbf{V} \int \mathbf{f}(\theta) \vec{\mathbf{p}}_F \, \mathrm{d}\, \Omega'$$

 $d\Omega'$ being the element of solid angle. Multiplying (3.13) by \vec{p} and dividing by p_F^2 , we obtain the Landau relation between the mass m, the effective mass m^{*} and the interaction function $f(\theta)$:

$$\frac{1}{m} = \frac{1}{m^*} + \frac{2p_F}{(2\pi\hbar)^3} \nabla \int f(\theta) \cos\theta \, d\Omega$$
(3.14)

In a real metal we do not have Galilean invariance but only the invariance under lattice translations. I am not aware of any analogue of (3.14) for the case of periodic systems.

We wish to give just a few results of the Landau theory to show how the theory works. A very thorough discussion is given by Pines and Nozières [2], to which I refer for further study.

Let us first consider the <u>specific heat</u> at constant volume. We obtain in a straightforward and rather self-explanatory manner that

$$C_{V} = \frac{\partial E}{\partial T} \bigg|_{V} = \frac{\partial}{\partial T} \left\{ E(\{n_{k}^{0}\}) + \sum_{k} \epsilon(k) \delta n_{k} \right\}$$
$$= \frac{\partial}{\partial T} \left\{ E(\{n_{k}^{0}\}) + \sum_{k} \epsilon(k)(n_{k} - n_{k}^{0}) \right\} = \frac{\partial}{\partial T} \sum_{k} \epsilon(k)n_{k}$$
$$\simeq \sum_{k} \epsilon_{0}(k) \frac{\partial n_{k}}{\partial T}$$

to leading order in the temperature dependence. From the last step the calculation is identical with that for an ideal gas of fermions and we obtain

$$C_{V} = \frac{1}{3} k_{B}^{2} \frac{m^{*} p_{F}}{\hbar^{3}} T$$
 (3.15)

Thus, the specific heat has the same form as for the ideal gas but with m^* replacing the bare mass m. Actually, the specific heat is related to the density of states rather than to a dynamical mass and we also give the alternative form

$$C_{V} = \frac{1}{3} \pi^{2} k_{B}^{2} N(\epsilon_{F}) T$$
 (3.16)

where $N(\epsilon_{F})$ is the density of states at the Fermi level.

We next proceed to calculate the <u>compressibility</u> of the system, or, what amounts to the same, the velocity of sound. The pressure is defined as

$$P = -\frac{\partial E}{\partial V}$$

and the compressibility by

$$\frac{1}{\kappa} = -V \frac{\partial \dot{P}}{\partial V}$$

The mass density of the system is $\rho = Nm/V$ and the square of the sound velocity s is

$$s^2 = \frac{\partial P}{\partial \rho} = -\frac{V^2}{Nm} \frac{\partial P}{\partial V}$$

We prefer not to try to calculate directly the change in total energy when we change the volume of the system. Instead we use the Duhem relation of thermodynamics, which for dT = 0 gives that $Nd\mu$ = -Vdp. Now the chemical potential μ depends on N and V only through the ratio $\frac{N}{V}$ so that

$$\frac{\partial \mu}{\partial N} = -\frac{V}{N} \frac{\partial \mu}{\partial V} = -\frac{V^2}{N^2} \frac{\partial P}{\partial V}$$

 $s^2 = \frac{N}{m} \frac{\partial \mu}{\partial N}$

and thus

We now have to calculate the change in the chemical potential when we change the number of particles. This causes a shift in the Fermi momentum and hence in the distribution function. μ changes for two

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reasons: (a) the Fermi energy changes when we change the radius of the Fermi sphere, (b) the interaction energy changes when we change the distribution. Thus

$$\delta \mu = \frac{\partial \epsilon_{\rm F}}{\partial p_{\rm F}} \delta p_{\rm F} + \sum_{\rm p^*} f(p, p^{\rm t}) \delta n_{\rm p^{\rm t}}$$

The density of quantum states in momentum space relates δp_F and δN :

$$2 \frac{4\pi p_F^2 \delta p_F}{(2\pi\hbar)^3} = \frac{\delta N}{V}$$

Next we calculate the change in interaction energy

$$\sum_{p'} f(p, p') \delta n_{p'} \simeq V \int f(p, p') d\Omega' \frac{2p_F^2 \delta p_F}{(2\pi\hbar)^3}$$
$$= \int f(p, p') \frac{d\Omega'}{4\pi} \frac{\delta N}{V}$$

Using $\frac{\partial \epsilon_F}{\partial p_F} = \frac{p_F}{m^*}$ we find that

$$\frac{\partial \mu}{\partial N} = \frac{(2\pi\hbar)^3}{8\pi p_F m^* V} + \frac{1}{V} V \int f(\mathbf{p}, \mathbf{p'}) \frac{d\Omega'}{4\pi}$$

Finally we use the Landau formula (3.14) for m^{*} and multiply by

$$\frac{N}{m} = \frac{2}{3} \frac{4\pi p_F^3}{(2\pi\hbar)^3} \frac{V}{m}$$

to obtain the final formula

$$s^{2} = \frac{p_{F}^{2}}{3m^{2}} + \frac{2}{3m} \left(\frac{p_{F}}{2\pi\hbar}\right)^{3} V \int d\Omega f(\theta) (1 - \cos\theta) \qquad (3.17)$$

The first term gives the result for an ideal gas and the second term gives an important contribution from the interaction.

In the case of non-interacting fermions the <u>spin susceptibility</u> is only related to the density of states, which is no longer true in an interacting system. When we apply a magnetic field we create an unbalanced distribution of spins. This is important because the effective interaction is spin-dependent. Even if the fundamental interaction between the

particles does not depend on spin, the exclusion principle will give rise to a spin dependence in the effective interaction. We must therefore write

$$f(\vec{p}\sigma, \vec{p}'\sigma') = f_o(\vec{p}, \vec{p}') + \delta_{\sigma\sigma'} f_e(\vec{p}, \vec{p}')$$

The term f_e , which occurs only when the spins are parallel, is the <u>effective exchange interaction</u> between quasi-particles. If we apply a magnetic field the single particle levels will shift by an amount of $\pm\beta H$, where $\beta = e\hbar/2mc$ (minus or plus for spins parallel or antiparallel to the field). The readjustment of the distribution will give an additional shift and the total shift of the level \vec{p} , σ is given by

$$\delta \epsilon(\mathbf{p}) = \pm \beta H + \sum_{\mathbf{p}'} f(\mathbf{p}, \mathbf{p}') \delta n(\mathbf{p}')$$

The shift in the distribution of the electrons is illustrated in Fig.1.



FIG.1. The distribution of electrons of different spins in the presence of a magnetic field.

The change in the Fermi momentum is of the absolute magnitude

$$\left| \delta \mathbf{p}_{\mathrm{F}} \right| = \frac{\left| \delta \epsilon \right|}{\mathrm{v}_{\mathrm{F}}} = \frac{\mathrm{m}^{*}}{\mathrm{p}_{\mathrm{F}}} \left| \delta \epsilon \right|$$

and in good metals $\delta p_F \ll p_F$ even for very high fields. The energy shift, because of the interaction with the other electrons, becomes

$$\sum_{\mathbf{p}'} f(\mathbf{p}, \mathbf{p}') \delta \mathbf{n}(\mathbf{p}') = \frac{\mathbf{p}_F^2 \left| \delta \mathbf{p}_F \right|}{(2\pi \hbar)^3} \sqrt{\int} d\Omega \left\{ f(\theta, \sigma, \uparrow) - f(\theta, \sigma, \downarrow) \right\}$$
$$= \pm \frac{\mathbf{m}^* \mathbf{p}_F}{(2\pi \hbar)^3} \left| \delta \epsilon \right| \int d\Omega f_e(\theta)$$

We can now solve for $|\delta\epsilon|$ and obtain explicit results for $\delta\epsilon$ and $\delta p_{\rm F}$:

$$\delta \epsilon = \frac{F\beta H}{1 + \frac{m^* P_F}{(2\pi\hbar)^3} V \int d\Omega f_e(\theta)}$$

and

$$\left| \delta \mathbf{p}_{\mathrm{F}} \right| = \frac{\mathrm{m}^{*}}{\mathrm{p}_{\mathrm{F}}} \frac{\beta \mathrm{H}}{1 + \frac{\mathrm{m}^{*} \mathrm{p}_{\mathrm{F}}}{(2\pi \hbar)^{3}} \mathrm{V} \int \mathrm{d} \Omega \ \mathrm{f}_{\mathrm{e}}(\theta)}$$

We can then calculate the magnetic momentum of the electrons

$$M = \sum_{p} \beta \left(\delta n_{p}^{\dagger} - \delta n_{p}^{\downarrow} \right) \frac{1}{V} = \beta 2 \frac{4\pi p_{F}^{2} \left| \delta p_{F} \right|}{\left(2\pi \hbar \right)^{3}}$$

$$=\beta^2 \frac{\mathbf{m}^{*}\mathbf{p}_{\mathrm{F}}}{\pi^2\hbar^3} \frac{1}{1+\frac{\mathbf{m}^{*}\mathbf{p}_{\mathrm{F}}}{(2\pi\hbar)^3} \mathrm{V}\int \mathrm{d}\,\Omega\,\mathbf{f}_{\mathrm{e}}(\theta)}\,\mathrm{H}$$

From the relation M = X H we get the paramagnetic spin susceptibility in the form

$$\chi = \beta^2 \frac{m^* P_F}{\pi^2 \hbar^3} \frac{1}{1 + \frac{m^* P_F}{(2\pi \hbar)^3} V \int d\Omega f_e(\theta)}$$
(3.18)

or, introducing the density of states,

$$X = \beta^2 N(\epsilon_F) \frac{1}{1 + \frac{m^* P_F}{(2\pi\hbar)^3} V \int d\Omega f_e(\theta)}$$
(3.19)

If we put $f_e = 0$ we retrieve, of course, the result of the one-electron theory. The electron-electron interaction gives a very important modification of the Fermi gas result. Theoretical estimates from many-body theory shows that the correction seems to be in the range 20 - 200%, depending on the metal.

We would like to add the remark that our formula for the susceptibility says something about the stability of the system. The exchange interaction is negative so that we have an enhancement of the susceptibility. Increasing the strength of the exchange interaction would make the susceptibility become infinite and then be negative. An infinite susceptibility indicates a dynamical instability of the system, which would then

make a transition to an ordered magnetic state. Similar conditions for the dynamical stability can also be derived for other quantities, for example the effective interaction must be such that the sound waves are stable excitations and that the effective mass is positive. We have given a brief account of some important results of the Landau theory. It provides the basis for the theory of conduction electrons in metals and gives the physical explanation of how the concepts of oneelectron theory such as the existence of a Fermi surface, the results for specific heat, transport properties etc., can be given a proper meaning. It also shows, as for the sound velocity and the spin susceptibility, how the effect of many-body interactions will modify the results. The effective mass m^{*} and the quasi-particle interaction f are parameters of the theory. They can (in principle) be calculated from a complete many-body theory, however, the difficulties, particularly in calculating the Landau f-function, are quite serious and much work still remains to be done.

4. THE MANY-BODY WAVE FUNCTION AND OPERATORS IN SECOND QUANTIZATION

We start from the conventional description of an N-body system of identical particles in terms of wave functions in configuration space. One constructs a set of one-particle wave functions $u_k(\vec{x})$, k being the quantum number, which are assumed to be orthogonal, i.e.,

$$\int u_{k'}^{*}(\vec{x}) u_{k}(\vec{x}) d^{3}x = \delta_{kk'}$$

and have the closure property

$$\sum_{k} u_{k}^{*}(\vec{x}^{\prime}) u_{k}(\vec{x}) = \delta(\vec{x} - \vec{x}^{\prime})$$

From this set of one-particle functions we can first form a product wave function $% \left({{{\left[{{{{\bf{n}}_{{\rm{c}}}}} \right]}_{{\rm{c}}}}} \right)$

$$\Phi = u_{k_1}(\vec{x}_1) u_{k_2}(\vec{x}_2) \dots u_{k_N}(\vec{x}_N)$$

which physically describes the motion of n independent numbered particles. However, we have to introduce the proper symmetry. For fermions we must work with antisymmetric functions and so we replace the product by

$$\Phi_{\mathbf{k}_1 \cdot \mathbf{k}_2 \dots \cdot \mathbf{k}_N} = \mathscr{A} \mathbf{u}_{\mathbf{k}_1} (\vec{\mathbf{x}_1}) \mathbf{u}_{\mathbf{k}_2} (\vec{\mathbf{x}_2}) \dots \mathbf{u}_{\mathbf{k}_N} (\vec{\mathbf{x}_N})$$

where $\mathscr{A} = 1/\sqrt{N!} \sum (-1)^p P$ (summation over all permutations P, p being

the order of the permutation). This function is the well-known <u>Slater</u> determinant

$$\begin{array}{c} u_{k_1}(\vec{x}_1) \ \dots \ u_{k_1}(\vec{x}_N) \\ u_{k_2}(\vec{x}_2) \ \dots \ u_{k_2}(\vec{x}_N) \\ \vdots \\ u_{k_{n_1}}(\vec{x}_1) \ \dots \ u_{k_{n_1}}(\vec{x}_N) \end{array}$$

For bosons we consider instead the symmetrized product

$$\Phi_{k_1k_2...k_N} = S u_{k_1}(\vec{x}_1) u_{k_2}(\vec{x}_2) ... u_{k_N}(\vec{x}_N)$$

 $S = \frac{1}{\sqrt{N!}} \sum P$

with

In this way we build up a set of properly symmetrized functions. We normalize them to unity and they are by construction orthogonal. They form a <u>complete set</u> for the system of N particles, so that an arbitrary state vector can be expanded as follows:

$$\Psi(\vec{x}_1, \vec{x}_2 \dots \vec{x}_N) = \sum_{k_1, k_2 \dots k_N} A_{k_1, k_2 \dots k_N} \Phi_{k_1, k_2 \dots k_N}(\vec{x}_1, \vec{x}_2 \dots \vec{x}_N)$$

The coefficients $A_{k_1k_2...k_N}$ can be interpreted as the wave function

in the "quantum number representation". We wish to make a transition to such a representation, but the notation is too cumbersome. What we really need is to know the <u>number of fermions in each quantum state</u>. We therefore make the following change in enumerating the states:

 $k_1 k_2 \dots k_N \longrightarrow n_1 n_2 \dots n_p \dots$

where n_1 is the number of particles in quantum state 1, etc.

We wish to introduce the occupation numbers n_p as the dynamical variables of the theory. A scattering of a particle from state i to state j is then described by decreasing the occupation of state i by one unit and increasing that of j by one unit, i.e., $n_i \rightarrow n_i - 1$ and $n_j \rightarrow n_j + 1$. In making the transition to the occupation number representation we note that each Slater determinant or permanent corresponds to exactly one state in the occupation number representation. We introduce the corresponding new normalized vectors by giving the mapping from configuration space to n-space.

$$\Phi_{n_1n_2...n_p...}(\vec{x}_1\vec{x}_2...\vec{x}_N) \longrightarrow \left| n_1n_2...n_p... \right\rangle$$

These vectors form an orthogonal set and give a complete description of the N-particle system. However, we wish to do more. We make experiments in which we are sending particles in or take particles out, so we wish to consider situations in which the total number of particles changes.

With our construction we have one complete set of basis vectors for N particles, another for N' particles and so on. Let us now consider the enormous vector space obtained when combining these for all possible volumes of N. A complete set of basis vectors would be the following:

- a) The vacuum state with no particle present.
- b) All single particle states, describing a system with only one particle.
- c) All two-particle states describing a system with two particles and so on.

The operators on the states $|n_1 n_2 \dots n_p \dots \rangle$ change the occupation numbers, or in other words, they "create" or "annihilate" particles in the various quantum states. Let us first consider the case of fermions and define a creation operator a_k^* , which adds a fermion in the state k, and its conjugate a_k which has the opposite effect, i.e., it destroys one particle in state k.

$$a_{k}^{*}|n_{1}n_{2}...n_{k}...\rangle = (1 - n_{k})(-1)^{\sum_{i < k}^{n_{i}}}|n_{1}n_{2}...n_{k}+1...\rangle$$
(4.1)

$$\mathbf{a}_{k} | \mathbf{n}_{1} \mathbf{n}_{2} \dots \mathbf{n}_{k} \dots \rangle = \mathbf{n}_{k} (-1)^{\sum n_{i}} | \mathbf{n}_{1} \mathbf{n}_{2} \dots \mathbf{n}_{k} - 1 \dots \rangle$$

The properties of the a_k^* and a_k are fixed by the requirement of antisymmetry. The factors in the right-hand side of (4.1) guarantee that we have no more than one particle in each quantum state, which implies that $(a_k^*)^2 = (a_k)^2 = 0$. The antisymmetry also implies that

$$a_{k}^{*}a_{k}^{*}| > = -a_{k}^{*}a_{k}^{*}| >$$

for arbitrary states k, k', so that

$$a_{k}^{*}a_{k'}^{*} + a_{k'}^{*}a_{k}^{*} = 0$$

By the same argument we obtain that

$$a_k a_{k'} + a_{k'} a_k = 0$$

It follows from Eq.(4.1) that

$$\mathbf{a}_{\mathbf{k}}^{*}\mathbf{a}_{\mathbf{k}} | \mathbf{n}_{1}\mathbf{n}_{2} \dots \mathbf{n}_{\mathbf{k}} \dots \rangle = \mathbf{n}_{\mathbf{k}} | \mathbf{n}_{1}\mathbf{n}_{2} \dots \mathbf{n}_{\mathbf{k}} \dots \rangle$$

and hence we can define the <u>number operator</u> $N_k = a_k^* a_k$, which measures the number of particles in state k. We can also construct the <u>total</u> number operator N

$$N = \sum_{k} N_{k} = \sum_{k} a_{k}^{*} a_{k}$$
(4.2)

By straightforward calculation we find that

$$(a_{k}a_{k}^{*}+a_{k}^{*}a_{k})|n_{1}...n_{k}...\rangle = \{(n_{k}+1)(1-n_{k})+n_{k}\}|n_{1}...n_{k}...\rangle$$
$$= 1|n_{1}...n_{k}...\rangle$$

and that $a_k a_k^* + a_k^* a_k = 0$.

We now summarize the important relations for a_k^* and a_k using the notation { A, B} for the anticommutator AB+BA:

$$\{a_{k}, a_{k'}^{*}\} = \delta_{k, k'}, \ \{a_{k}, a_{k'}^{*}\} = \{a_{k}^{*}, a_{k'}^{*}\} = 0$$
(4.3)

Up to this point we have only constructed a set of basis vectors and introduced creation and annihilation operators a* and a, which change vectors into new vectors or destroy them. We must now find the proper form of operators describing the physics of the system. For each operator in the configuration-space language there is a corresponding operator in second quantization, which has the same matrix elements between any pair of basis vectors in n-space as the "old" operator between the corresponding Slater determinants. We use this requirement as a guide to find the right form of the operators.

We consider first a very simple situation in which a particle is scattered by an ordinary potential $V(\vec{x})$ from state k into a state k', illustrated graphically in Fig. 2.



FIG.2. Scattering of a particle by a potential.

In configuration space we know the answer. The matrix elements are taken between the Slater determinants where the final state differs from the initial one only through the replacement $k \rightarrow k'$. This matrix element is just $\langle k' | V | k \rangle$ and furthermore k must be an occupied state and the final state must be empty. Thus, the full answer is simply

$$\langle k' | V | k \rangle (1 - n_{k'}) n_{k}$$
 (4.4)

In second quantization this is described by first destroying the particle in state k and then creating it again in the final state k'. The diagram in Fig. 2 illustrates the scattering process as a particle coming in with momentum k, interacting with the potential V at the interaction point at the centre of the diagram and then going out in state k'. It is obvious that the annihilation-creation part of the process must be $a_{k'}^* a_k$ and that the part representing the potential must be essentially the matrix element $\langle k' | V | k \rangle$. Indeed if we choose the following expression for the process shown in Fig. 2

$$\langle \mathbf{k}' | \mathbf{V} | \mathbf{k} \rangle \mathbf{a}_{\mathbf{k}'}^* \mathbf{a}_{\mathbf{k}}$$
 (4.5)

and take the matrix elements between the n-states, we immediately retrieve the result in (4.4).

In this example we just studied a special case. By summing over all possible initial and final states we allow all possible scattering processes to happen and this will give us all the possible matrix elements in the correct way. In this way we obtain the following correspondence

$$\sum_{i=1}^{N} V(\vec{x}_{i}) \Longrightarrow \sum_{kk'} \langle k' | V | k \rangle a_{k'}^{*} a_{k}$$

The same argument holds, of course, for any single-particle operator (momentum, angular momentum, kinetic energy, etc.). Thus, if a single-particle operator F has matrix elements $\langle k^{\dagger} | F | k \rangle$ between the corresponding Slater determinants then the operator in n-space will be

$$\mathbf{F} = \sum_{\mathbf{k}\mathbf{k}'} \langle \mathbf{k}' | \mathbf{F} | \mathbf{k} \rangle \mathbf{a}_{\mathbf{k}'}^* \mathbf{a}_{\mathbf{k}}$$
(4.6)

These arguments can easily be extended to two-body operators. Let us consider the two-body scattering by an interaction potential $v(\vec{x}_1 - \vec{x}_2)$ as pictured in Fig. 3.



FIG.3. A two-body scattering process.

The matrix element between single-particle states is given by

$$\langle \mathbf{k}'_{1} \ \mathbf{k}'_{2} | \mathbf{v} | \mathbf{k}_{2} \mathbf{k}_{1} \rangle = \int d^{3} \mathbf{x}_{1} d^{3} \mathbf{x}_{2} \ \mathbf{u}^{*}_{\mathbf{k}'_{1}}(\vec{\mathbf{x}}_{1}) \ \mathbf{u}^{*}_{\mathbf{k}'_{2}}(\vec{\mathbf{x}}_{2}) \ \mathbf{v}(\vec{\mathbf{x}}_{1} - \vec{\mathbf{x}}_{2}) \ \mathbf{u}_{\mathbf{k}_{2}}(\vec{\mathbf{x}}_{2}) \ \mathbf{u}_{\mathbf{k}_{1}}(\vec{\mathbf{x}}_{1})$$

In analogy with the preceding case, the second-quantization form corresponding to the diagram shown in Fig. 3 will be

$$< k_1' k_2' | v | k_2 k_1 > a_{k_1'}^* a_{k_2'}^* a_{k_2} a_{k_1}$$

The general form is found by summing over all states and in this way we establish the correspondence

$$\frac{1}{2} \sum_{ij} \mathbf{v}(\vec{x}_i - \vec{x}_j)$$

 $\implies \frac{1}{2} \sum_{k_{3}' k_{2}' k_{1} k_{2}} \langle k_{1}' k_{2}' | v | k_{2} k_{1} \rangle a_{k_{1}'}^{*} a_{k_{2}'}^{*} a_{k_{2}} a_{k_{1}} \qquad (4.7)$

We can now write down the Hamiltonian, represented in the ordinary language by

$$H = \sum_{i} \frac{p_{i}^{2}}{2m} + \sum_{i} V_{1}(\vec{x}_{i}) + \frac{1}{2} \sum_{i,j} V_{2}(\vec{x}_{i}, \vec{x}_{j})$$

Using Eqs (6) and (7) we obtain

$$H = \sum_{kk'} \langle k' | H_1 | k \rangle a_{k'}^* a_k$$

$$+\frac{1}{2}\sum_{k_{1}'k_{2}'k_{1}'k_{2}}\left|V_{2}\right|k_{2}k_{1} > a_{k_{1}'}^{*}a_{k_{2}'}^{*}a_{k_{2}}a_{k_{1}} \qquad (4.8)$$

where

$$\left< k' \left| H_1 \right| k \right> = \int u_{k'}^*(\vec{x}) \left\{ \frac{p^2}{2m} + V_2(\vec{x}) \right\} u_k(\vec{x}) d^3x$$

and

$$< k_{1}' k_{2}' | V_{2} | k_{2} k_{1} > = \int u_{k_{1}}^{*}(\vec{x}_{1}) u_{k_{2}}^{*}(\vec{x}_{2}) V_{2}(\vec{x}_{1}, \vec{x}_{2}) u_{k_{2}}(\vec{x}_{2}) u_{k_{1}}(\vec{x}_{1}) d^{3}x_{1} d^{3}x_{2}$$

If the functions $u_k(\vec{x})$ are chosen as eigenfunctions of H_1 , we have that $\langle \mathbf{k'} | H_1 | \mathbf{k} \rangle = \epsilon_k \, \delta_{kk'}$, and the first term in the Hamiltonian then becomes

$$\mathbf{H}_{1} = \sum_{k} \boldsymbol{\epsilon}_{k} \mathbf{a}_{k}^{*} \mathbf{a}_{k} = \sum_{k} \boldsymbol{\epsilon}_{k} \mathbf{N}_{k}$$

This discussion has been given for fermions, but the treatment of Bose particles follows the same lines with the fundamental difference caused by the different symmetry requirements. For bosons we define creation and destruction operators as follows:

$$\begin{aligned} \mathbf{a}_{k}^{*}|\ldots \mathbf{n}_{k} \ldots \rangle &= \sqrt{\mathbf{n}_{k}+1}|\ldots \mathbf{n}_{k}+1 \ldots \rangle \\ \mathbf{a}_{k}|\ldots \mathbf{n}_{k} \ldots \rangle &= \sqrt{\mathbf{n}_{k}}|\ldots \mathbf{n}_{k}-1 \ldots \rangle \end{aligned} \tag{4.9}$$

and they obey the following commutations relations:

$$[a_{k}^{*}, a_{k}^{*}] = \delta_{kk}^{*}, \ [a_{k}^{*}, a_{k}^{*}] = [a_{k}^{*}, a_{k}^{*}] = 0$$
(4.10)

The operators a_i^* and a_i always refer to a certain chosen basis of single-particle states. It is very useful to introduce operators which do not depend upon the states but depend rather on the coordinates \vec{x}

$$\Psi(\vec{x}) = \sum_{k} u_{k}(\vec{x}) a_{k}$$

$$\Psi^{*}(\vec{x}) = \sum_{k} u_{k}^{*}(\vec{x}) a_{k}^{*}$$
(4.11)

 $\Psi(\vec{x})$ annihilates a particle at the point \vec{x} and $\Psi^*(\vec{x})$ creates one. These so-called wave field operators satisfy the following commutation relations

Fermions:
$$\begin{cases} \{\Psi(\vec{x}), \Psi^{*}(\vec{x}')\} = \delta(\vec{x} - \vec{x}') \\ \{\Psi(\vec{x}), \Psi(\vec{x}')\} = \{\Psi^{*}(\vec{x}), \Psi^{*}(\vec{x}')\} = 0 \end{cases}$$
Bosons:
$$\begin{cases} [\Psi(\vec{x}), \Psi^{*}(\vec{x}')] = \delta(\vec{x} - \vec{x}') \\ [\Psi(\vec{x}), \Psi(\vec{x}')] = [\Psi^{*}(\vec{x}), \Psi^{*}(\vec{x}')] = 0 \end{cases}$$
(4.12)

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In terms of the wave field $\Psi(\vec{x})$ the total Hamiltonian can be written as

$$H = \int d^{3} x \Psi^{*}(\vec{x}) H_{1}(\vec{x}) \Psi(\vec{x}) + \frac{1}{2} \int d^{3} x d^{3} x' \Psi^{*}(\vec{x}) \Psi^{*}(\vec{x'}) V_{2}(\vec{x}, \vec{x'}) \Psi(\vec{x'}) \Psi(\vec{x'})$$
(4.13)

We notice that the operator for the density of particles is simply

$$\rho = \Psi^*(\vec{\mathbf{x}}) \Psi(\vec{\mathbf{x}}) \tag{4.14}$$

the number operator becomes

$$N = \int \Psi^*(\vec{x}) \Psi(\vec{x}) d^3x \qquad (4.15)$$

and the total momentum operator is

$$\vec{\mathbf{P}} = \int d^3 \mathbf{x} \ \Psi^*(\vec{\mathbf{x}}) \ (-i \ \hbar \nabla) \ \Psi(\vec{\mathbf{x}})$$
(4.16)

5. SOME USEFUL RESULTS FROM GENERAL QUANTUM MECHANICS

Now that we have set up a framework of state vectors and operators, we have to determine how the state of the system changes in time. To do this, we solve the Schrödinger equation

$$i \frac{\partial \Phi^S}{\partial t} = H \Phi^S$$

We write the solution in the symbolic form

$$\Phi^{S} = e^{-iHt} \Phi^{H}$$

with

 $\Phi^{\mathsf{H}}=\Phi^{\mathsf{S}}(0)$

Using this formula, we can find the time variation of the matrix elements of any operator ${\rm F}$

$$\mathbf{F}_{ij}(\mathbf{t}) = \left\langle \Phi_i^{S}(\mathbf{t}) \operatorname{F} \Phi_j^{S}(\mathbf{t}) \right\rangle = \left\langle \Phi_i^{H} e^{iHt} \operatorname{F} e^{-iHt} \Phi_j^{H} \right\rangle$$

This can be interpreted as the matrix elements with respect to the functions Φ^{H} of the operator

$$F(t) = e^{iHt} F e^{-iHt}$$
(5.1)

This corresponds to going over to a new representation called the <u>Heisenberg picture</u>. Here the state vector is independent of time, $\Phi^{H} = \Phi^{S}(0)$, but instead the operators change with time according to the Heisenberg equation of motion

$$\frac{\mathrm{dF}}{\mathrm{dt}} = \mathrm{i} \left(\mathrm{HF} - \mathrm{FH}\right) = \mathrm{i} \left[\mathrm{H}, \mathrm{F}\right] \tag{5.2}$$

In the Schrödinger picture, the wave functions vary with time, whereas the operators do not. The connection between Heisenberg and Schrödinger operators and vectors is given by

$$\mathbf{F}^{H} = \mathbf{e}^{\mathbf{i}H\mathbf{t}} \mathbf{F}^{S} \mathbf{e}^{-\mathbf{i}H\mathbf{t}}$$

$$\Phi^{H} = \mathbf{e}^{\mathbf{i}H\mathbf{t}} \Phi^{S}$$
(5.3)

The wave field operator $\Psi(\mathbf{x}, t)$ in the Heisenberg picture is thus related to that in the Schrödinger picture through

$$\Psi(\vec{x}, t) = e^{iHt} \Psi(\vec{x}) e^{-iHt}$$

The commutation relations for Ψ and Ψ^* at equal time are the same as those derived earlier and the Hamiltonian is unchanged in form, thus

$$H = \int d^3x \ \Psi^*(\vec{x}, t) \ H_1(\vec{x}) \ \Psi(\vec{x}, t) + \frac{1}{2} \int d^3x \ d^3x' \ \Psi^*(\vec{x}, t) \ \Psi^*(\vec{x'}, t) \ V(\vec{x}, t') \ \Psi(\vec{x'}, t) \ \Psi(\vec{x}, t)$$

We can now derive the equation of motion for the annihilation operator by calculating

$$-i\frac{\partial\Psi}{\partial t} = [H,\Psi]$$

Evaluating the commutator (which is left as an exercise) one obtains

$$i \frac{\partial \Psi}{\partial t} = H_1(\vec{x}) \Psi(\vec{x}, t) + \int d^3 x' V(\vec{x}, \vec{x'}) \Psi^*(\vec{x'}, t) \Psi(\vec{x'}, t) \Psi(\vec{x}, t)$$
(5.4)

which forms the starting point for some of our later discussions.

A particularly useful picture in quantum field theory is an intermediate type, called the <u>interaction picture</u>. We divide the Hamiltonian into two parts

$$H = H_0 + H_1$$

and consider the following transformation of the Schrödinger wave function $\Phi(t)$:

$$\Psi(t) = e^{iH_0 t} \Phi(t)$$

Differentiating $\Psi(t)$ with respect to time, gives us

$$i \frac{\partial}{\partial t} \Psi(t) = H_I(t) \Psi(t)$$
 (5.5)

with

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$$H_{I}(t) = e^{iH_{0}t}H_{1}e^{-iH_{0}t}$$

 $H_I(t)$ is the interaction energy operator in the interaction picture and is <u>explicitly time-dependent</u>, in contrast to the Schrödinger operator. A general operator Q^S in the Schrödinger picture is transformed into

$$\mathsf{Q}^{\mathrm{I}}(\mathsf{t}) = \mathsf{e}^{\mathsf{i}\mathsf{H}_{0}\mathsf{t}} \, \mathsf{Q}^{\mathrm{S}} \mathsf{e}^{-\mathsf{i}\mathsf{H}_{0}\mathsf{t}}$$

and, thus, its time evolution obeys the equation

$$\frac{\partial}{\partial t} Q^{I}(t) = i [H_0 Q^{I}(t) - Q^{I}(t) H_0]$$

We now consider how to determine the state vector in the interaction picture. Suppose we know the value of $\Psi(t)$ at $t = t_0$. We then go from the differential Eq.(5) to an integral equation

$$\Psi(t) = \Psi(t_0) - i \int_{t_0}^{t} dt' H_I(t') \Psi(t')$$
 (5.6)

Eq.(6) can be formally solved by iteration. We, however, first introduce the operator $U(t, t_0)$ describing the change of the state vector with time from t_0 to t

$$\Psi(t) = U(t, t_0) \Psi(t_0)$$

$$U(t_0, t_0) = 1$$
(5.7)

One can show that $U(t, t_0)$ is a unitary operator. It obviously satisfies the same differential equation as $\Psi(t)$ and the integral equation

$$U(t, t_0) = 1 - i \int_{t_0}^{t} dt' H_I(t') U(t_0', t_0)$$
 (5.8)

Solving by iteration gives the series

$$U(t, t_{0}) = 1 + (-i) \int_{t_{0}}^{t} dt_{2} H_{I}(t_{1}) + (-i)^{2} \int_{t_{0}}^{t} dt_{1} \int_{t_{0}}^{t_{1}} dt_{2} H_{I}(t_{1}) H_{I}(t_{2})$$

+ ... $(-i)^{n} \int_{t_{0}}^{t} dt_{1} \int_{t_{0}}^{t_{1}} dt_{2} \dots \int_{t_{0}}^{t_{n-1}} dt_{n} H_{I}(t_{1}) H_{I}(t_{2}) \dots H_{I}(t_{n})$ (5.9)

Note that the operators ${\rm H}_{\rm I}(t)$ taken at a later time always appear to the left of operators taken at earlier times, since the inequality

$$t > t_1 > t_2 \dots > t_0$$

always holds. Let us consider the nth integral

$$\int_{t_0}^{t} dt_1 \int_{0}^{t_1} dt_2 \dots \int_{0}^{t_{n-1}} dt_n H_I(t_1) H_I(t_2) \dots H_I(t_n)$$

This expression does not change if we permute the variables $t_1 \ldots t_n \rightarrow t_{\rho_1} t_{\rho_2} \ldots t_{\rho_n}$. Considering all such permutations, adding the resulting expressions and finally dividing by n!, we can extend the range of integration of each variable from t_0 to t_1 . However, in doing so it is important that the operators H_I in the integral are always ordered from left to right in the order of decreasing times. Dyson formally removed this restriction by introducing the chronological product P

$$P\{H_{I}(t_{1}) H_{I}(t_{2}) \dots H_{I}(t_{n})\} = H_{I}(t_{i}) H_{I}(t_{j}) \dots H_{I}(t_{k})$$

where $t_i, t_j \dots t_k$ are permutations of $t_1, t_2 \dots t_r$ such that

$$t_i \geqslant t_j \geqslant \ldots \geqslant t_k$$

Thus the nth order term becomes

$$\frac{1}{n!} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \dots \int_{t_0}^t dt_n \operatorname{P} \{ H_I(t_1) H_I(t_2) \dots H_I(t_n) \}$$

and the expansion of U becomes

$$U(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^t \dots \int_{t_0}^t dt_1 \dots dt_n P \{H_I(t_1) \dots H_I(t_n)\}$$
(5.10)

or in a compact though not very practical form

$$U(t, t_0) = P \exp \{-i \int_{t_0}^{t} H_I(t') dt'\}$$
(5.11)

6. HOW "GREEN" IS MY VALLEY

In this section we shall introduce the single-particle Green function and choose once more a metal as a model for our considerations. Let $|0\rangle$ denote the ground state of the metal. Then, if we send in an electron in a Bloch state k at t = 0, we produce the state $a_k^*|0\rangle = |k, 0\rangle$. The added electron will interact with the rest of the system and undergo scattering as well as various inelastic processes. Therefore, we do not expect $|k, 0\rangle$ to be an exact eigenstate but rather a form of decaying state as it develops in time. Let us ask what the state $|k, t\rangle$ is at a late time t. From quantum mechanics we know that the answer is formally given by

$$|\mathbf{k}, \mathbf{t}\rangle = e^{-iHt} |\mathbf{k}, 0\rangle$$

Let us now ask for the probability that the system, after a time t, should still be in the same state as at t = 0, i.e., with an electron in the Bloch state \vec{k} and the rest in the ground state. This probability is $\langle k, 0 | k, t \rangle$. Closely related is the one-electron Green function, which we define as

$$G(k,t) = \begin{cases} -i \langle k, 0 | k, t \rangle & t > 0 \\ 0 & t < 0 \end{cases}$$
(6.1)

We write this in the form it is mostly used by introducing explicitly the Heisenberg operators for creating and annihilating an electron in Bloch state ${\bf k}$

$$G(k, t) = \begin{cases} -i \langle 0 | a_{k}(t) a_{k}^{*}(0) | 0 \rangle & t > 0 \\ 0 & t < 0 \end{cases}$$
(6.2)

We do some rewriting of this formula

$$G(k, t) = -i \langle 0 | a_{k}(t) a_{k}^{*}(0) | 0 \rangle \approx \sum_{n} -i \langle 0 | a_{k}(t) | n \rangle \langle n | a_{k}^{*}(0) | 0 \rangle$$
$$= \sum_{n} -i \langle 0 | e^{-iHt} a_{k}(0) e^{-iHt} | n \rangle \langle n | a_{k}^{*}(0) | 0 \rangle$$

$$= \sum_{n} -i \left| \langle n \left| a_{k}^{*} \right| 0 \rangle \right|^{2} e^{-i(E_{n}(N+1)-E_{0}(N))t}$$
$$= \sum_{n} -i \left| \langle n \left| a_{k}^{*} \right| 0 \rangle \right|^{2} e^{-i\epsilon_{n}t} ; t > 0$$
(6.3)

In Eq.(6.3) $\epsilon_n = E_n(N+1) - E_0(N)$. We can, if we wish, make the subdivision

$$\epsilon_n = [E_n(N+1) - E_0(N+1)] + E_0(N+1) - E_0(N)$$

= $\omega_n + \mu$

where ω_n is the excitation energy. The smallest value of ϵ_n equals μ as it should.

Fourier transforming (6.3) into energy space we obtain

$$G(k,\omega) = \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \ G(k,t) = \sum_{n} \frac{\left| \langle n | a_{k}^{*} | 0 \rangle \right|^{2}}{\omega - \epsilon_{n} + i \delta}$$
(6.4)

where δ is a positive infinitesimal, needed to ensure that G(k,t) = 0 for negative times, if we transform back from ω to t again.

We can make the same discussion of <u>hole injection</u>. The probability amplitude related to the <u>hole Green function</u> is $\langle 0 | a_k^*(t) a_k(0) | 0 \rangle$. For conventional reasons one uses the negative time-axis for holes and defines the hole Green function as

$$G(k, t) = \begin{cases} 0 & t > 0 \\ i < 0 | a_{k}^{*}(0) a_{k}(t) | 0 > t < 0 \end{cases}$$
(6.5)

We do the analogous rewriting of this formula and obtain

$$\begin{aligned} \mathbf{G}(\mathbf{k}, \mathbf{t}) &= \mathbf{i} \langle \mathbf{0} | \mathbf{a}_{\mathbf{k}}^{*}(\mathbf{0}) \mathbf{a}_{\mathbf{k}}(\mathbf{t}) | \mathbf{0} \rangle &= \sum_{n} \mathbf{i} \langle \mathbf{0} | \mathbf{a}_{\mathbf{k}}^{*}(\mathbf{0}) | \mathbf{n} \rangle \langle \mathbf{n} | \mathbf{a}(\mathbf{t}) | \mathbf{0} \rangle \\ &= \sum_{n} \mathbf{i} \langle \mathbf{0} | \mathbf{a}_{\mathbf{k}}^{*}(\mathbf{0}) | \mathbf{n} \rangle \langle \mathbf{n} | \mathbf{e}^{\mathbf{i}H\mathbf{t}} \mathbf{a}_{\mathbf{k}}(\mathbf{0}) | \mathbf{e}^{-\mathbf{i}H\mathbf{t}} | \mathbf{0} \rangle \\ &= \sum_{n} \mathbf{i} | \langle \mathbf{n} | \mathbf{a}_{\mathbf{k}} | \mathbf{0} \rangle |^{2} \mathbf{e}^{-\mathbf{i}(\mathbf{E}_{0}(\mathbf{N}) \cdot \mathbf{E}_{\mathbf{n}}(\mathbf{N}-\mathbf{1}))\mathbf{t}} = \sum_{n} \mathbf{i} | \langle \mathbf{n} | \mathbf{a}_{\mathbf{k}} | \mathbf{0} \rangle |^{2} \mathbf{e}^{-\mathbf{i}\epsilon_{\mathbf{n}}\mathbf{t}} \end{aligned}$$
(6.6)
where $\epsilon_{\mathbf{n}} = \mathbf{E}_{0}(\mathbf{N}) - \mathbf{E}_{\mathbf{n}}(\mathbf{N}-\mathbf{1})$ and, of course, $\epsilon_{\mathbf{n}} < \mu$.

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Fourier transforming (6.6) into energy space we obtain

$$G(k, \omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} G(k, t) = + \sum_{n} \frac{\left| \langle n | a_k | 0 \rangle \right|^2}{\omega - \epsilon_n - i\delta}$$
(6.7)

It is convenient to combine the particle and the hole Green function into one single function which is called the <u>time-ordered</u> or <u>causal</u> Green function defined by

$$G(k, t) = -i \langle 0 | T \{ a_{k}(t) a_{k}^{*}(0) \} | 0 \rangle$$

$$= \begin{cases} -i \langle 0 | a_{k}(t) a_{k}^{*}(0) | 0 \rangle & t > 0 \\ \\ i \langle 0 | a_{k}^{*}(0) a_{k}(t) | a \rangle & t < 0 \end{cases}$$
(6.8)

The time-ordering symbol T means that we should order the operators chronologically so that operators with earlier times are placed to the right; furthermore, for fermions we should include the minus signs arising from the anticommutations.

We can combine (6.4) and (6.7) into one single formula which gives the so-called <u>spectral representation</u> of the Green function. As a preliminary, we note that for electrons $\epsilon(k) > \mu$ and for holes $\epsilon(k) < \mu$. It is convenient to shift the energy scale and measure energies from the Fermi energy so that <u>particles have positive energies</u> and <u>holes</u> have negative energies.

Next we introduce the probability distribution to find the N+1 or N-1 system excited to a given excitation energy. For particles we can define, from (6.3), a function

$$A^{+}(\mathbf{k},\omega) = \sum_{n} \left| \langle n | \mathbf{a}_{\mathbf{k}}^{*} | \mathbf{0} \rangle \right|^{2} \delta(\omega - \epsilon_{n})$$
(6.9)

with the property that $\underline{A}^{+}(k,\omega)d\omega$ gives the probability to find the N+1particle system excited to an energy in the interval $[\omega, \omega + d\omega]$. Similarly, for hole injection we define the quantity

$$A^{-}(\mathbf{k},\omega) = \sum_{n} \left| \langle n | \mathbf{a} | 0 \rangle \right|^{2} \delta(\omega - \epsilon_{n})$$
(6.10)

with an analogous interpretation (note that ϵ_n is negative for holes). In terms of these quantities we can combine (6.4) for particles and (6.7) for

holes into the following relation:

$$G(\mathbf{k},\omega) = \int_{0}^{\infty} d\omega' \frac{A^{\dagger}(\mathbf{k},\omega')}{\omega - \omega' + i\delta} + \int_{-\infty}^{0} d\omega' \frac{A^{\dagger}(\mathbf{k},\omega')}{\omega - \omega' - i\delta}$$

$$= \int_{-\infty}^{\infty} d\omega^{\dagger} \frac{A(k, \omega^{\dagger})}{\omega - \omega^{\dagger} + i\omega\delta}$$
(6.11)

where we have defined the total spectral weight function

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$$A(k, \omega) = A^{\dagger}(k, \omega) + A^{\dagger}(k, \omega)$$
(6.12)

Eq.(6.11) is called the spectral representation for $G(k, \omega)$ which is exact and from which we can deduce various analytic properties and relations.

According to its definition $A(k, \omega)$ is a <u>positive real quantity</u>. Furthermore it fulfills the <u>sum</u> rule

$$\int_{-\infty}^{\infty} A(k, \omega) d\omega = 1$$
 (6.13)

This follows from inserting (6.9) and (6.10) in the integral

+ 00

$$\int_{-\infty}^{\infty} A(k, \omega) d\omega = \sum_{n} \{ |\langle n | a_{k}^{*} | 0 \rangle|^{2} + |\langle n | a_{k} | 0 \rangle|^{2} \}$$
$$= \sum_{n} \{ \langle 0 | a_{k} | n \rangle \langle n | a_{k}^{*} | 0 \rangle + \langle 0 | a_{k}^{*} | n \rangle \langle n | a_{k} | 0 \rangle \}$$
$$= \langle 0 | a_{k} a_{k}^{*} + a_{k}^{*} a_{k} | 0 \rangle = 1$$

where we have used the anticommutation relation.

The spectral weight function $A(k, \omega)$ is the general distribution function with regard to both momentum and energy of the system. The positive frequency part $A^{+}(k, \omega)$ is related to processes involving the addition of an electron, whereas the negative frequency part $A^{-}(k, \omega)$ describes processes involving holes. Integration over the momenta gives the energy distribution in the system and integration over (negative) frequencies gives the momentum distribution.

In actual calculations one often determines G directly, rather than first calculating A. We shall derive a couple of useful formulas by simple application of the "well-known relation"

$$\frac{1}{x\pm i\epsilon} = P \frac{1}{x} \mp i \pi \delta(x)$$

 ϵ being a positive infinitesimal. The meaning is that if we multiply by any reasonable function f(x) and integrate from $-\infty$ to ∞ and let P mean the principal value, then the answer corresponding to the formula is obtained.

Applying this to the spectral representation (6.11) one obtains

Im G(k,
$$\omega$$
) =

$$\begin{cases}
-\pi A(k, \omega) & \omega > 0 \\
\pi A(k, \omega) & \omega < 0
\end{cases}$$
(6.14)

Inserting this result in (6.11), we obtain a dispersion relation connecting the real and imaginary parts of G

Re
$$G(k, \omega) = -\frac{1}{\pi} P \int_{0}^{\infty} \frac{\operatorname{Im} G(k, \omega') d\omega'}{\omega - \omega'}$$

 $+\frac{1}{\pi} P \int_{-\infty}^{0} \frac{\operatorname{Im} G(k, \omega') d\omega'}{\omega - \omega'}$ (6.15)

We shall conclude this section by making some remarks about extension of the treatment indicated here to more general situations.

i) We can of course define the space-time Green function by means of the Heisenberg operators for the wave fields:

$$G(\vec{x}, t, \vec{x'}, t') = -i \langle 0 | T \{ \Psi(\vec{x}, t) \Psi^*(\vec{x'}, t') \} | 0 \rangle$$

$$= \begin{cases} -i \langle 0 | \Psi(\vec{x}, t) \Psi^*(\vec{x'}, t') | 0 \rangle & t > t' \\ \\ i \langle 0 | \Psi^*(\vec{x'}, t') \Psi(\vec{x}, t) | 0 \rangle & t < t' \end{cases}$$
(6.16)

 We can generalize the notion of a Green function to n-particles, defining the n-particle Green function by

$$G(\vec{x}_{1}, t_{1}, \ldots, \vec{x}_{n}, t_{n}, \vec{x}_{1}', t_{1}', \ldots, \vec{x}_{n}', t_{n}')$$

= $(-i)^{n} < 0 | T(\Psi(\vec{x}_{1}, t_{1}) \ldots \Psi(\vec{x}_{n}, t_{n}) \Psi^{*}(\vec{x}_{1}', t_{n}') \ldots \Psi^{*}(\vec{x}_{1}', t_{1}')) | 0 > (6.17)$

- iii) The time-ordered Green functions are particularly useful in connection with perturbation theory. In many physical applications, however, one has use for functions with different properties with regard to time evolution. The <u>retarded</u> and <u>advanced</u> Green functions are often used and examples of this will be given later.
- iv) The Green functions introduced are defined as expectation values with regard to the ground state of the system. The appropriate generalization to finite temperatures is obtained by replacing this by appropriate statistical averages for the temperature T:

$$\langle 0 | \dots | 0 \rangle \longrightarrow \sum_{s} \rho_{s} \langle s | \dots | s \rangle = \langle \rangle_{T}$$

where s denotes the state of the system and $\rho_{\rm s}$ is the probability that the state s is realized.

7. SOME EXAMPLES OF GREEN'S FUNCTIONS AND THEIR USE

(a) A gas of free fermions

This is a particularly simple special case of the results in the preceding section. For the time-dependence we obtain

$$G(k,t) = \begin{cases} -i \langle a_k a_k^* \rangle e^{-i\epsilon(k)t} & t > 0 \\ \\ i \langle a_k^* a_k \rangle e^{-i\epsilon(k)t} & t < 0 \end{cases}$$
(7.1)

 \mathbf{or}

$$G(k, t) = \begin{cases} -i(1-n_k^0) e^{-i\epsilon(k)t} & t > 0 \\ & & \\ i n_k^0 e^{-i\epsilon(k)t} & t < 0 \end{cases}$$
(7.2)

Thus the Green function describes electrons <u>outside</u> the Fermi sea for <u>positive</u> times and holes in the Fermi sea for <u>negative</u> t.

Transforming to energy space, we obtain

$$G(k, \omega) = \frac{1}{\omega - \epsilon(k)}$$

where we must add the prescription of how to treat the singularity. It is left as an exercise to show that one retrieves (7.1), (7.2) if one chooses

$$G(k, \omega) = \frac{1}{\omega - \epsilon(k) + i\omega\delta}$$
(7.3)

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Thus, we have to add small imaginary parts to the single particle energies. Their location in the complex ω -plane is shown in Fig.4.



FIG.4. Location of singularities for electrons and holes for the time-ordered Green function.

Had we considered instead the retarded rather than the time-ordered Green functions, we would have used the boundary condition

$$G(\mathbf{k}, \omega) = \frac{1}{\omega - \epsilon(\mathbf{k}) + i\delta}$$
(7.4)

for all k. All the singularities are here shifted below the real axis i.e., the retarded Green function is analytic in the upper half-plane.

(b) Decaying particle

In this case the amplitude $|k, t\rangle$ decays in time and we have that

$$G(k, t) = \begin{cases} -i < k, 0 | k, t > \approx e^{-\Gamma t} e^{-i\epsilon(k)t} & t > 0 \\ = 0 & t < 0 \end{cases}$$
(7.5)

Calculating the Fourier transform of this we get

$$G(k, \omega) = \frac{1}{\omega - \epsilon(k) + i\Gamma}$$
(7.6)

From the imaginary part we obtain the expected Lorentzian form for the spectral function

$$A(k,\omega) = \frac{1}{\pi} \left| \operatorname{Im} G(k,\omega) \right| = \frac{1}{\pi} \frac{\Gamma}{(\omega - \epsilon(k))^2 + \Gamma^2}$$
(7.7)

(c) The one-phonon Green function

In complete analogy we can introduce the one-phonon Green function defined by

$$D_{s}(\vec{q}, t) = -i \langle 0 | T \{ \phi_{qs}(t) \phi_{qs}^{*}(0) \} | 0 \rangle$$
 (7.8)

where we restrict the momenta to the first Brillouin zone. The phonon field is related to the creation and annihilation operators by

$$\varphi_{qs} = a_{qs} + a_{-qs}^*$$

We observe that for bosons no change in sign is associated with the timeordering symbol T.

We can obtain a spectral representation of (7.8) by introducing the spectral weight function

$$B_{s}(\vec{q},\omega) = \sum_{n} |\langle n | \varphi_{qs}^{*} | 0 \rangle|^{2} \delta(\omega - \omega_{n})$$
$$- \sum_{n} |\langle n | \varphi_{qs} | 0 \rangle|^{2} \delta(\omega + \omega_{n})$$
(7.9)

where ω_n is the excitation energy of the system. The spectral representation is then given by

$$D_{s}(\vec{q},\omega) = \int_{-\infty}^{+\infty} \frac{B_{s}(\vec{q},\omega') d\omega'}{\omega - \omega' + i\omega \delta}$$
(7.10)

where δ is a positive infinitesimal. Again using the formula

$$\frac{1}{\mathbf{x}=\mathrm{i}\delta}=\mathrm{P}\,\frac{1}{\mathbf{x}}\,\overline{+}\,\mathrm{i}\pi\delta(\mathbf{x})$$

we obtain the relations

$$\operatorname{Im} D_{s}(\vec{q}, \omega) = -\pi B_{s}(\vec{q}, \omega) \operatorname{sgn} \omega \qquad (7.11)$$

and the dispersion relation

$$D_{s}(\vec{q},\omega) = -\frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega' \frac{\text{Im } D_{s}(\vec{q},\omega') \text{ sgn } \omega'}{\omega - \omega' + i\omega\delta}$$
(7.12)

For a system of free undamped phonons the spectral function is simply

.

$$\mathbf{B}_{s}(\vec{\mathbf{q}},\omega) = \begin{cases} \cdot \delta(\omega - \omega_{s}(\mathbf{q})) & \omega > 0 \\ \\ \\ -\delta(\omega + \omega_{s}(\mathbf{q})) & \omega < 0 \end{cases}$$

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and the phonon Green function is

$$D_{0s}(\vec{q},\omega) = \frac{2\omega_s(q)}{\omega^2 - \omega_s^2(q) + i\delta}$$
(7.13)

(d) Calculation of expectation values

From the preceding sections it is clear that the Green functions in the first place contain information about excitations of the system. However, taking the appropriate limits one can also calculate the ground state properties from the Green functions.

For example from the operator for the density of particles we obtain the average density of particles

$$\rho(\vec{\mathbf{x}}) = \langle 0 | \psi^*(\vec{\mathbf{x}}, t) \psi(\vec{\mathbf{x}}, t) | 0 \rangle = -i \ G(\vec{\mathbf{x}}, t; \vec{\mathbf{x}'}, t')_{\vec{\mathbf{x}} \to \vec{\mathbf{x}}}$$
(7.14)
$$t' \to t + 0$$

The momentum distribution is given by

$$N(k) = \langle 0 | a_{k}^{*} a_{k} | 0 \rangle = -i G(k, t)_{t \to -0}$$
$$= -i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} G(k, \omega) e^{i\omega\delta} = \int_{-\infty}^{0} A(k, \omega) d\omega \qquad (7.14')$$

Similarly the energy distribution of electrons is obtained by summing $A(k,\omega)$ over all momenta

$$N(\omega) = \sum_{k} A(k, \omega)$$
(7.15)

The kinetic energy can be expressed in terms of the single-particle Green function as follows

$$<0 \left| \int \psi^{*}(\vec{\mathbf{x}}, \mathbf{t}) \left(-\frac{\nabla^{2}}{2m} \right) \psi(\vec{\mathbf{x}}, \mathbf{t}) d^{3}\mathbf{x} \right| 0 >$$

$$= \int d^{3}\mathbf{x} \left[i \frac{\nabla^{2}_{\mathbf{x}}}{2m} G(\vec{\mathbf{x}}, \mathbf{t}, \vec{\mathbf{x}'}, \mathbf{t'}) \right]_{\vec{\mathbf{x}'} \to \vec{\mathbf{x}}}_{\mathbf{t'} \to \mathbf{t} + 0}$$

$$(7.16)$$
For a system with particles interacting via a two-body interaction, the interaction energy can be expressed in terms of the two-particle Green function

$$< 0 \left| \frac{1}{2} \int \psi^{*}(\vec{x}, t) \psi^{*}(\vec{x}', t) v(\vec{x} \cdot \vec{x}') \psi(\vec{x}', t) \psi(\vec{x}, t) d^{3}x d^{3}x' \left| 0 \right\rangle$$

$$= -\frac{1}{2} \int d^{3}x d^{3}x' v(\vec{x} \cdot \vec{x}') G(\vec{x}t, \vec{x}'t, \vec{x}t', \vec{x}'t')_{t' \to t}$$

$$(7.17)$$

8. PERTURBATION SERIES EXPANSIONS. THE USE OF DIAGRAMS

Much of the work up to now has been based upon the use of perturbation expansions, systematized with the help of diagrams. Many of the important earlier results such as the so-called "linked cluster expansion" were obtained in this way. The perturbation expansion is based on the <u>adiabatic hypothesis</u>, which implies that the ground state of the noninteracting system is assumed to go over adiabatically to the ground state of the interacting system as the interactions are adiabatically switched on in time. One also assumes that the energy shift in the ground state as well as the Green functions of the system can be expanded as a power series in the strength of the interaction.

The key theorem that gives the systematic way of writing down the expectation value of any time-ordered product is known as <u>Wick's theorem</u>. I am not going to prove this theorem because proofs can be found in most texts on quantum field theory or many-body theory. The analysis results in a set of rules, and once the rules are written down one need not keep the derivation in mind.

We shall give the rules only for the simplest case where we assumed crystal momentum to be conserved by the interactions, i.e., we neglect umklapp processes. This means that the Green functions are diagonal in momentum, that is they are of the form $G(k, \omega)$ we have already used in Section 7. We assume that the particles move in a common potential U. Because of our assumption this potential will only have diagonal matrix elements $\langle k | U | k \rangle$. The electrons are interacting via their Coulomb interaction. We introduce as a further approximation the replacing of the full matrix element $\langle k^{t}, p^{t} | V | p, k \rangle$ by a matrix element for plane waves. The matrix element then depends only on the momentum transfer $\vec{q} = \vec{k} - \vec{k}'$ of one of the electrons, i.e.,

$$v(q) = \frac{4\pi}{|\vec{q}|^2}$$

It is convenient to use four-vector notation and write $k = (\vec{k}, \omega)$, $G(k) = G(\vec{k}, \omega)$, $d^4 k = d^3 k d\omega$ etc.

The rules to calculate the one-electron Green function will now be listed:

(i) Draw all diagrams in which an electron \vec{k}, ω enters from the right and goes to the left undergoing all distinct interactions during the process. Only topologically non-equivalent diagrams should be

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considered and we consider only "connected diagrams", i.e., those which cannot be separated into two or more unconnected parts without cutting any lines. The Coulomb interaction is represented by a dashed line ---- and the external potential U is represented by a dotted line \times connected to a cross (the source).

- (ii) Assign momentum, energy and spin in such a way that they are conserved at each vertex of a diagram.
- (iii) For every electron line \underbrace{k}_{k} include a factor i $G_0(k)$, where $G_0(k)$ is the Green function for the non-interacting system

$$G_0(k) = \frac{1}{k_0 - \epsilon(\vec{k}) + i k_0 \delta}$$
(8.1)

(iv) For every Coulomb line ---- include a factor

$$\langle \mathbf{k}_1' \mathbf{k}_2' | \nabla | \mathbf{k}_2 \mathbf{k}_1 \rangle$$
 or just $\mathbf{v}(\vec{\mathbf{q}})$ (8.2)

(v) For every interaction with the external potential include a factor

$$\langle \mathbf{k} | \mathbf{U} | \mathbf{k} \rangle$$
 (8.3)

- (vi) Include a factor $(-i)^n$, where n is the number of interactions 4 and 5, and a factor $(-1)^{\ell}$ where ℓ is the number of closed electron loops in the graph.
- (vii) Multiply all the factors together and integrate over all free internal four-momenta according to

$$\int \frac{d^4k}{(2\pi)^4} \int \frac{d^4p}{(2\pi)^4} \dots \times \text{ (all factors form rules iii) to vi)}$$

We illustrate the rules by calculating a few diagrams of low order.

(a) Particle scattered by the external potential



 $(-i) iG_0(p) \langle \vec{p} | U | \vec{p} \rangle iG_0(p) = i[G_0(p)]^2 \langle \vec{p} | U | \vec{p} \rangle$

(b) Particle scattered by the Fermi sea



- $(-1)(-i) \ iG_{0}(p) \left\{ \int \frac{d^{4}p'}{(2\pi)^{4}} < pp' \left| V \right| p'p > iG_{0}(p') \right\} iG_{0}(p)$ $= -i \left[G_{0}(p) \right]^{2} \int \frac{d^{4}p'}{(2\pi)^{4}} < pp' \left| V \right| p'p > iG_{0}(p')$
- (c) Lowest order Coulomb interaction correction



(-i)
$$iG_0(p) \int \frac{d^4q}{(2\pi)^4} iG_0(p-q) v(\vec{q}) iG_0(p)$$

=
$$i [G_0(p)]^2 \int \frac{d^4q}{(2\pi)^4} iG_0(p-q) v(\vec{q})$$

(d) Interaction with a density fluctuation (an electron-hole pair)



$$(-i)^{2} 2 (-1) \int \frac{d^{4} q}{(2\pi)^{4}} \int \frac{d^{4} p'}{(2\pi)^{4}} iG_{0}(p) v(\vec{q}) iG_{0}(p-q) iG_{0}(p') iG_{0}(p'+q) v(\vec{q}) iG_{0}(p)$$

= $i [G_{0}(p)]^{2} \int \frac{d^{4} q}{(2\pi)^{4}} iG_{0}(p-q) v(\vec{q}) (-2i v(\vec{q})) \int \frac{d^{4} p'}{(2\pi)^{4}} G_{0}(p') G_{0}(p'+q)$

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This diagram can be thought of as a modification of the interaction in diagram (c) and indeed the particle hole excitations give rise to screening of the bare Coulomb interaction. This screening must be included to infinite order, and we can illustrate here how this can be done in terms of diagrams. The next process we consider corresponds to the diagram with two particle-hole excitations:



Applying the rules as in the preceding graph we find for this case the contribution $% \left({{{\left[{{{L_{\rm{s}}}} \right]}_{\rm{s}}}} \right)$

$$i[G_{0}(p)]^{2} \int \frac{d^{4}q}{(2\pi)^{4}} i G_{0}(p-q) v(\vec{q}) \left[-2i v(\vec{q}) \int \frac{d^{4}p'}{(2\pi)^{4}} G_{0}(p') G_{0}(p'+q) \right]^{2}$$

Generalizing the argument we obtain for the diagram with n particle hole pairs



We can now sum the whole sequence of diagrams

$$= i[G_{0}(p)]^{2} \int \frac{d^{4}q}{(2\pi)^{4}} i G_{0}(p-q) v(\vec{q}) \left\{ 1 - 2i v(\vec{q}) \int \frac{d^{4}p'}{(2\pi)^{4}} G_{0}(p') G_{0}(p'-q) + \left[-2i v(\vec{q}) \int \frac{d^{4}p'}{(2\pi)^{4}} G_{0}(p') G_{0}(p'+q) \right]^{2} + \dots \right\}$$

$$= i[G_{0}(p)]^{2} \int \frac{d^{4}q}{(2\pi)^{4}} i G_{0}(p-q) \frac{v(\vec{q})}{1 + 2i v(\vec{q}) \int \frac{d^{4}p'}{(2\pi)^{4}} G_{0}(p') G_{0}(p'+q)}$$

This result has the same \underline{form} as the first diagram but with an $\underline{effective}$ interaction

$$v_{eff}(q) = \frac{v(\vec{q})}{1 + 2i v(\vec{q}) \int \frac{d^4 p'}{(2\pi)^4} G_0(p') G_0(p'+q)}$$
(8.4)

replacing the bare Coulomb interactions.

In terms of graphs, the effective interaction is obtained as the series



which corresponds to the so-called <u>random phase approximation</u>. Higher approximations are obtained by including graphs in which the electron and hole interact, e.g.,



One usually writes

$$v_{eff}(q) = \frac{v(\vec{q})}{\epsilon(q)}$$

where $\epsilon(q)$ is the wave-number and frequency-dependent dielectric function. In the random phase approximation we find that

$$\epsilon(q) = 1 + 2i v(\vec{q}) \int \frac{d^4 p'}{(2\pi)^4} G_0(p') G_0(p'+q)$$
(8.5)

Evaluating the right-hand term member one obtains what is essentially the Lindhard dielectric function [3].

We shall not at this moment comment on the dielectric properties of metals; the motive is rather to illustrate in a simple case how certain infinite sequences of diagrams may be summed to infinite order to renormalize quantities like interactions, single-particle energies, etc.

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We conclude this section by indicating a couple of important generalizations.

- (i) We can equally well use a diagrammatic representation in a space-time picture where each vertex is marked with the corresponding four-vector \vec{x} , t. The identification will now be made with the <u>space-time</u> Green function $G_0(x, x')$, the interactions in space $U(\vec{x})$ and $v(\vec{x} \vec{x'})$, etc., and the integrations have to be carried out over all free <u>space-time</u> variables of each diagram.
- (ii) The diagrammatic representation is easily extended to include further interactions. For example, if phonons are included we should consider the electron-phonon interaction. Phonons may be represented by a wavy line. For a process in which a phonon of momentum \vec{q} and polarization s is emitted and an electron is scattered from \vec{k} to $\vec{k'}$ we have a coupling constant $g_{\vec{k},\vec{k'},s}$ which should be attached to each electron-phonon vertex.

9. GREEN'S FUNCTIONS AND EXPERIMENTS: INELASTIC SCATTERING

We consider the interaction between our system and external probes like beams of neutrons or charged particles, electromagnetic radiation, etc. In such experiments the probe goes from an initial state $|p\rangle$ to a final state $|p'\rangle$ and the system makes a transition from $|s\rangle$ to $|s'\rangle$ as illustrated in Fig.5.



If the interaction between the probe and the system is weak, we can treat it in first order and use the Golden Rule for the transition probability per unit time

$$\frac{\mathrm{dW}_{\mathbf{p} \to \mathbf{p}'}}{\mathrm{dt}} = \frac{2\pi}{\hbar^2} \sum_{\mathbf{s}'} \left| \left\langle \mathbf{s}' \; H_{\mathrm{int}}^{\mathbf{p}'\mathbf{p}} \middle| \mathbf{s} \right\rangle^2 \delta(\omega - \omega_{\mathbf{s}'\mathbf{s}}) \right|$$
(9.1)

where $\omega_{s's} = \omega_{s'} - \omega_s$ is the excitation energy of the system and $\omega = \omega_p - \omega_{p'}$ is the change of energy of the probe (positive change for loss of energy in the process). H_{int} is the interaction between the probe and the system and $\langle s' | H_{int}^{p p} | s \rangle$ is the matrix element for the transition.

In most cases we do not have one single initial state but rather a statistical distribution ρ_s over initial states. We therefore replace (9.1) by the more general formula

$$\frac{\mathrm{d}W_{\mathbf{p}\to\mathbf{p}'}}{\mathrm{d}t} = \frac{2\pi}{\hbar^2} \sum_{\mathbf{s}} \rho_{\mathbf{s}} \left\{ \sum_{\mathbf{s}'} \left| \left\langle \mathbf{s}' \right| \mathbf{H}_{\mathrm{int}}^{\mathbf{p}'\mathbf{p}} \right| \mathbf{s} \right\rangle^2 \delta(\omega - \omega_{\mathbf{s}'\mathbf{s}}) \right\}$$
(9.2)

This standard expression is not very useful for practical purposes because of the difficulty in performing the summation and it is not easy to interpret. However, a simple transformation using the formula

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} dt$$

makes it possible to perform the summation over final states and gives a form more suggestive for physical interpretation. The transformation goes as follows:

$$\begin{split} &\sum_{ss'} \rho_{s} \leqslant s \left| H_{int}^{*pp'} \right| s^{*} \geqslant \leqslant s' \left| H_{int}^{p'p} \right| s \geqslant \delta(\omega - \omega_{s's}) \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \left\{ \sum_{ss'} \rho_{s} \leqslant s \left| H_{int}^{*pp'} \right| s^{*} \geqslant \leqslant s' \left| H_{int}^{p'p} \right| s \geqslant e^{-i\omega_{s'}t} \ e^{i\omega_{s}t} \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \left\{ \sum_{ss'} \rho_{s} \leqslant s \left| e^{iHt} \right| H_{int}^{*pp'} e^{-iHt} \right| s' \geqslant \leqslant s' \left| H_{int}^{p'p} \right| s \geqslant \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \sum_{s} \rho_{s} \leqslant s \left| H_{int}^{*pp'}(t) \right| H_{int}^{p'p}(0) \right| s \geqslant \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \leqslant \left| H_{int}^{*pp'}(t) \right| H_{int}^{p'p}(0) \right| s \geqslant \end{split}$$

H denotes the total Hamiltonian of the scattering system. We have used that $\sum_{s'} |s' \rangle \langle s'| = 1$ and the definition of a Heisenberg operator.

The transition probability per unit time now becomes

$$\frac{\mathrm{dW}_{p \to p'}}{\mathrm{dt}} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \mathrm{dt} \, \mathrm{e}^{\mathrm{i}\omega \mathrm{t}} < \left| \mathrm{H}_{\mathrm{int}}^{*\mathrm{pp'}}(\mathrm{t}) \, \mathrm{H}_{\mathrm{int}}^{\mathrm{p'p}}(0) \right| > \qquad (9.3)$$

This formula shows that the scattering depends on a certain time correlation function of the interaction operator taken with itself at two different times. The transition probability itself is, except for a constant, just the Fourier transform of the time correlation function.

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As an explicit illustration, let us consider the case where the probe is a particle without spin of mass M. The differential cross-section per unit solid angle per unit energy internal and per unit volume of the specimen is

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} = \left(\frac{\mathrm{M}}{2\pi}\right)^{2} \frac{\left|\vec{\mathbf{p}}^{\prime}\right|}{\left|\vec{\mathbf{p}}\right|} \sum_{\mathbf{s}^{\prime}} \left|\langle \mathbf{s}^{\prime}\right| \mathbf{H}_{\mathrm{int}} \left|\mathbf{s}\rangle\right|^{2} \delta(\omega - \omega_{\mathbf{s}^{\prime}\mathbf{s}})$$
(9.4)

We assume that the particles interact via a two-body interaction with the particles in the system,

$$H_{int}(\vec{x}) = \sum_{i=1}^{N} v(|\vec{x} - \vec{x}_i|)$$

or, in the form of second quantization

$$H_{int} = \int d^3 x' v(|\vec{x} - \vec{x}'|) \rho(\vec{x}') \qquad (9.5)$$

where $\rho(\vec{x}') = \sum_{\text{spin}} \psi_{\sigma}^{*}(\vec{x}') \psi_{\sigma}(\vec{x}')$ is the particle density operator.

In the Born approximation the initial and final states of the particle are taken as plane waves

$$|\mathbf{p}\rangle = \mathbf{e}^{\vec{\mathbf{p}}\cdot\vec{\mathbf{x}}}$$
 and $|\mathbf{p}'\rangle = \mathbf{e}^{\vec{\mathbf{p}}'\cdot\vec{\mathbf{x}}}$

The matrix element becomes, with $\vec{q} = \vec{p'} - \vec{p}$,

$$H_{int}^{p'p} = \int d^3 x \ e^{-i\vec{q}\cdot\vec{x}} H_{int}(\vec{x})$$
(9.6)

Thus, the interaction matrix is just the Fourier transform of (9.5) and, because (9.5) is a convolution (faltung) of $v(\vec{x} - \vec{x'})$ and $\rho(\vec{x'})$, we know that the Fourier transform is the product of the separate transforms, i.e.,

$$H_{int}^{p'p} = v(\vec{q}) \rho_{\vec{q}}$$
(9.7)

Inserting this formula in (9.4) we obtain

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} = \left(\frac{\mathrm{M}}{2\pi}\right)^{2} \left(\frac{|\vec{p}|}{|\vec{p}|}\right) |\mathbf{v}(\vec{q})|^{2} \sum_{\mathbf{s}'} |\langle \mathbf{s}'|\rho_{\mathbf{q}}|\mathbf{s}\rangle|^{2} \delta(\omega - \omega_{\mathbf{s}'\mathbf{s}})$$
(9.8)

Thus, the cross-section factorizes into two parts: one, which is concerned with the nature of the probe and its interaction with the system

and one describing the excitation of the system and which is entirely a property of the system. Thus we write

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} = \left(\frac{\mathrm{M}}{2\pi}\right)^{2} \left(\frac{\left|\vec{\mathbf{p}}'\right|}{\left|\vec{\mathbf{p}}\right|}\right) \left|\mathbf{v}(\vec{\mathbf{q}})\right|^{2} \mathrm{S}(\vec{\mathbf{q}},\omega) \tag{9.9}$$

with

$$S(\vec{q},\omega) = \sum_{s^{*}} \left| \langle s^{*} | \rho_{\vec{q}} | s \rangle \right|^{2} \delta(\omega - \omega_{s^{*}s})$$

 $S(\vec{q}, \omega)$ is the dynamic form factor of the system and contains all the information about the system that can be obtained in a scattering experiment.

We notice that it has the form of a spectral weight function, where the strength in this case is determined by the matrix element $\langle s' | \rho_{\vec{d}} | s \rangle$.

Going from energy to time representation, using the arguments leading up to (9.3), we find that

$$S(\vec{q}, t) = \left\langle \rho_{\vec{t}}(t) \rho_{\vec{t}}(0) \right\rangle$$
(9.10)

Thus this scattering experiment is related to the <u>density-density corre-</u> lation function and the <u>dynamic form factor is the spectral weight function</u> for <u>density fluctuation</u>. In order to calculate this function one has then to go back to the two-particle Green function. However, it should be observed that the result depends on only two times and this implies that only part of the information contained in the two-particle Green function is actually needed to obtain the density fluctuation spectrum.

Analogous considerations apply for other scattering mechanisms. In the case of magnetic scattering between neutrons and the electrons we have instead the interaction between the magnetic field from the neutron and the <u>spin density</u> of electrons or in other words the microscopic density of magnetization. This interaction leads, by precisely parallel considerations, to a study of correlation functions describing fluctuations in the spin density of the system. In the case of electromagnetic radiation, the vector potential of the electromagnetic field couples to the <u>current operator</u> of the system, and we are in this case led to study the current-current correlation function.

We can summarize and generalize these scattered remarks by noting that there is a class of situations with a linear coupling between the probe and the system, such that the scattering cross-section factorizes as in (9.9). The corresponding dynamic form factor will describe the properties of the system and it will be related to a certain time correlation function. From Eq.(9.3) we see that only two times occur rather than the full number of times contained in the corresponding Green function. For this reason one often refers to these objects as double-time Green functions, and we shall say more about their properties in a later section.

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10. GREEN'S FUNCTIONS AND EXPERIMENTS: THE DRIVEN RESPONSE OF A SYSTEM

In this section we turn towards another familiar type of experiments in which we drive the system with an external field and measure the response of the system. As in the preceding section we are going to study only the first order efforts, i.e., the <u>linear response</u> to the external disturbance. Typically we deal in these experiments with a steady state operation. The external field couples to the system via some operator A and we measure the average value of some other operator B of the system, as schematically illustrated in Fig. 6.



Typical examples are when you apply a frequency-dependent electric field and measure the induced electric moment, which gives you the polarizability, or when you determine the frequency dependent susceptibility by measuring the induced moment when applying an external magnetic field.

For simplicity we consider the case where the interaction part of the Hamiltonian has the form

$$H_{int} = \int d^3x A(\vec{x}) f(\vec{x}, t)$$
 (10.1)

We wish to calculate the forced motion of some dynamical variable B. It is convenient to work in the <u>interaction picture</u>, which was briefly described in section 5.

We shall assume that the external force has been switched on slowly, formally from $t = -\infty$, and this can be taken care of by multiplying f by a factor $\exp(\delta t)$, δ being a positive infinitesimal. In the absence of interaction the Heisenberg operators A and B are given by

$$A^{0}(\vec{x}, t) = e^{i H_{0} t} A(\vec{x}) e^{-i H_{0} t}; \qquad B^{0}(\vec{x}, t) = e^{i H_{0} t} B(\vec{x}) e^{-i H_{0} t}$$
(10.2)

Switching on the perturbation adiabatically, starting from $t = -\infty$, the time dependence of B will change in the presence of the perturbation into

$$B(\vec{x}, t) = U^{*}(t, -\infty) B^{0}(\vec{x}, t) U(t, -\infty)$$
(10.3)

To first order in the perturbation we have

$$U(t, -\infty) = 1 - i \int_{-\infty}^{t} dt' \int d^{3}x' A^{0}(\vec{x}', t') f(\vec{x}', t')$$
$$U^{*}(t, -\infty) = 1 + i \int_{-\infty}^{t} dt' \int d^{3}x' A^{0}(\vec{x}', t') f(\vec{x}', t')$$

and so

$$B(\vec{x},t) = \left\{1 + i \int_{-\infty}^{t} dt' \int d^{3}x' A^{0}(\vec{x}',t') f(\vec{x}',t')\right\} B^{0}(\vec{x},t) \left\{1 - i \int_{-\infty}^{t} dt' \int d^{3}x' A^{0}(\vec{x}',t') f(\vec{x}',t')\right\}$$

$$= B^{0}(\vec{x},t) - i \int_{-\infty}^{t} dt' \int d^{3}x' \left[B^{0}(\vec{x},t) A^{0}(\vec{x'},t') - A^{0}(\vec{x'},t') B^{0}(\vec{x},t) \right] f(\vec{x'},t')$$

plus second-order terms

$$\approx B^{0}(\vec{x},t) - i \int_{-\infty}^{t} dt' \int d^{3}x' [B^{0}(\vec{x},t),A^{0}(\vec{x}',t')] f(\vec{x}',t')$$

Finally we average over the ground state or a statistical distribution, which we assume can be taken as that of the system in equilibrium before we applied the external field. Assuming B to be a quantity not explicitly depending on time, its average over an ensemble will be constant in time and so we have that

$$\langle B(\vec{x},t) \rangle - \langle B^{0}(\vec{x}) \rangle = -i \int_{-\infty}^{t} dt' \int d^{3}x' \langle [B^{0}(\vec{x},t), A^{0}(\vec{x}',t')] \rangle f(\vec{x}',t') \quad (10.4)$$

giving the change in B proportional to the force f.

The formula has a nice physical interpretation. It shows that a disturbance in the system of the point $\vec{x'}$ at time t' causes a change in $\langle B \rangle$ at another point \vec{x} at a later time t, indicating that the disturbance propagates through the system.

It is convenient to introduce the propagator

$$h_{BA}(\vec{x}, t; \vec{x'}, t') = \begin{cases} -i \langle [B^{0}(\vec{x}, t), A^{0}(\vec{x'}, t')] \rangle_{T} & \text{for } t > t' \\ 0 & \text{for } t < t' \end{cases}$$
$$= -i \Theta(t-t') \langle [B^{0}(\vec{x}, t), A^{0}(\vec{x'}, t')] \rangle_{T} \qquad (10.5)$$

It has the following properties:

(i) It can only depend on the time difference t-t'.

(ii) For a uniform system it depends only on the relative distance $\vec{x} \cdot \vec{x}'$. In a crystal lattice it is unchanged if we change both \vec{x} and \vec{x}' with the same lattice vector.

(iii) It satisfies the condition of causality, which means, for instance, that no polarization will be seen before we apply an electric field. This appears explicitly from our derivation of (10.4) and was explicitly included in (10.5).

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We are often interested in the response to a <u>periodic external field</u> in which the response is given by the frequency dependent conterpart of (10.5), defined by the Fourier transform

$$h(\vec{x}, \vec{x}', \omega) = \int_{-\infty}^{+\infty} dt \ h(\vec{x}, \vec{x}', t) \ e^{i\omega t}$$
(10.5')

(We have made a slight change in notation, replacing $h_{BA}(\vec{x}, t; \vec{x'}, t')$ by $h(\vec{x}, x', t-t')$.)

Resonances in the response indicate the presence of approximate eigenmodes of the system. A pole in $h(\vec{x}, \vec{x}', \omega)$ means that we can have a response without a driving field, and signifies that we have a stable elementary excitation in the system. The structure of $h(\vec{x}, \vec{x}', \omega)$ with regard to its frequency-dependence is therefore of great importance in studying the excitation spectrum of the system.

The condition of <u>causality</u>, i.e., that $h(\vec{x}, \vec{x}', t) = 0$ for t < 0 imposes an important property on the structure of $h(\vec{x}, \vec{x}', \omega)$ as a function of the complex frequency ω . If we calculate $h(\vec{x}, \vec{x}', t)$ from $h(\vec{x}, \vec{x}', \omega)$ using the formula

$$h(\vec{x}, \vec{x}', t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} h(\vec{x}, \vec{x}', \omega) e^{i\omega t}$$
(10.6)

we can do this by going over to a contour integration and use Cauchy's theorem. We must close the contour with a semicircle in the lower half-plane for t>0, but in the upper half-plane for t<0. In order to have $h(\vec{x}, \vec{x}', t) = 0$ for t<0 we must require that $h(\vec{x}, \vec{x}', \omega)$ be analytic in the whole upper half-plane. All the singularities representing excitations of the system must thus be located in the lower half-plane.

From this property it also follows that

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$$\int_{-\infty}^{+\infty} d\omega' \frac{h(\vec{x}, \vec{x}', \omega')}{\omega - \omega' - i\delta} = \int_{-\infty}^{+\infty} d\omega' \frac{h(\vec{x}, \vec{x}', \omega')}{\omega - \omega' - i\delta} = 0$$

Taking real and imaginary parts of this we find that the real and imaginary parts of $h(\vec{x}, \vec{x}', \omega)$ satisfy the dispersion relations

Re h(
$$\vec{x}, \vec{x}', \omega$$
) = $\frac{1}{\pi} P \int_{-\infty}^{+\infty} d\omega' \frac{\text{Im h}(\vec{x}, \vec{x}', \omega')}{\omega' - \omega}$

Im
$$h(\vec{x}, \vec{x}', \omega) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} d\omega' \frac{\operatorname{Re} h(\vec{x}, \vec{x}', \omega)}{\omega' - \omega}$$
 (10.7)

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Examples of retarded response functions are the polarizability, conductivity, dielectric functions, magnetic susceptibility, etc. Their properties will be discussed in detail by other lecturers during this course.

The retarded response functions form a class of functions closely related to experiments. Although they may contain four and more wavefield operators, they only depend on two times (actually only on the difference), and again, as in the case of scattering, belong to the class of <u>double-time Green's functions</u> which we shall briefly discuss in the next section.

11. DOUBLE-TIME GREEN FUNCTIONS AND THEIR EQUATIONS OF MOTION

We have encountered several kinds of Green functions in the preceding sections. One example has been the <u>time-ordered</u> or <u>causal</u> Green functions, defined as

$$G_{c}(t, t') = \langle \langle A(t) ; B(t') \rangle \rangle = -i \langle T\{A(t) B(t')\} \rangle$$

$$(11.1)$$

where T denotes the time-ordering symbol defined as

T A(t) B(t') =
$$\Theta(t-t')$$
 A(t) B(t') + $\eta \Theta(t'-t)$ B(t') A(t)

where $\eta = \pm 1$, depending on the nature of the operators A and B.

In connection with the driven response of a system exerted to an external force we encountered the <u>retarded</u> Green function defined from the retarded commutator

$$G_{r}(t,t') = \langle \langle A(t) ; B(t') \rangle \rangle_{r} = -i \Theta(t-t') \langle [A(t), B(t')] \rangle \qquad (11.2)$$

We can of course also define an advanced Green function $G_a(t, t')$ as

$$G_{a}(t,t') = \langle \langle A(t); B(t') \rangle \rangle_{a} = +i \Theta(t'-t) \langle [A(t), B(t')] \rangle \qquad (11.3)$$

Finally we have encountered the time correlation functions

$$F(t, t') = \langle A(t), B(t') \rangle \qquad (11.4)$$

They do not contain the discountinuous factor $\Theta(t-t^1)$ and are also defined at $t=t^1$. Because of this property they are not Green functions but they are in practice often calculated from the corresponding Green function.

We should mention that A(t) and B(t') need not be simple annihilation and creation operators, but are usually composite operators such as density, current density, spin density and so on. The alternative procedure of writing down the equations for the full n-particle 2n-time Green functions will not be discussed in these notes.

Next we shall indicate the nature of the equations satisfied by the double-time Green functions. The operators A(t) and B(t) both satisfy

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the equation of motion of quantum theory

$$i \frac{dA}{dt} = [A, H]$$
(11.4')

We now differentiate any of the Green functions (11.1), (11.2) or (11.3) with respect to t and obtain

$$i \frac{dG}{dt} = i \frac{d}{dt} \langle \langle A(t), B(t') \rangle \rangle$$
$$= \frac{d\Theta(t-t')}{dt} \langle [A(t), B(t')]_{\eta} \rangle + \langle \langle i \frac{dA(t)}{dt}; B(t') \rangle \rangle \qquad (11.5)$$

In obtaining (11.5) we have used $\frac{d\Theta(-t)}{dt} = -\frac{d\Theta(t)}{dt}$ In the next step we use the formula

$$\Theta(t) = \int_{-\infty}^{t} \delta(t') dt'$$

and the equation of motion (11.4') to obtain

$$\frac{\mathrm{dG}(\mathbf{t}-\mathbf{t}')}{\mathrm{dt}} = \langle [\mathbf{A}(\mathbf{t}), \mathbf{B}(\mathbf{t})]_{\eta} \rangle \delta(\mathbf{t}-\mathbf{t}') + \langle \langle [\mathbf{A}(\mathbf{t}) | \mathbf{H}(\mathbf{t}) - \mathbf{H}(\mathbf{t}) | \mathbf{A}(\mathbf{t})]; \mathbf{B}(\mathbf{t}') \rangle \rangle$$
(11.6)

In (11.6) $[]_n$ means either the commutator or the anticommutator, depending on the choice of η . The last term in (11.6) is in general a function of higher complexity than G(t-t') itself: it is related to a higher-order Green function. We can proceed to derive for this quantity a new equation of the form given in (11.6) and this in turn will depend on some higher-order correlation for which we again construct its equation of motion and so on. In this way we generate a chain of coupled equations describing successively more and more complicated motions and correlations in the system. The full chain of equations will of course give the formal description of the complete many-body problem, but is of course as intractable as trying to solve the many-particle Schrödinger equation itself. One way of finding approximate solutions is equivalent to what has been used in the theory of liquids (compare the lectures by Professor N. March in this course) where one assumes some kind of factorization or decoupling whereby the chain is broken and reduced to a small number of equations. The simple-minded decoupling procedure seems to be frowned upon by a number of many-body theorists and certainly for some good reasons. In discussing many important aspects of these problems, however, this method of obtaining approximate solutions seems to work as well as any other.

Going back to (11.6), the first term shows the delta-function behaviour in time which is characteristic of any Green function and the second term gives the change in time because of the interactions. The time-correlation functions have no discontinuity in the time dependence and satisfy (11.6) with only the second term included. Usually one rather determines the corresponding Green function first and then proceeds to calculate the time correlation function from the spectral weight function.

We again emphasize that (11.6) holds for all three types of Green functions: retarded, advanced and time-ordered. The equation must be supplemented by specifying the <u>boundary conditions</u>. These boundary conditions are best incorporated by using the spectral properties. As in the preceding cases we can introduce <u>spectral representations</u> for the various Green functions which are of the form

$$G_{r,a}(\omega) = \int_{-\infty}^{+\infty} \frac{A(\omega')d\omega'}{\omega - \omega' \pm i\delta}$$

for the retarded and advanced Green functions and of the form

$$G_{c}(\omega) = \int_{-\infty}^{+\infty} \frac{A(\omega')d\omega'}{\omega - \omega' + i\omega\delta}$$

for the time-ordered Green functions.

As a simple illustration we shall once more consider the case of free fermions. The Hamiltonian of the system is

$$H = \sum_{k} \epsilon(k) a_{k}^{*} a_{k}$$

From the commutation relations we obtain

$$i \frac{da_k}{dt} = \epsilon(k) a_k$$
 $i \frac{da_k^*}{dt} = -\epsilon(k) a_k^*$

Next we introduce the Green function

$$G(k, t-t') = \langle \langle a_k(t); a_k^*(t) \rangle \rangle$$

The equation of motion is obtained from (11.6)

$$i \frac{d}{dt} G(k, t-t') = \delta(t-t') + \epsilon(k) G(k, t-t')$$
(11.7)

This equation is immediately solved using the Fourier transformations

$$G(k, t-t') = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} G(k, \omega) e^{-i\omega(t-t')}$$
$$\delta(t-t') = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')}$$

and so we get

$$\{\omega - \epsilon(\mathbf{k})\} \mathbf{G}(\mathbf{k}, \omega) = 1$$

or

$$G(k,\omega) = \frac{1}{\omega - \epsilon(k)}$$
(11.8)

The spectral weight function in this case is simply

$$A(k, \omega) = \delta(\omega - \epsilon(k))$$

and we obtain for the retarded and advanced Green function the solution

$$G_{r/a}(k,\omega) = \int_{-\infty}^{+\infty} \frac{d\omega' A(k,\omega')}{\omega - \omega' \pm i\delta}$$
(11.9)

and for the time-ordered Green function, the solution

$$G_{c}(k,\omega) = \int_{-\infty}^{+\infty} \frac{d\omega' A(k,\omega')}{\omega - \omega' + i\omega\delta}$$
(11.10)

12. THE DIELECTRIC FUNCTION

We introduced in passing a dielectric function in Section 8 when we summed a particular class of diagrams which served to replace the bare Coulomb interaction by a frequency-dependent screened interaction. In this section we shall start from the point of view taken in Section 10, where we discussed the linear response of a system to an external disturbance.

Let us consider a system of electrons perturbed by a time-dependent external potential $V_{ext}(\vec{x},t)$ caused by a test charge $\rho_0(\vec{x},t)$ of small (formally infinitesimal) strength. This causes a first-order change in the average particle density

$$\langle \delta \rho(\vec{x}, t) \rangle = \langle \rho(\vec{x}, t) \rangle - \langle \rho^{0}(\vec{x}) \rangle$$

given by the equation

$$\langle \delta \rho(\vec{\mathbf{x}}, \mathbf{t}) \rangle = \int d^3 \mathbf{x}' \, d\mathbf{t}' \, h(\vec{\mathbf{x}}, \mathbf{t}; \vec{\mathbf{x}'}, \mathbf{t}') \, V_{\text{ext}}(\vec{\mathbf{x}'}, \mathbf{t}')$$
(12.1)

where

$$h(\vec{x}',t;\vec{x}',t') = -i\theta(t-t') \left\langle \left[\rho(\vec{x}t), \rho(\vec{x}',t')\right] \right\rangle$$

In order to avoid cumbersome notations we consider $h(\vec{x}t; \vec{x'}t')$ as a continuous matrix and write (12.1) in the shorter notation

$$\rho_{\text{ind}} = \langle \delta \rho \rangle = h \, V_{\text{ext}} = h \, v \, \rho_{\text{ext}} \tag{12.2}$$

where the Coulomb potential is written in the form

$$v(\vec{x}, t; \vec{x}', t') = \frac{e^2}{\left|\vec{x} \cdot \vec{x}'\right|} \delta(t-t')$$

In macroscopic theory we have the following connection between the external and induced charges:

$$\rho_{\rm ind} = \left(\frac{1}{\epsilon} - 1\right) \rho_{\rm ext} \tag{12.3}$$

where ϵ is the dielectric constant. This allows us to define a generalized dielectric function

 $\frac{1}{\epsilon} - 1 = h v \tag{12.4}$

Now the effective field V_{eff} inside a system which gives rise to the classical force on a charged test particle differs from the external field because of the induced charges and is given by

$$V_{eff} = V_{ext} + v \langle \delta \rho \rangle = (1 + hv) V_{ext} = \frac{1}{\epsilon} V_{ext}$$
(12.5)

This shows that the induced charges screen the external potential by the factor $1/\epsilon$.

The definition of a dielectric function is very general and we now specialize to a uniform system. The dielectric function $\epsilon(\vec{x} - \vec{x'}, t - t')$ has a <u>non-locality range</u> $|\vec{x} - \vec{x'}|$ and a <u>retardation</u> in time (t-t'). In momentumenergy space this means that the <u>dielectric function $\epsilon(\vec{q}, \omega)$ depends on</u> wave-length as well as on frequency.

We shall only briefly remark on how we shall calculate the function h. A straightforward attack is physically not very meaningful. One major reason for this difficulty is that the response of any small part of the system to the external field is heavily masked by the field created by the

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induced charges. It is indeed much easier if we try to disentangle this by asking for the response to the <u>effective field</u> in the first place and then use the relation between external and effective fields to calculate h.

The response theory, of course, works for this case as well and we can write

$$\langle \delta \rho \rangle = h_{\text{eff}} V_{\text{eff}}$$
 (12.6)

The connection between h and h_{eff} is found by using (12.5) and gives

$$h = h_{eff} \frac{1}{1 - vh_{eff}}$$
(12.7)

For the dielectric functions this gives simply

$$\epsilon = 1 - vh_{eff} \tag{12.8}$$

We still have the problem of how to calculate h_{eff} . However, when we have removed the difficulties of the self-consistent effective field, it is reasonable to assume that we can obtain a sensible answer by using the lowest order approximation for h_{eff} . We therefore put $h_{eff} = h_0$ where h_0 is the density-density correlation function for a gas of independent fermions. Thus

$$h_{0}(\vec{q}, t-t') = -i \theta(t-t') \langle 0 | [\rho_{q}(t), \rho_{-q}(t')] | 0 \rangle$$

$$= -i \theta(t-t') \sum_{n} \{ \langle 0 | \rho_{q}(t) | n \rangle \langle n | \rho_{-q}(t') | 0 \rangle - \langle 0 | \rho_{-q}(t') | n \rangle \langle n | \rho_{q}(t) | 0 \rangle \}$$

$$(12.9)$$

The density fluctuation operator is

$$\rho_{\mathbf{q}} = \int d^3 \mathbf{x} \ \psi^*(\vec{\mathbf{x}}) e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{x}}} \ \psi(\vec{\mathbf{x}}) = \sum_{\mathbf{k}} a^*_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}}$$
(12.10)

The matrix element for the transition out of the Fermi sea has the form

$$\langle \vec{k}, \vec{k} + \vec{q} \mid a_{k+q}^{*}(t) a_{k}(t) \mid 0 \rangle = n_{k}^{0}(1 - n_{k+q}^{0}) e^{i\{\epsilon(k+q) - \epsilon(k)\}t}$$

We then obtain the formula by summing over all momentum states and spins

$$h_{0}(\vec{q}, t-t') = -2i \sum_{k} \{ n_{k}^{0}(1-n_{k+q}^{0}) e^{-i(\epsilon(k+q)-\epsilon(k)(t-t')} - n_{k+q}^{0}(1-n_{k}^{0}) e^{-i(\epsilon(k+q)-\epsilon(k)(t-t')} \}$$

Writing $\tau = t - t'$ we next calculate $h_0(\vec{q}, \omega)$

$$h_{0}(\vec{q}, \omega) = \int_{0}^{\infty} d\tau e^{i\omega\tau} h_{0}(q, \tau) = -2\sum_{k} \frac{n_{k+q}^{0} - n_{k}^{0}}{\omega - \epsilon(k+q) + \epsilon(k) + i\delta}$$

For the dielectric function we finally obtain, using (12.8),

$$\epsilon(\mathbf{q},\omega) = 1 + \frac{4\pi e^2}{q^2} 2\sum_{\mathbf{k}} \frac{n_{\mathbf{k}+\mathbf{q}}^0 - n_{\mathbf{k}}^0}{\omega - \epsilon(\mathbf{k}+\mathbf{q}) + \epsilon(\mathbf{k}) + i\delta}$$
(12.11)

This result was first derived by Lindhard (loc. cit.). The integral can be performed analytically but the result is a rather lengthy mathematical expression. The many applications of this formula to physical problems of screening, plasmons, stopping power, etc., will be discussed in other lectures during this course. Instead we shall comment a little further on the physical assumptions leading up to the formula (12.11).

We recapitulate that we started out from the formula (12.4) expressing the dielectric function in terms of the density-density correlation function h. We next changed the point of view and found it more reasonable to calculate first the response to an effective field, thus introducing the new function h_{eff} , and then using the relation between external and effective potentials to obtain Eq.(12.8). The response function h_{eff} has a precise meaning and the formula (12.8) is of course an exact formal result. The approximation consisted in the replacement $h_{eff} \rightarrow h_0$, where h_0 is the response function for an ideal Fermi gas. This is precisely the same result as if we had directly calculated (12.6) using straightforward first-order perturbation theory, which indeed was what Lindhard did in his pioneering work on this problem.

Next we ask this question. By summing this set of diagrams



in section 8 we introduced a dielectric function

$$\epsilon(\mathbf{q}) = 1 + \frac{4\pi e^2}{\left|\vec{\mathbf{q}}\right|^2} 2i \int \frac{d^4 p}{(2\pi)^4} G_0(\mathbf{p}) G_0(\mathbf{p}+\mathbf{q})$$
 (12.12)

Is this the same as (12.11) or not? Evaluating the right-hand member we can show that the real parts are the same and the imaginary parts coincide only for positive frequencies but are equal with opposite signs for negative frequencies.

We should remember that the dielectric response function is a <u>retarded</u> function, whereas the expansion in terms of diagrams refer to time-ordered quantities, and therefore we have to distinguish between

the response dielectric function ϵ_r , which is connected to the retarded commutator of the density fluctuation, and the propagating dielectric function ϵ_c , which is connected to the time-ordered density correlations. These considerations hold, of course, for the exact results as well as the approximate formulas (12.11) and (12.12).

The approximations leading to (12.11) and (12.12) are often referred to as the <u>random phase approximations</u> or RPA. In perturbation theory the RPA means that we sum over this particular sequence of diagrams to obtain the propagating dielectric function. Some more physical insight was given in the steps leading up to (12.11), showing that RPA corresponds to lowest order perturbation theory supplemented with the self-consistency condition on the effective potential V_{eff}.

Next we would like to comment how we can go beyond the RPA. Let us introduce what is called the <u>irreducible polarization propagator</u> P(q)related to the dielectric function through

$$\epsilon_{\rm c}({\rm q}) = 1 + \frac{4\pi{\rm e}^2}{{\rm q}^2} {\rm P}({\rm q})$$
 (12.13)

We note that P(q) is closely related to the response function h_{eff} which measures the response to the ellective field.

In the RPA we have simply that

$$P^{RPA}(q) = \sum = 2i \int \frac{d^4p}{(2\pi)^4} G_0(p) G_0(p+q)$$
 (12.14)

This describes processes in which electron-hole pairs are excited and where they travel as free particles until they fall back and annihilate. Higher approximations are obtained by including processes in which they interact and indeed we can generate the full structure of P(q) as a perturbation series of the form



which is a formally exact but practically untractable procedure to obtain P(q). In fact not very much is understood about how to go an essential step beyond the RPA approximation.

We finally turn to the question of spectral representations. We start from the formula

$$\frac{1}{\epsilon_{\mathbf{c}}(\vec{\mathbf{q}},\omega)} - 1 = -i \frac{4\pi e^2}{q^2} \int_{-\infty} d\tau e^{i\omega\tau} \langle 0 | \mathbf{T} \{ \rho_{\mathbf{q}}(\tau) \rho_{\mathbf{q}}(0) \} | 0 \rangle \qquad (12.16)$$

By inserting a complete set of eigenstates and following the same steps as in section 6, we obtain

$$\frac{1}{\epsilon_{c}(\vec{q},\omega)} - 1 = \frac{4\pi e^{2}}{q^{2}} \sum_{n} \left| \langle n \left| \rho_{-q} \right| 0 \rangle \right|^{2} \left\{ \frac{1}{\omega - \omega_{n0} + i\delta} - \frac{1}{\omega + \omega_{n0} - i\delta} \right\}$$
(12.17)

Introducing a spectral weight function

$$A(\vec{q},\omega) = \sum_{n} \left| \langle n | \rho_{-q} \right| 0 \rangle \right|^{2} \delta(\omega - \omega_{n0}) \quad \text{for} \quad \omega > 0 \quad (12.18)$$

and

$$A(\vec{q}, \omega) = -A(\vec{q}, -\omega)$$
 for $\omega < 0$

we obtain the spectral representation

$$\frac{1}{\epsilon_{c}(\vec{q},\omega)} - 1 = \frac{4\pi e^{2}}{q^{2}} \int_{-\infty}^{\infty} \frac{A(\vec{q},\omega')d\omega'}{\omega - \omega' + i\omega\delta}$$
$$= \frac{4\pi e^{2}}{q^{2}} \int_{0}^{\infty} d\omega' A(q,\omega') \left\{ \frac{1}{\omega - \omega' + i\omega\delta} - \frac{1}{\omega + \omega' + i\omega\delta} \right\}$$
(12.19)

As mentioned earlier, the various Green functions differ only with respect to boundary conditions and for the dielectric response function which is related to the retarded commutator rather than to the timeordered product we obtain simply

$$\frac{1}{\epsilon_{\mathbf{r}}(\vec{q},\omega)} - 1 = \frac{4\pi e^2}{q^2} \int_{-\infty}^{+\infty} \frac{A(q,\omega') d\omega'}{\omega - \omega' + i\delta}$$
(12.20)

We finally add that the spectral representation of the density fluctuations has the same form as the corresponding one for phonons. The poles of these functions give the boson-like excitations of the system, which can be either ordinary particle-hole excitations similar to those in a noninteracting gas or, in the long wave length limit, they represent collective waves of density-fluctuations, the plasmons.

13. THE ONE-ELECTRON GREEN FUNCTION FOR AN INTERACTING FERMI GAS

We should like to discuss in a little more detail the properties and structure of the one-electron Green function. The physical problem we

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are concerned with is the motion of an electron interacting in a complicated way with the rest of the system. Let us first approach the problem in an intuitive way. In the case of no interactions the Green function has the form

$$G_0(\vec{k},\omega) = \frac{1}{\omega - \epsilon(\vec{k}) + i\omega\delta}$$
(13.1)

Let us now ask what happens if the effect of the interactions is accounted for by a potential $V(\vec{k})$. It is obvious that this will only shift the energy of each level by an amount $V(\vec{k})$ in (13.1), so we need only make the replacement $\epsilon(\vec{k}) \rightarrow \epsilon(\vec{k}) + V(\vec{k})$ to obtain

$$G(\vec{k},\omega) = \frac{1}{\omega - \epsilon(\vec{k}) - V(\vec{k}) + i\omega\delta}$$
(13.2)

We add the almost trivial remark that from the point of view of perturbation theory such a result can only be obtained by summing a perturbation series to infinite order. In this case it corresponds to summing the infinite sequence of diagrams

A momentum dependent potential corresponds to an interaction in space which is <u>non-local</u>, i.e., in an ordinary Schrödinger equation picture we have to make the replacement

$$V(\vec{x})\psi(\vec{x},t) \longrightarrow \int d^3x' V(\vec{x}\cdot\vec{x}')\psi(\vec{x}',t)$$

However, the most general interaction must also be <u>non-local in time</u>, i.e., we must consider the generalization to

$$V(\vec{x})\psi(\vec{x},t) \longrightarrow \int d^3x' dt' M(\vec{x}\cdot\vec{x}',t-t')\psi(\vec{x}',t')$$
(13.4)

In momentum-energy space, therefore, it must have the form $M(\vec{k}, \omega)$. This quantity, which takes over the role of an ordinary average potential

and includes the full interaction between the particle and the rest of the system, is what we call the <u>self-energy</u> or <u>mass operator</u>. Because we defined it to be the generalization of an ordinary potential, the Green function shall have the form

$$G(\vec{k},\omega) = \frac{1}{\omega - \epsilon(\vec{k}) - M(\vec{k},\omega) + i\omega\delta}$$
(13.5)

Again this can be considered to be a sum over infinite series of terms

or as the solution of the integral equation with $iG(k, \omega) = -$ thus



 \mathbf{or}

$$G(\vec{k},\omega) = G_0(\vec{k},\omega) + G_0(\vec{k},\omega) \quad M(\vec{k},\omega) \quad G(\vec{k},\omega)$$
(13.6)

The self-energy can be defined in terms of diagrams and we go back to the expansion of $G(\vec{k},\omega)$ discussed in section 8. Instead of expanding in terms of the bare Coulomb interaction, one should first perform the summations over the polarization graphs and then consider the expansion in terms of the screened interaction $v_{Coul.}/\epsilon_c(\vec{q},\omega)$ which we represent by a wavy line. In this way we obtain



which is a formally well-defined procedure but practically quite intractable. $M(\vec{k},\omega)$ is, in general, a <u>complex function</u>. If $M(\vec{k},\omega)$ is known we can calculate the spectral weight function

$$A(\vec{k},\omega) = \frac{1}{\pi} \left| \operatorname{Im} G(\vec{k},\omega) \right| = \frac{1}{\pi} \frac{\left| \operatorname{Im} M(\vec{k},\omega) \right|}{\left[\omega - \epsilon(\vec{k}) - \operatorname{Re}M(\vec{k},\omega) \right]^2 + \left\{ \operatorname{Im} M(\vec{k},\omega) \right\}^2}$$
(13.8)

Furthermore

Im
$$M(\vec{k}, \omega) = \begin{cases} < 0 & \text{for } \omega > 0 \\ \\ > 0 & \text{for } \omega < 0 \end{cases}$$
 (13.9)

In the absence of interactions the function A takes the form

$$A(\vec{k}, \omega) = \delta(\omega - \epsilon(\vec{k}))$$

i.e., only one term remains from the entire superposition. When taking interactions into account the spectral function does not reduce to a δ -function; it is non-zero for all values of \cdot . It may turn out, however, that the function $A(\vec{k}, \omega)$ has a more or less sharply defined maximum near a point $\omega = \tilde{\epsilon}(k)$ with a width $\Gamma(\vec{k}) << \tilde{\epsilon}(\vec{k})$.

This resonance behaviour means formally that the analytical contribution into the complex ω -plane has a pole near the real axis. Near the pole we can put

$$G(\vec{k},\omega) = \frac{Z(\vec{k})}{\omega - \tilde{\epsilon}(\vec{k}) + i\Gamma(\vec{k})}$$
(13.10)

and the spectral function becomes, as expected,

$$A(\vec{k},\omega) \approx \frac{1}{\pi} \frac{Z(\vec{k}) \Gamma(\vec{k})}{\left[\omega - \tilde{\epsilon}(\vec{k})\right]^2 + \Gamma^2(\vec{k})}$$
(13.11)

where

$$Z(\vec{k}) = \left\{ 1 - \frac{\partial M(\vec{k}, \omega)}{\partial \omega} \bigg|_{\omega = \widetilde{a}(k)} \right\}^{-1}$$

and

$$\tilde{\epsilon}(\vec{k}) = \epsilon(\vec{k}) + \text{Re } M(\vec{k}, \tilde{\epsilon}(k))$$

Assuming that no more poles occur for the same values of \vec{k} , the rest of the spectrum will contribute in an incoherent way and we can write

$$G(\vec{k},\omega) = \frac{Z(\vec{k})}{\omega - \tilde{\epsilon}(\vec{k}) + i\Gamma(k)} + \varphi(\vec{k},\omega)$$
(13.12)

where the (smooth) function $\varphi(\vec{k},\omega)$ takes care of the remaining part.

Transforming to the time-variable, the singular part in (13.12) will describe a <u>quasiparticle</u> with lifetime Γ , thus

$$G(\vec{k},t) = \begin{cases} -i \ Z(\vec{k}) \ e^{-i \ \widetilde{\epsilon}(\vec{k})t} \ e^{-\Gamma(\vec{k})t} + \text{incoherent contributions for } t > 0 \\ \\ +i \ Z(\vec{k}) \ e^{-\widetilde{\epsilon}(\vec{k})t} \ e^{-\Gamma(\vec{k})t} + \text{incoherent contributions for } t < 0. \end{cases}$$
(13.13)

We compare this with the corresponding relations for non-interacting fermions

$$G_0(\vec{k}, t) = \begin{cases} -i e^{-i \epsilon(k)t} & \text{for } t > 0 \\ \\ +i e^{-i \epsilon(k)t} & \text{for } t < 0 \end{cases}$$

We observe the differences caused by the interactions:

- (i) The single particle energies have changed: $\epsilon(\vec{k}) \rightarrow \tilde{\epsilon}(\vec{k})$
- (ii) We have a finite damping $\Gamma(\vec{k})$, however $\Gamma \rightarrow 0$ when we approach the Fermi surface.
- (iii) A renormalization factor $Z(\vec{k})$, (<1) appears in the quasiparticle propagator.

We next calculate the momentum distribution function $\underline{n}(\vec{k})$, defined by

$$n(\vec{k}) = \langle 0 | a_{k}^{*}a_{k} | 0 \rangle = -i \lim_{t=0} G(\vec{k}, t)$$
$$= -i \int_{\infty} G(k, \omega) \frac{d\omega}{2\pi}$$
(13.14)

The location of the singularities is illustrated in Fig.7.



FIG. 7. Position of quasiparticle poles.

The contribution from the quasiparticle gives $Z(\vec{k})$ as long as we are inside the Fermi sea. As soon as we pass the Fermi momentum the pole falls outside the contour and therefore we have a discontinuity of magnitude $Z(k_{\rm F})$ at the Fermi surface. The incoherent contributions will add a smooth background. Thus $n(\vec{k})$ will have the shape given in Fig.8.



FIG.8. Momentum distribution in interacting Fermi systems.

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We finally ask: What is the physical structure in the self-energy operator? In order to see the gross features it is instructive to calculate first the self-energy of a <u>heavy charged particle</u> moving through the medium with velocity \vec{v} . The difference in the potential from the particle between the medium and in vacuum is given by the formula

$$\Phi(\vec{\mathbf{x}} - \vec{\mathbf{vt}}) = \int \frac{d^3 q}{(2\pi)^3} \mathbf{v}(\vec{\mathbf{q}}) \left\{ \frac{1}{\epsilon(\vec{\mathbf{q}}, \vec{\mathbf{q}}, \vec{\mathbf{v}})} - 1 \right\} e^{i\vec{\mathbf{q}}(\vec{\mathbf{x}} - \vec{\mathbf{vt}})}$$
(13.15)

In order to get the self-energy we evaluate the potential at the position of the particle, and remember that we should consider its charge as having gradually built up from zero to its full value, thus

$$M = \frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} v(\vec{q}) \left\{ \frac{1}{\epsilon(\vec{q}, \vec{q}, \vec{v})} - 1 \right\}$$
(13.16)

The factor $1/\epsilon(\vec{q}, \vec{q}, \vec{v})$ -1 describes the <u>Coulomb hole</u> around the electron and the self-energy describes just the <u>Coulomb interaction</u> with the induced hole around the particle.

This classical calculation ignores a couple of effects which should be included for electrons:

- (i) The effect of recoil which must be taken into consideration for a light particle and
- (ii) the effect of quantum statistics, i.e., the effect of exchange.

The effects will all be included in an approximate way if one considers the lowest order diagram in terms of the screened interaction

$$M(\vec{k}) = \underbrace{\int \frac{d^4q}{(2\pi)^4} \frac{v(\vec{g})}{\epsilon_0(q)} G(\vec{k} \cdot \vec{q})}_{(13.17)}$$

This can be written out explicitly as a sum of a <u>Coulomb hole contribution</u> plus an exchange term.

If, instead, we consider the lowest order graph in terms of the bare Coulomb interaction, we obtain the well-known <u>Hartree-Fock exchange</u> interaction

$$M_{HF}(\vec{k}) = -\int \frac{d^3q}{(2\pi)^3} v(\vec{q}) n^0_{\vec{k}+\vec{q}}$$
(13.18)

The effect of using the dynamical screened interaction is to make the correlation hole narrower and deeper. This is illustrated in Fig.9 where we have reproduced results for the non-local potential for particles on the Fermi surface from work by Hedin [4].

The effect of the dynamic interaction is not only to screen the Coulomb interaction but also to give strong resonance effect. due to the coupling, to the longitudinal field of density fluctuations. Indeed, the occurrence of plasmon resonances at long wave lengths for which $\epsilon_{\rm c}(\vec{q},\omega) = 0$ gives a strong resonance in the M(k) which is strongly reflected in the shape of the spectral function, as illustrated in the following figure taken from work by L. Hedin, B.I. Lundqvist, and S. Lundqvist [5].



FIG.9. Self-energy operator as a non-local potential. We have multiplied $M(r, \mu)$ by a factor $4\pi r^2 a_0 r_s$ from the volume element $4\pi r^2 dr = 4\pi r^2 a_0 r_s dx$ and by an extra r_s to make the HF curve r_s independent.



FIG.10. A typical example of the spectral function for electrons in an electron gas, for moment $0.6k_F$ I.u.k_F and I.y.k_F, respectively.

It should be added that the results of Figs 9 and 10 are based upon the first order graph (13.17). Although higher-order effects will undoubtedly change the quantitative results, the first-order results will already give a good qualitative insight in the structure of correlation and spectrum in an interacting Fermi system.

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THE LIQUID STATE

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Abstract

1. Distribution function theory of the liquid state. 1.1. Definition of distribution functions (canonical ensemble). 1.2. Radial distribution function and structure factor. 1.3. Internal energy and equation of state in terms of g(r). 1.4. Structure and forces. 2. Approximate theories of structure, 2.1. Born-Green theory. 2.1.1. Properties of E. 2.2. Abe's approximate form of Born-Green theory. 2.3. Asymptotic solution of Born-Green equation for van der Waals forces. 2.4. Ornstein-Zernike direct correlation function. 2.5. Density fluctuations and correlation functions. 2.6. Random-phase approximation. 2.7. Effective interatomic potential and the Percus-Yevick theory. 2.8. Direct correlation function for fluid argon. 2.9. Form of c(1) and equation of state of fluid argon. 2.10. Summary and comments on approximate 3. Fluctuations, compressibility and structure. 3.1. Grand partition function. 3.2. Long theories wavelength limit of structure factor in terms of fluctuations. 3.3. Specific heat at constant volume. **3.3.1.** Fluctuations in $\langle \Phi_{\rm N} | \Psi_{\rm N} \rangle$. **4.** Liquid dynamics and time-dependent correlation functions. 4.1. Relation to density operator. 4.2. Van Hove correlation function. 4.3. Intermediate scattering function, 4.4. Moments of van Hove correlation function and short-time expansions, 4.5. Asymptotic form of $G(\vec{r}, t)$ at large r and short times for van der Waals forces, 5. Elementary transport theory: particularly self-diffusion. 5.1. Solution of diffusion equation for $G_{s}(r, t)$. 5.2. Diffusion constant as a limit of $S_{s}(k, \omega)$. 5.3. Velocity correlation function, 5.4. Calculation of D for hard spheres. 5.5. Fourier transform of velocity correlation function. 6. Collective motions and $S(k, \omega)$. 6.1. Euler equation for trial function. 6.2. Solution for fluid and connection with Vlasov equation. 7. Liquid-gas critical point. 7.1. Phenomenology. 7.2. Ornstein-Zernike theory. 7.3. Specific heat at constant volume. 8. Quantal fluids. 8.1. Form of $S(k, \omega)$ for ground-state of ⁴He. 8.2. Use of structure data to determine $\omega(k)$ and form of ground-state wave function. 8.3. Preliminary remarks on the structure of ³He. APPENDICES. 1. Rushbrooke's form of Born-Green equation, 2. Exact relation between radial

distribution function and equation of state for hard spheres. 3. Relations between time-dependent correlation functions. 4. Sketch of theory for general transport coefficients. 5. Density matrices and two-body correlation function for free Fermions, 6. Velocity correlation function for Brownian motion and other cases, 7. Decay time of velocity correlation function for hard spheres. 8. Solution of linearized Vlasov equation for $S(k, \omega)$. 9. Phonon Hamiltonian for fluid.

1. DISTRIBUTION FUNCTION THEORY OF THE LIQUID STATE

The basic problem of the liquid state is to calculate the liquid properties from the intermolecular potential energy function $\Phi(\vec{r}_1 \ldots \vec{r}_N)$. These properties may refer either to equilibrium or non-equilibrium situations. In the first case, we can deal with the situation from probability distributions in position, whereas in the second we need to consider timedependent correlation functions, which reflect the molecular dynamical motions.

1.1. Definition of distribution functions (canonical ensemble)

We shall be thinking exclusively of monatomic liquids, like liquid argon or liquid metals. Suppose we have classical conditions at first;

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we shall discuss quantal fluids later in the lactures. Since the probability distribution in the phase space is given by exp (- H/k_BT), where H is the classical Hamiltonian, and k_B is Boltzmann's constant, we can integrate over momenta immediately and confine our attention to distribution functions in co-ordinate space. If we have N atoms in a volume Ω at

temperature T, then the probability $P^{(N)}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ that atom 1 will be found in volume element $d\vec{r}_1$ around \vec{r}_1 , atom 2 in $d\vec{r}_2$ around \vec{r}_2 , ... atom N in $d\vec{r}_N$ around \vec{r}_N is evidently given by

$$P^{(N)}(\vec{r}_{1} \quad \vec{r}_{2} \quad \dots \quad \vec{r}_{N}) \, d\vec{r}_{1} d\vec{r}_{2} \dots \quad d\vec{r}_{N}$$

$$= \frac{\exp\left[-\Phi(\vec{r}_{1}, \dots \quad \vec{r}_{N})/k_{B}T\right] \, d\vec{r}_{1} \, d\vec{r}_{2} \dots \quad d\vec{r}_{N}}{\int \dots \quad \int \exp\left[-\Phi/k_{B}T\right] \, d\vec{r}_{1} \, d\vec{r}_{2} \dots \quad d\vec{r}_{N}} \qquad (1.1)$$

The denominator in (1.1) is the so-called configurational integral, and will be denoted by Z.

Let us next define the probability that a given number $n(n \le N)$ atoms will be in $d\vec{r}_1$ around $\vec{r}_1, \ldots d\vec{r}_n$ around \vec{r}_n , regardless of the positions of the remaining N-n molecules. This is evidently given by integrating (1.1) over all co-ordinates \vec{r}_{n+1} to \vec{r}_N , and we find

$$P^{(n)}(\vec{r}_{1}\vec{r}_{2}...\vec{r}_{n}) = \frac{\int ... \int \exp\left[-\Phi(\vec{r}_{1}...\vec{r}_{N})/k_{B}T\right] d\vec{r}_{n+1}... d\vec{r}_{N}}{Z}$$
(1.2)

We shall often find it convenient to normalize the distribution functions differently from the above definitions. For example, consider $P^{(1)}(\vec{r_1})$, which is such that the probability that molecule 1 will be found at $\vec{r_1}$,

within $d\vec{r}_1$ is $P^{(1)}(\vec{r}_1) d\vec{r}_1$. This evidently satisfies

$$\int P^{(1)}(\vec{r}_1) \, d\vec{r}_1 = 1 \tag{1.3}$$

and since, in contrast to a crystal where $P^{(1)}(\vec{r_1})$ would be a periodic function of $\vec{r_1}$, $P^{(1)}(\vec{r_1})$ is constant in a fluid (except very near the surfaces, which we neglect generally), say $P^{(1)}$, we see from (1.3) that

$$P^{(1)}\Omega = 1$$
 (1.4)

Since we generally wish to take the limit $\Omega \to \infty$, $N \to \infty$, such that the density $N/\Omega = \rho^{(1)}$ remains finite, the normalization of $P^{(1)}$ in (1.4) is not very

convenient, and NP⁽¹⁾, which from (1.4) is equal to the density $\rho^{(1)}$, is more convenient. In general

$$\rho^{(n)} = \frac{N!}{(N-n)!} P^{(n)}$$
(1.5)

defines distribution functions normalized more conveniently than the $\mathbf{P}^{\left(n\right)}$.

The reason for introducing the factor N!/(N - n)! is to avoid labelling the molecules. In other words, there are N choices for the molecule at $\vec{r_1}$ in volume $d\vec{r_1}$, (N - 1) for $d\vec{r_2}$, (N - n+1) for $d\vec{r_n}$. Thus the total number of possibilities is

$$N(N-1)...(N-n+1) = \frac{N!}{(N-n)!}$$

and this factor is just the difference between $o^{(n)}$ and $P^{(n)}$.

1.2. Radial distribution function and structure factor

Perhaps the most central quantity in the theory of the liquid state is then the distribution function $\rho^{(2)}$ $(\vec{r}_1\vec{r}_2)$, which is such that $\rho^{(2)}(\vec{r}_1\vec{r}_2)d\vec{r}_1d\vec{r}_2$ is the probability that one molecule of the system will be found at \vec{r}_1 in $d\vec{r}_1$ and another in $d\vec{r}_2$ at \vec{r}_2 . In a fluid, $\rho^{(2)}$ depends only on $|\vec{r}_1 - \vec{r}_2|$. Since in the case of zero interatomic forces, $Z = \Omega^N$ and

$$\rho^{(n)} = \frac{N!}{(N-n)!} \frac{\Omega^{N-n}}{\Omega^N}$$
(1.6)

we find for a random system

$$\rho^{(2)} = \frac{N(N-1)}{\Omega^2}$$
(1.7)

We shall drop the superscript on $\rho^{(1)}$ generally and denote the particle density N/Ω by ρ . Thus, as $N \rightarrow \infty$, $\rho^{(2)} \rightarrow \rho^2$ in this case¹. We expect this to be true, with non-zero interatomic forces, as $|\vec{r_1} - \vec{r_2}| \equiv r_{12}$ gets very large and hence, writing

$$\rho^{(2)}(r_{12}) = \rho^2 g(r_{12}) \tag{1.8}$$

we see that $g(r_{12}) \rightarrow 1$ at very large interatomic separations. $g(r_{12})$ is the <u>radial distribution function</u>, the Fourier transform of which, from the work of Debye, is known to characterize the X-ray scattering from a fluid. It will be convenient at this point to define the <u>structure factor</u> S(k), by writing

$$S(k) = 1 + \rho \int [g(r) - 1] \exp(i\vec{k} \cdot \vec{r}) d\vec{r} \qquad (1.9)$$

¹ This is, from (1.7), only true to O(1/N).

and, utilizing the fact that g(r) is isotropic in a fluid, we can integrate over angles in (1.9) to obtain the alternative form

$$S(k) = 1 + \rho \int [g(r) - 1] 4\pi r^2 \frac{\sin kr}{kr} dr \qquad (1.10)$$

The inverse relations are immediately obtained and are given by

$$g(\mathbf{r}) = 1 + \frac{1}{8\pi^3\rho} \int [S(\mathbf{k}) - 1] \exp((\mathbf{i}\mathbf{k}\cdot\mathbf{\vec{r}})d\mathbf{\vec{k}}]$$

$$= 1 + \frac{1}{2\pi^2 \rho r} \int_{0} [S(k) - 1] k \sin kr dk \qquad (1.11)$$

Then, in treatises on X-ray scattering, it is shown that the intensity I of X-rays, measured in units defined by the scattering from a single electron, is given by

$$I = Nf^2S(k)$$
 (1.12)

where f is the usual atomic scattering factor, and $k = 4\pi \sin \theta / \lambda$, where θ is half the scattering angle, and λ is the wavelength of the radiation.

Thus, if we could calculate g(r) or S(k) from the interatomic forces, then a knowledge of f, essentially the Fourier transform of the electron density in an atom of the liquid, would allow the intensity of X-ray scattering to be predicted. So far, however, the main progress has come from using X-ray scattering as a tool for determining S(k) from (1.12), and hence g(r) from (1.11). A typical experimental curve of S(k) for liquid tin at 530°K is shown in Fig. 1. The corresponding (schematic) form of g(r) is indicated in Fig. 2. It is worth commenting at this stage that g(r) must be zero within an atomic diameter, due to the very strong repulsive forces then obtaining between atoms. This feature is reflected in the wavelength of the oscillations in S(k) at large k, the hard core diameter being 2π divided by this wavelength. These statements will be made quantitative later.

It is the short-range order, revealed by the peaks in g(r), which is the characteristic property of the liquid state. In contrast, for a dilute gas $S(k) \rightarrow 1$, $g(r) \rightarrow 1$ and we have to a good approximation an essentially random system.

1.3. Internal energy and equation of state in terms of g(r)

As a first application of the radial distribution function g(r), we shall show how the internal energy E and the equation of state may be obtained, provided we can assume that the intermolecular potential energy Φ can be decomposed into a sum of pair potentials $\phi(r_{ij})$. This assumption was thought for a long time to be realistic for liquid argon and similar fluids,



FIG. 1. Structure factor S(k) measured by X-ray scattering for liquid tin just above the melting point.



FIG. 2. Typical form of radial distribution function g(r), as obtained from an S(k) of the form shown in . Fig. 1.

but not to work for liquid metals, because of the electron gas. However, recent work on liquid metals suggests that the effects of the electron gas can be incorporated into a pair potential model, though $\phi(\mathbf{r})$ must then

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show an explicit density dependence. For the moment, however, we shall . consider $\phi(\mathbf{r})$ to be essentially the potential energy of interaction of two (argon) atoms in a vacuum. If we write

$$\Phi(\vec{r}_{1},\vec{r}_{2},\ldots,\vec{r}_{N}) = \sum_{i < j} \phi(r_{ij}) \qquad (1.13)$$

then we wish to obtain the internal energy E in terms of g(r) and $\phi(r)$. We note first that

$$E = \frac{3}{2} Nk_{B}T + \langle \Phi \rangle \qquad (1.14)$$

where the kinetic energy is immediately written down for classical atoms in equilibrium at temperature T. On the other hand, the mean potential energy is simply

$$\langle \Phi \rangle = \frac{\int \dots \int e^{-\Phi/k_{\rm B}T} \Phi \, d\vec{\mathbf{r}}_1 \dots d\vec{\mathbf{r}}_{\rm N}}{Z}$$
 (1.15)

From (1.13), the sum consists of N(N-1)/2 terms, all of which contribute equally to (1.15), and hence we find

$$\langle \Phi \rangle = \frac{N(N-1)}{2} \iint \phi(\mathbf{r}_{12}) \left[\frac{\int \dots \int e^{-\Phi/k_{B}T} d\vec{\mathbf{r}}_{3} \dots d\vec{\mathbf{r}}_{N}}{Z} \right] d\vec{\mathbf{r}}_{1} d\vec{\mathbf{r}}_{2} \qquad (1.16)$$

But from the definition of the distribution functions, the quantity in square brackets on the right-hand side of (1.16) is simply $P^{(2)}(\vec{r}_1 \cdot \vec{r}_2)$, and using (1.5) and (1.8) we find

$$\langle \Phi \rangle = \frac{N(N-1)}{2} \int \int \phi(\mathbf{r}_{12}) \frac{(N-2)!}{N!} \rho^2 g(\mathbf{r}_{12}) d\vec{\mathbf{r}}_1 d\vec{\mathbf{r}}_2$$
$$= \frac{\rho^2 \Omega}{2} \int_0^\infty \phi(\mathbf{r}) g(\mathbf{r}) 4\pi r^2 d\mathbf{r}$$
(1.17)

one of the integrations giving us immediately the volume of the fluid. Hence, from (1.14) and (1.17), we have

$$E = \frac{3}{2} N k_{B} T + \frac{N \rho}{2} \int_{0}^{\infty} \phi(r) g(r) 4 \pi r^{2} dr \qquad (1.18)$$

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In fact the potential energy term could have been written down directly on physical grounds, since the number of molecules on average within a distance between r and r+dr of a given molecule is $\rho g(r) 4\pi r^2 dr$ and the factor $\frac{1}{2}$ is present to avoid counting interactions twice.

To obtain the equation of state, we shall work from the classical virial theorem. This relates the kinetic energy \overline{K} to the virial of the forces. It is well known that the virial of the pressure p is $3p\,\Omega$, giving for a perfect gas

$$2\overline{K} = 3p\Omega \qquad (1.19)$$

When there is a force \vec{F}_i acting on the ith molecule at \vec{r}_i we have to calculate the average of $-\sum_i \vec{r}_i \cdot \vec{F}_i$, the sum extending over all the molecules.

For central forces, this becomes the average of N(N-1)/2 terms again, each of which is given by

$$\int \mathbf{r}_{12} \frac{\partial \phi(\mathbf{r}_{12})}{\partial \mathbf{r}_{12}} \, \mathrm{d}\vec{\mathbf{r}}_1 \mathrm{d}\vec{\mathbf{r}}_2 \begin{bmatrix} \frac{-\Phi/k_B T}{\mathbf{d}\vec{\mathbf{r}}_3 \dots \mathbf{d}\vec{\mathbf{r}}_N}{Z} \end{bmatrix}$$
(1.20)

Writing this again in terms of the radial distribution function g(r), using (1.5) and (1.8) we have, since $\overline{K} = (3/2) \operatorname{Nk}_{B}T$

$$3p\Omega = 3Nk_{B}T - \frac{N(N-1)}{2} \int r_{12} \frac{\partial \phi(\mathbf{r}_{12})}{\partial r_{12}} \cdot \frac{(N-2)!}{N!} \rho^{2}g(\mathbf{r}_{12}) d\vec{r}_{1} d\vec{r}_{2}$$

or

$$p = \rho k_{B}T - \frac{\rho^{2}}{6} \int r \frac{\partial \phi}{\partial r} g(r) d\vec{r}$$
(1.21)

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In principle then, from an assumed law of force and a measured (or, hopefully, calculated) g(r), we can estimate the internal energy and the fluid pressure from (1.18) and (1.22).

1.4. Structure and forces

We wish next to consider how we can, in principle, derive the radial distribution function $g(\mathbf{r})$ from the pair potential $\phi(\mathbf{r})$. As we shall see below, an exact equation exists which connects the distribution functions $\rho^{(2)}$ (α g(r)) and $\rho^{(3)}$, with $\phi(\mathbf{r})$. Unfortunately, so far we have no exact theory of $\rho^{(3)}$ to insert into this equation. We shall consider several approximations which we can make to enable us to estimate g(r) from the pair force law.

We have

$$g(\vec{r}_1 \vec{r}_2) = \frac{\Omega^2 \int \dots \int e^{-\Phi(\vec{r}_1 \dots \vec{r}_N)/k_B T} d\vec{r}_3 \dots d\vec{r}_N}{Z}$$
(1.22)
We wish to form $\partial g / \partial \vec{r}_1$, and thus we write

$$\Phi = \sum_{s=2}^{N} \phi(1, s) + \begin{array}{c} \text{terms independent of} \\ \text{co-ordinate } \vec{r_1} \end{array}$$
(1.23)

We then find

$$\frac{\partial g}{\partial \vec{r_1}} = \frac{\Omega^2}{Z} \int \dots \int \frac{\partial}{\partial \vec{r_1}} \left[\sum_{s=2}^{N} \phi(1, s) \right] \left[\frac{-1}{k_B T} \right] e^{-\Phi/k_B T} d\vec{r_3} \dots d\vec{r_N}$$
$$= \frac{-\Omega^2}{k_B T Z} \int \dots \int \left(\frac{\partial \phi(r_{12})}{\partial \vec{r_1}} + (N-2) \frac{\partial \phi(r_{13})}{\partial \vec{r_1}} \right) e^{-\Phi/k_B T} d\vec{r_3} \dots d\vec{r_N} \qquad (1.24)$$

Now we recall the definitions of g and $\rho^{(3)},$ and we can rewrite this equation in the form

$$\frac{\partial g(\mathbf{r}_{12})}{\partial \vec{r}_{1}} = \frac{-1}{k_{B}T} \frac{\partial \phi(\mathbf{r}_{12})}{\partial \vec{r}_{1}} g(\mathbf{r}_{12})$$

$$\frac{-1}{k_{B}T} \int \frac{\rho^{(3)}(\vec{r}_{1} \vec{r}_{2} \vec{r}_{3})}{\rho^{2}} \frac{\partial \phi(\mathbf{r}_{13})}{\partial \vec{r}_{1}} d\vec{r}_{3} \qquad (1.25)$$

This is the desired equation and we can rewrite it in a physically significant form by dividing both sides by $g(r_{12})$ and introducing a quantity $U(r_{12})$ through

$$g(r_{12}) = e^{-U(r_{12})/k_{\rm B}T}$$
(1.26)

Then we find

$$\frac{-\partial U(\mathbf{r}_{12})}{\partial \vec{r}_1} = \frac{-\partial \phi(\mathbf{r}_{12})}{\partial \vec{r}_1} - \int \frac{\rho^{(3)}(\vec{r}_1 \vec{r}_2 \vec{r}_3)}{\rho^2 g(r_{12})} \frac{\partial \phi(r_{13})}{\partial \vec{r}_1} d\vec{r}_3 \qquad (1.27)$$

This has the direct interpretation that, with $U(\mathbf{r}_{12})$ from (1.26) interpreted as a 'potential of mean force,' the left-hand-side is the total force on atom 1. This is split into two parts, a 'direct' part $-\partial\phi(\mathbf{r}_{12})/\partial\vec{\mathbf{r}_1}$, plus a part from the other atoms. Thus $\rho^{(3)}(\vec{\mathbf{r}_1}\vec{\mathbf{r}_2}\vec{\mathbf{r}_3})/\rho^2 g(\mathbf{r}_{12})$ is pro-

portional to the probability that a third atom is at $\vec{r_3}$ if there are certainly atoms at $\vec{r_1}$ and $\vec{r_2}$. This is simply multiplied by the force between atoms 1 and 3 and integrated over all positions of the third atom. This equation is valuable in giving us a handle on the relation between g(r) [or U(r)] and the pair potential $\phi(r)$.

We shall use this as a basis for our approximate theories of the liquid state. Before proceeding to discuss them, we should remark that the preceding argument is rather general and could have been applied to $\rho^{(n)}$, with n > 2. We shall not have occasion to use these more general relations in these lectures and so we shall not give the details.

2. APPROXIMATE THEORIES OF STRUCTURE

The basic equation (1.25), or its equivalent, (1.27) which we shall call the 'force equation', provides us with a starting point for a theory of liquid structure. We mean by this a theory which will allow us to calculate g(r) from a given pair potential $\phi(r)$.

The presence of $\rho^{(3)}$ ($\vec{r}_1 \vec{r}_2 \vec{r}_3$), the three-atom correlation function, means that we have to make approximations. However, it is worthwhile examining $\rho^{(3)}$ a little further to see just what part of $\rho^{(3)}$ is actually involved in the relation between ϕ and g. To see this, it is useful to take the scalar product of $\vec{r}_2 - \vec{r}_1$ with (1.25). Then we find,

$$-r_{12} \frac{\partial g(r_{12})}{\partial r_{12}} - \frac{r_{12}}{k_B T} g(r_{12}) \frac{\partial \phi(r_{12})}{\partial r_{12}}$$

$$= \frac{1}{k_{\rm B}T} \int \rho^{(3)}(\vec{r}_1 \vec{r}_2 \vec{r}_3) r_{12} \cos \theta \frac{\partial \phi(r_{13})}{\partial r_{13}} d\vec{r}_3$$
(2.1)

where (see Fig.3), θ is the angle between $\vec{r}_3 - \vec{r}_1$ and $\vec{r}_2 - \vec{r}_1$.



It will be convenient to simplify the notation as in Fig.3 when evidently r_{12} = s, r_{13} = t. Furthermore, $\rho^{(3)}$ will only depend on s, t and cos θ , for, in a fluid, it cannot depend on the choice of origin. Exploiting this fact, we may write

$$\rho^{(3)} (\vec{r}_1 \vec{r}_2 \vec{r}_3) = \rho^{(3)} (s, t, \cos \theta)$$
$$= \sum_{\ell=0}^{\infty} p_{\ell}^{(3)} (s, t) P_{\ell} (\cos \theta)$$
(2.2)

where the quantities $p_{\ell}^{(3)}$ (s,t), as indicated, are now independent of $\cos \theta$, after the expansion in Legendre polynomials $P_{\ell}(\cos \theta)$. If we now insert (2.2) in (2.1), then because of the presence of $\cos \theta$ ($\equiv P_1 (\cos \theta)$), only the $\ell = 1$ term in (2.2) contributes (see, for example, Hutchinson [1]). This shows that much less than complete knowledge of the three-body function is required in relating <u>structure</u> and forces. In particular, we

could add any terms with $\ell \neq 1$ to $\rho^{(3)}$ in (2.1) and not affect the final equation. We shall use this fact below; in discussing approximate theories.

2.1. Born-Green theory

All that we have said so far is exact for classical fluids with pair interactions. However, to obtain $p_1^{(3)}$ (s,t) or $\rho^{(3)}$ we must make approximations. As a starting point, we shall argue that we will treat pair correlations precisely through g(r), but shall assume that $\rho^{(3)}$ can be built up as a product of pair terms. Thus, we write

$$\rho^{(3)} (\vec{r_1} \cdot \vec{r_2} \cdot \vec{r_3}) = \rho^3 g(r_{12})g(r_{23})g(r_{31})$$
(2.3)

the factor ρ^3 following from the fact that for large interatomic separations of the three atoms we must get the random value ρ^3 given by (1.6), with N = 3. It should be noted from Fig. 3 that only the term g(r₂₃) depends on cos θ , and because of the argument given above, we can substitute

$$ho^3 g(r_{12}) g(r_{31})[g(r_{23}) - 1]$$

in (2.1), without changing the result from that obtained using (2.3). This latter substitution will be convenient, because g(r)-1 is a well behaved function, tending to zero at infinity. It is often useful, and we shall call it the total correlation function and denote it by h(r). Thus we find, after a simple calculation from (2.1),

$$\frac{\mathrm{d}}{\mathrm{ds}}\left[\ln g(s) + \frac{\phi(s)}{k_{\mathrm{B}}T}\right] = \frac{-\rho}{k_{\mathrm{B}}T} \int h(\mathbf{r}_{23})g(t) \frac{\partial\phi(t)}{\partial t} \cdot \frac{\mathrm{d}z}{t} \,\mathrm{d}\vec{r}_{3}$$
(2.4)

where, from Fig.3, we see that t_Z is the resolved part of \vec{t} on \vec{s} . It is shown in Appendix 1 that this equation may be rewritten, after some manipulation, in the form

$$\ln g(s) + \frac{\phi(s)}{k_B T} = \frac{\rho}{k_B T} \int E(|\vec{r} - \vec{s}|) h(r) d\vec{r} \qquad (2.5)$$

where

$$E(t) = \frac{1}{k_B T} \int_{t}^{\infty} g(x) \phi'(x) dx \qquad (2.6)$$

This is the Born-Green equation, and gives us an explicit integral equation connecting structure g(r) and the pair potential $\phi(r)$.

We shall consider some solutions of this for different physical cases below, but for the moment let us comment on two properties of E(t) which will be useful later.

2.1.1. Properties of E

i) At sufficiently large t, we can evidently replace g(x) by unity in (2.5) when we immediately obtain

$$E(t) \sim -\frac{\phi(t)}{k_B T}$$
(2.7)

ii) We can calculate $\int E(r) d\vec{r}$ over the volume of the fluid, in terms of the fluid pressure p. Defining the Fourier transform $\tilde{E}(k)$ of E(r) by

$$\widetilde{E}(\mathbf{k}) = \rho \int E(\mathbf{r}) e^{i \vec{\mathbf{k}} \cdot \vec{\mathbf{r}}} d\vec{\mathbf{r}}$$
(2.8)

then evidently

$$\tilde{\mathbf{E}}(0) = \rho \int \mathbf{E}(\mathbf{r}) d\vec{\mathbf{r}}$$
(2.9)

and substituting from (2.5) we may write

$$\widetilde{E}(0) = \rho \int d\vec{r} \int_{0}^{\infty} H(rt) g(t) \frac{\phi'(t)}{k_{B}T} dt \qquad (2.10)$$

where

$$H(rt) = 1, t > r$$

= 0, t < r (2.11)

We can now interchange the order of integration and we find

$$\int H(rt) d\vec{r} = \int_{0}^{t} 4\pi r^{2} dr = \frac{4\pi t^{3}}{3}$$
 (2.12)

and hence

$$\widetilde{E}(0) = \frac{4\pi\rho}{3} \int_{0}^{\infty} \frac{g(t)\phi'(t)}{k_{B}T} t^{3} dt \qquad (2.13)$$

But we saw in the first lecture (Eq. (1.22)) that the fluid pressure p involved this integral and we find (Gaskell, 1965)

$$\widetilde{E}(0) \approx 2 \left[1 - \frac{p}{\rho k_B T} \right]$$
(2.14)

For a perfect gas, with $p = \rho k_B T$, we see that $\tilde{E}(0)$ vanishes, which is evidently correct from (2.10) when $\phi = 0$.

Before turning to use these results in an explicit asymptotic solution of the Born-Green equation for van der Waals interactions, we shall discuss a further approximate equation of liquid state theory, given by Abe and many other workers (often called the hyperchain equation).

2.2. Abe's approximate form of Born-Green theory

To see how Abe's method results from the Born-Green equation we rewrite E(t) from (2.6) in the form

$$E(\mathbf{r}) = \frac{1}{k_{B}T} \int_{\mathbf{r}}^{\infty} ds g(s) \frac{d}{ds} [\phi(s) - U(s)] + \frac{1}{k_{B}T} \int_{\mathbf{r}}^{\infty} ds g(s) \frac{dU}{ds}$$
(2.15)

Then, since $g(r) = exp(-U/k_BT)$, the last term can be integrated explicitly and is simply the total correlation function h(r). Thus we find

$$E(\mathbf{r}) = \frac{1}{k_B T} \int_{\mathbf{r}}^{\infty} d\mathbf{s} \ g(\mathbf{s}) \frac{d}{d\mathbf{s}} \left[\phi(\mathbf{s}) - U(\mathbf{s})\right] + h(\mathbf{r})$$
(2.16)

Abe's approximation is now obtained (see Gaskell [2]) by putting g(s) in the integral term in (2.16) as unity, that is, replacing it by its asymptotic form. Such a procedure would seem to lead to a less accurate theory than the Born-Green theory, though the possibility exists that this second approximation could counteract the superposition assumption of the Born-Green theory. We shall see that, in at least one respect, this latter circumstance seems to exist. Then, we replace the function E(r) of (2.16) by c(r), say, defined by

$$c(r) = \frac{1}{k_B T} [U(r) - \phi(r)] + h(r) \qquad (2.17)$$

This leads to the second approximate equation of structure theory, namely,

$$\ln g(\mathbf{r}) + \frac{\phi(\mathbf{r})}{k_{B}T} = \rho \int c(|\vec{\mathbf{r}} - \vec{\mathbf{r}}|)h(\vec{\mathbf{r}}|)d\vec{\mathbf{r}}$$
(2.18)

This equation and the Born-Green theory are so similar in structure that we can apply essentially the same method of solution to both. We shall now show that both equations can be solved asymptotically for van der Waals interactions, to give an interesting result for the range of the correlations in g(r) in this case.

2.3. Asymptotic solution of Born-Green equation for van der Waals forces

In general, we have to solve the Born-Green and the Abe equations numerically for realistic pair potentials. But for van der Waals interactions, occurring in insulating fluids like argon, we can get interesting information on the range of the correlations, that is, the range of g(r). It will also show us that for short-range forces of this kind, we must make some modifications to the Born-Green theory, such as that made by Abe, to have a good theory asymptotically.

Thus, we return to (2.5) and look at the solution when, at large r,

$$\phi(\mathbf{r}) \sim -\frac{A}{r^6} \tag{2.19}$$

where A is the strength of the van der Waals interaction. From (2.6) we have then, since $g(x) \rightarrow 1$ for large x,

$$E(r) \sim \frac{A}{r^{6}k_{B}T}$$
(2.20)

Now it will prove convenient to work in \vec{k} space, and large \vec{r} implies that we look at small \vec{k} . Thus we can imagine $\tilde{E}(k)$, defined by

$$\widetilde{E}(\mathbf{k}) = \rho \int E(\mathbf{r}) e^{i \vec{\mathbf{k}} \cdot \vec{\mathbf{r}}} d\vec{\mathbf{r}}$$
(2.21)

expanded in a Taylor series about $\vec{k} = 0$. The question is what information can we gain about this expansion from the asymptotic form (2.20). The answer is provided by a nice theorem of Lighthill [3] which states that if a function F(k) is well behaved, with its derivatives, then

$$\int_{0}^{r} F(k) \sin kr \, dk \sim \frac{F(0)}{r} - \frac{F'(0)}{r^3} + \frac{F^{IV}(0)}{r^5} - \dots$$
+ terms decaying exponentially with r. (2.22)

Noticing that the inverse of (2.21) may be written

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$$E(\mathbf{r}) = \frac{1}{2\pi^2 \rho \mathbf{r}} \int_0^\infty \mathbf{k} \, \widetilde{E}(\mathbf{k}) \sin \mathbf{k} \mathbf{r} \, d\mathbf{k}$$
 (2.23)

we can immediately show from (2.20) and (2.22) that $\widetilde{\mathrm{E}}(k)$ must have the form

$$\widetilde{E}(k) = \widetilde{E}(0) + b_2 k^2 + b_3 k^3 + b_4 k^4 + \dots$$
 (2.24)

at small k, where

$$b_{3} = \frac{A\pi^{2}\rho}{|2k_{B}T|}$$
(2.25)

No term in k can appear in the expansion (2.24), because, in fact, it would lead to $E(r) \propto r^{-4}$ at large r, in conflict with (2.20). By analogy we can expand

$$S(k) = S(0) + a_2 k^2 + a_3 k^3 + \dots$$
 (2.26)

where, although we have not proved it here, we can show from the Born-Green equation that if we include a term a_1k , then the only solution must have $a_1 = 0$. Inverting the above argument, we find

$$h(r) \sim \frac{12a_3}{\pi^2 \rho r^6}$$
(2.27)

showing that, if we verify that (2.26) is a consistent expansion, the range of the correlations is the same as the range of the van der Waals interaction. We now must determine a_3 from the Born-Green equation and since the right-hand-side of (2.5) is a convolution (cf. Appendix 1) it involves, in Fourier transform, the product $\tilde{E}(k)$ [S(k) - 1]. Clearly, once again, the large r behaviour of the right-hand-side is determined by the coefficient of k^3 in this product, and this is simply

$$a_3 \tilde{E}(0) + b_3 [S(0) - 1]$$

Assembling then the leading terms on each side of (2.5) we have

$$\frac{12a_3}{\pi^2\rho r^6} - \frac{A}{r^6k_BT} = \frac{12}{\pi^2\rho r^6} \left[a_3 \tilde{E}(0) + b_3 \{S(0) - 1\}\right]$$
(2.28)

and hence

$$a_{3} = \frac{A \pi^{2} \rho S(0)}{12 k_{B} T[1 - \tilde{E}(0)]}$$
(2.29)

This result is due to Gaskell (1966), while the fact that S(k) at small k has the form (2.26) for van der Waals forces was shown by Enderby, Gaskell and March [4].

It is perfectly clear that the same argument applies to the Abe equation (2.18) with $\tilde{E}(0)$ in (2.29) replaced by $\tilde{c}(0)$, with c(r) defined by (2.17). We shall return to (2.29) when we have discussed the physical significance of c(r).

2.4. Ornstein-Zernike direct correlation function

Let us substitute for $(U - \phi)$ from (2.17) into the left-hand-side of (2.18) when we find

$$h(\mathbf{r}) = c(\mathbf{r}) + \rho \int c(|\vec{r} - \vec{r}|)h(\vec{r}) d\vec{r} \qquad (2.30)$$

We see that this equation relates c(r) to h(r) for a given density and we take it as the <u>fundamental</u> definition of c(r), independently of approximate theories. Clearly, if we measure S(k) by X-ray or neutron

scattering and hence get h(r), we can obtain c(r) directly from experiment. c(r) as defined by (2.30) was first introduced by Ornstein and Zernike in connection with critical fluctuations. We shall see in Part III of these lectures that it does indeed play a central role in any discussion of critical phenomena. Most usually, c(r) is referred to nowadays as the <u>direct</u> correlation function, for reasons we shall briefly discuss at this point.

From (2.5), we see that the potential of mean force U is split into a direct part ϕ and a convolution of E and h. Asymptotically as we have seen, $E \sim \phi$ and $h \sim U$, and if we make these replacements, we see that (2.30) and the Born-Green equation (2.5) have then the same form. We are then, in defining c, splitting the total correlation function h into a direct part c and an indirect part. Strictly, by analogy with the force equation, some three-body correlation function should be involved, and we can expect c(r) to have physical significance, at most, asymptotically,

From the Abe theory, we then find

$$h - c = \frac{U - \phi}{k_B T}$$
(2.31)

and hence, for large r,

$$c(r) \sim - \frac{\phi(r)}{k_{\rm B}T}$$
 (2.32)

provided $h^2 < |c|$. This is true well away from the critical point. Since c(r) is, in fact, defined in terms of h(r), we can calculate it from the measured structure factor. Taking the Fourier transform of (2.30) we find

$$\hat{h}(k) = \hat{c}(k) + \hat{h}(k) \hat{c}(k)$$
 (2.33)

or

$$\tilde{c}(k) = \frac{\tilde{h}(k)}{1 + \tilde{h}(k)} = \frac{S(k) - 1}{S(k)}$$
 (2.34)

Thus the direct correlation function in \vec{k} space is simply $1 - S^{-1}$, but since S(0) is typically 0.01-0.03 in liquid metals, the form $\tilde{c}(k)$ is very different from S(k) as can be seen by comparing Fig. 1 for S(k) with the form of $\tilde{c}(k)$ shown in Fig.4 for liquid thallium just above its melting point, as measured by neutron experiments.

Having discussed the Born-Green and the Abe (or often called hypernetted chain because of its connection with diagrammatic analysis) theories, and noting that they are most conveniently discussed in \vec{r} space, we turn now to two further treatments which are more basically formulated in \vec{k} space, though they will turn out to have a close relation to the Abe theory.

2.5. Density fluctuations and correlation functions

To define the density fluctuations, let us start out from the particle density $\rho(\vec{r})$ corresponding to an "instantaneous snap-shot" of the liquid, with atoms at $\vec{r}_1, \vec{r}_2 \dots \vec{r}_N$. Then

$$\rho(\vec{\mathbf{r}}) = \sum_{i=1}^{N} \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{i}) \qquad (2.35)$$

and evidently if we take the ensemble average we get



and clearly each of the N terms makes the same contribution. We then find

$$\frac{N\int\ldots\int e^{\frac{-\Phi}{k_{B}T}(\vec{r_{1}},\vec{r_{2}},\ldots,\vec{r_{N}})}}{Z}$$

and this is just $\rho^{(1)}(\mathbf{r})$ as it should be. Now we take the Fourier components $\rho_{\vec{k}}$ of the density $\rho(\vec{\mathbf{r}})$ and we immediately find

$$\rho_{\overrightarrow{k}} = \sum_{i=1}^{N} e^{i \overrightarrow{k} \cdot \overrightarrow{r_{i}}}$$
(2.36)

The $\rho_{\vec{k}}$ are the density fluctuations and, since they involve the positions of all the atoms, they may be viewed as collective co-ordinates.

Let us now briefly consider how the two-particle distribution function $\rho^{(2)}(\vec{r}) \equiv \rho^2$ g(r) may be expressed in terms of the density fluctuations. This time we are interested in the separation $\vec{r_i} - \vec{r_j}$ of two particles i and j. Thus we expect the essential element to be $\delta(\vec{r} - \vec{r_i} + \vec{r_j})$ and again it is readily verified that

$$\rho g(\mathbf{r}) = \left\langle \frac{1}{N} \sum_{i \neq 1} \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}_i + \vec{\mathbf{r}}_j) \right\rangle \qquad (2.37)$$

We now show that the Fourier transform of this, the structure factor S(k), is simply related to the density fluctuations $\rho_{\vec{k}}$.

To do this, we form

$$\rho_{\overrightarrow{k}}\rho_{\overrightarrow{-k}} = \sum_{i=1}^{N} e^{\overrightarrow{ik} \cdot \overrightarrow{r_{i}}} \sum_{j=1}^{N} e^{-\overrightarrow{ik} \cdot \overrightarrow{r_{j}}}$$

 \mathbf{or}

$$\rho_{\vec{k}} \rho_{-\vec{k}} \rightarrow N = \sum_{i \neq j} e^{i \vec{k} \cdot \vec{r_j} - \vec{r_j}}$$
(2.38)

Thus, by Fourier transform of (2.37) we obtain the result

$$S(k) = \frac{\left\langle \rho_{k} \rightarrow \rho_{-k} \rightarrow N \right\rangle}{N}$$
(2.39)

Likewise, we can obtain the higher order distribution functions in terms of the $\rho_{\overrightarrow{k}}$. We now return to the exact force equation (1.25) and converting it into \overrightarrow{k} space we find

$$S(\mathbf{k}) = 1 + \frac{1}{Nk^2} \sum_{\vec{n}} \frac{\tilde{\phi}(\mathbf{n})}{k_{\rm B}T} \langle \rho_{\vec{k}+\vec{n}} \rho_{\vec{k}} \rho_{\vec{n}} \rangle \vec{k} \cdot \vec{n} \qquad (2.40)$$

where we have assumed, for the moment, that the pair potential $\phi(\mathbf{r})$ has a Fourier transform, given by

$$\widetilde{\phi}(\mathbf{k}) = \int \phi(\mathbf{r}) e^{i \vec{\mathbf{k}} \cdot \vec{\mathbf{r}}} d\vec{\mathbf{r}}$$
(2.41)

This equation is exact for a potential that can be Fourier transformed. $\langle \rho_{\overrightarrow{k}+\overrightarrow{n}}, \rho_{\overrightarrow{n}}\rho_{\overrightarrow{k}} \rangle$, involving three ρ 's comes from the three-body correlation function.

2.6. Random-phase approximation

As in the earlier theories based on the force equation, we must now approximate. Since we want to relate S(k) and $\phi(k)$, we must somehow reduce $\langle \rho_{\vec{k}+\vec{n}} \ \rho_{\vec{n}} \ \rho_{\vec{k}} \rangle$ to S(k) and if we pick out from the sum the term $\vec{n} = -\vec{k}$, this is evidently related to S(k). This is, in fact, the random-phase approximation which is discussed more fully in other lectures by Lundqvist and Thomas. The qualitative argument is that unless \vec{k} and \vec{n} bear this simple relation, destructive interference between the various oscillatory components will tend to annul the other terms. Actually, such an argument turns out to be a long wavelength approximation. We then find, collecting the terms in S(k),

$$S(k) = \frac{1}{1 + \frac{\rho \,\widetilde{\phi}(k)}{k_{p}T}}$$
(2.42)

Comparing this with the result

$$S(k) = \frac{1}{1 - \tilde{c}(k)}$$
 (2.43)

which follows from the definition of the direct correlation function, we see that

$$\widetilde{c}(k) = \frac{-\rho \phi(k)}{k_{B}T}$$
(2.44)

or in r space

$$c(r) = \frac{-\phi(r)}{k_B T}$$
(2.45)

This is the same result, for large r, as the Abe approximation yields.

Actually, without going through the \vec{k} space analysis, this same form arises from replacing $\rho^{(3)}$ inside the integration over \vec{r}_3 in the force equation by $h(r_{23})$. However, its basic theoretical justification for small \vec{k} comes from the random phase approximation.

2.7. Effective interatomic potential and the Percus-Yevick theory

The crippling limitation of the above approximation is that it assumes an interaction with a Fourier transform. For liquids, in general, the interaction has almost a hard core, and we cannot Fourier transform it. The Percus-Yevick method is an attempt to produce an effective potential which will replace the Fourier components $\tilde{\phi}(\mathbf{k})$ above [5].

The idea behind it is to use the $\rho_{\vec{k}}$ as collective co-ordinates. For them to afford an accurate approximation we must be able to express the Hamiltonian in terms of them and the corresponding momenta, and then solve as if they were "almost" independent. But a serious difficulty

immediately comes up; there are 3N co-ordinates, $\vec{r}_1 \dots \vec{r}_N$, in the original Hamiltonian and while, in a finite system with, say, periodic boundary conditions imposed over a large cube of side L, \vec{k} has discrete though dense values, all such discrete \vec{k} are allowed in enumerating the $\rho_{\vec{k}}$. Actually, we would transform naturally to centre of mass co-ordinates

 $\vec{X} = \frac{\sum_{i=1}^{i=1} \vec{r}_i}{N}$ (2.46)

and (3N-3) $\rho_{\vec{k}}$, and there are many redundant co-ordinates. However, this fact, while troublesome, suggests a method of procedure which we shall now outline.

Suppose we consider the potential energy. Then, in (1.18) we found it in terms of $\phi(\mathbf{r})$ and $g(\mathbf{r})$ and by Fourier transform we get

Potential energy =
$$\sum_{all \ \vec{k}} \widetilde{\phi}(\vec{k}) [\rho_{\vec{k}} \rho_{-\vec{k}} - N]$$
 (2.47)

where $\phi(\vec{k})$ is, as before, the (assumed) Fourier transform of the interaction. However, if $\phi(k)$ cannot be defined, we think of an effective interaction ϕ_{eff} (k) such that

Potential energy =
$$\sum_{(3N-3)\vec{k}s} \tilde{\phi}_{eff}(\vec{k})[\rho_{\vec{k}}\rho_{-\vec{k}} - N]$$
(2.48)

We can, at this stage, ask whether we can choose $\phi_{\text{eff}}(\mathbf{k})$ to get the "best" possible approximation. There is ambiguity in this statement, but we might require that the mean square difference between $\phi(\mathbf{r})$ and the effective potential

$$\phi_{\text{eff}}(\mathbf{r}) = \sum_{(3N-3)\vec{k}s} \widetilde{\phi}_{\text{eff}}(k) e^{i\vec{k}\cdot\vec{r}}$$
(2.49)

be a minimum. More precisely we could minimize

$$\langle \left\{ \phi(\vec{\mathbf{r}}_{i} - \vec{\mathbf{r}}_{j}) - \sum_{(3N-3)\vec{k}s} \widetilde{\phi}_{eff}(k) e^{-i\vec{k}\cdot(\vec{\mathbf{r}}_{i} - \vec{\mathbf{r}}_{j})} \right\}^{2} \rangle$$
(2.50)

A first-order approximation to this indicates that the choice is

$$\widetilde{\phi}_{eff}(\mathbf{k}) = [\phi(\mathbf{r})g(\mathbf{r})]$$
(2.51)

where, by the right-hand side, we mean the Fourier transform of the product of $\phi(\mathbf{r})$ and $g(\mathbf{r})$. We see already that we have avoided the very strong repulsive potential inside the core by weighting the interaction with the probability of the occurrence of the pair of atoms i, j at separation $\vec{\mathbf{r}} = \vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j$.

Actually, since we wish to calculate structure, it is better to minimize averages of $\rho_{\vec{k}}\rho_{-\vec{k}}$ with respect to the exact distribution function (involving ϕ) and the approximation to it (involving ϕ_{eff}). We then find, after numerous approximations,

$$\widetilde{\phi}_{eff} (k) = k_B T \left[g(r) \left\{ e^{\frac{\phi(r)}{k_B T}} - 1 \right\} \right]$$
(2.52)

which clearly reduces to the earlier choice if we take $\phi(\mathbf{r})/k_BT$ to be small. This is the choice of the $\tilde{\phi}_{eff}$ (k)'s generally referred to as the Percus-Yevick approximation. Thus we have, from (2.44)

$$\widetilde{\mathbf{c}}(\mathbf{k}) = -\rho \left[g(\mathbf{r}) \left\{ \mathbf{e}^{\frac{\phi(\mathbf{r})}{\mathbf{k}_{\mathrm{B}} \mathrm{T}}} - 1 \right\} \right]$$
(2.53)

and if we assume (doubtfully, because of the use of the random-phase approximation) that this is true for all \vec{k} , then we may write, finally,

$$\mathbf{c(r)} = \mathbf{g(r)} \begin{bmatrix} 1 & -\mathbf{e}^{\frac{\phi(r)}{k_B T}} \end{bmatrix}$$
(2.54)

Clearly again

 $c(\mathbf{r}) \sim -\frac{\phi(\mathbf{r})}{k_B T}$ (2.55)

for large r, and there is a direct equivalence with the Abe approximation if U and ϕ are small.

2.8. Direct correlation function for fluid argon

We are now in a position to construct an approximate c(r) for fluid argon. To do so simply, we shall divide the pair potential $\phi(r)$ into two parts, which we shall call ϕ_{sr} and $\phi_{\ell r}$. The short-range part we shall define as the part inside the atomic diameter R, as shown in Fig.5. If we take a Lennard-Jones (6-12) potential, to be quite specific, that is

$$\phi(\mathbf{r}) = \frac{D}{\mathbf{r}^{12}} - \frac{A}{\mathbf{r}^6}$$
(2.56)

then we define R by $\phi(R) = 0$ and then $D = AR^6$. However, for r < R, we assume a rigid hard core, as shown by the dotted line in the Fig.5. This is <u>not</u> essential, but we can now get an <u>exact</u> solution of the Percus-Yevick equation for hard spheres. While this is an important result, I shall not

derive it, but refer to the account in Frisch and Lebowitz [6]. However, it is immediately clear from (2.54) that





FIG. 5. Potential for fluid argon. The part inside R is replaced, for simplicity, by a hard core (dashed line).



FIG. 6. Schematic form of c(r) for fluid argon.
 c hs is the Percus-Yevick result for hard spheres.
 c 1r is the random-phase approximation for Lennard-Jones potential.

It turns out that c(r) is a polynomial inside R and if we use R as the unit of length and write x = r/R, then

$$c(x) = \alpha + \beta x + \gamma x^{3} \qquad x < 1$$

$$= 0 \qquad x > 1$$
(2.57)

where α , β and γ are functions of the packing density η given by

$$\eta = \frac{1}{6} \pi R^{3} \rho$$
 (2.58)

Substituting in the Percus-Yevick equation, it can be shown that $\alpha\,,\beta\,$ and $\gamma\,$ are defined by

$$(1 - \eta)^{4} \alpha = -(1 + 2\eta)^{2}$$

$$(1 - \eta)^{4} \beta = 6\eta (1 + 2\eta)^{2}$$

$$(2.59)$$

$$(1 - \eta)^{4} \gamma = -\frac{1}{2}\eta (1 + 2\eta)^{2}$$

c(r) has then the form shown schematically in Fig. 6 while, if we calculate the structure factor S(k), we find, for a chosen value $R^3 \rho = 0.4$, the upper curve in Fig.7. Actually, it seems likely that both the Born-Green



- (b) Born-Green theory
- (d) Abe theory

and Abe approximations would give similar results, but so far the corresponding equations have not been solved exactly. However, the lower part of Fig.7 shows density expansions of these three theories and, except at small k, the results are quite similar. However, the other theories do not give c(r) = 0 for r > R and, in fact, it may be shown that the exact c(r)for hard spheres $\neq 0$. But we expect it to be small and we now turn to discuss the final form the above theories suggest for c(r) in fluid argon.

The form of $\tilde{c}_{hs}(k)/\tilde{c}_{hs}(0)$ is shown in Fig.8 along with experimental results for fluid argon at 84°K. The model obviously has the general features of the experimental data.



FIG. 8. Direct correlation function in \vec{k} space for fluid argon at 84°K. Curve 1 - Experiment. Other curves are slightly different ways of calculating hard sphere result.

2.9. Form of c(r) and equation of state of fluid argon

We have seen in the Percus-Yevick theory that c_{hs} is zero outside r. On the other hand, if we use the result (2.45) for the long-range part, we have immediately the form shown in Fig. 6, the tail directly reflecting the Lennard-Jones potential. This general form of c(r) has been confirmed from scattering data by a number of workers. We do not expect the step at R, of course, in a real liquid, though we expect a rather steep rise which will lead to oscillations in $\tilde{c}(k)$ at large k.

One rather striking confirmation that this approach is highly appropriate to fluid argon comes from studying its equation of state at high density (i.e., near the triple point). A few years ago, Longuet-Higgins and Widom [7] pointed out that in this regime the equation of state was well represented by a modified van der Waals theory. Thus, in the van der Waals equation of state we have

$$p = \frac{\rho k_B T}{1 - b\rho} - a\rho^2 \qquad (2.60)$$

where a and b are constants, independent of ρ and T. The first term is designed to take account of the "finite size" of the molecules, i.e., it is the analogue of a hard sphere term, while the second term takes account of the attractive forces. In present terms, we want therefore to write

$$p = p_{hs}(\rho, T) - a\rho^2$$
 (2.61)

Longuet-Higgins and Widom [7] show that this equation of state gives a quantitative account of the properties of fluid argon near the triple point. To show this, we reproduce in Table 1 some results they obtained at the triple point, together with the corresponding experimental results.

	(Ω _ℓ /Ω _s)	$\ln(p\Omega_{\ell}/Nk_{B}T)$	(∆S/NkB)	(U _l /Nk _B T)
Theory	1.19	-5.9	1.64	-8.6
Experiment	1.11	-5.88	1.69	-8.53

TABLE I. PROPERTIES OF ARGON AT TRIPLE POINT

The dimensionless quantities shown in Table 1 are, first the ratio of the liquid and solid volumes at the triple point, second the pressure, third the entropy of fusion ΔS , in units of Nk_B and fourth the cohesive energy of the liquid. Certain second derivatives of the free energy are given less satisfactorily and, in particular, the configurational specific heat is zero. But the numbers above are given to illustrate that this is really a very good equation of state for the high density fluid.

The link with our calculation of c(r) may now be made by a formula for S(0) which we shall prove below. This says that S(0) is related to the isothermal compressibility K_T and given by

$$S(0) = \rho k_B T K_T$$
(2.62)

Now $K_T = -\frac{1}{\Omega} \left(\frac{\partial \Omega}{\partial p} \right)_T$ by definition, and hence

$$\left(\frac{\partial p}{\partial \rho}\right)_{T} = \frac{k_{B}T}{S(0)} = k_{B}T \left[1 - \tilde{c}(0)\right]$$
(2.63)

the last step following from (2.43). Now we return to our result for c(r), namely,

$$c(\mathbf{r}) \doteq c_{\rm hs}(\mathbf{r}) + c_{\ell r}(\mathbf{r}) \tag{2.64}$$

and

$$\tilde{c}(0) = \tilde{c}_{hs}(0) + \tilde{c}_{gr}(0)$$
 (2.65)

Hence it follows that

$$\left(\frac{\partial p}{\partial \rho}\right)_{T} = \left(\frac{\partial p_{hs}}{\partial \rho}\right)_{T} - k_{B}T \tilde{c}_{\ell r} (0)$$

$$= \left(\frac{\partial p_{hs}}{\partial \rho}\right)_{T} + \rho \tilde{\phi}_{\ell r} (0)$$

$$(2.66)$$

from (2.44). Differentiating (2.61) with respect to ρ at constant temperature we see immediately that these two expressions agree, provided

$$2a = -\widetilde{\phi}_{gr} (0) \tag{2.67}$$

But this quantity, from the definition (2.56) is simply given by

$$\int_{R}^{\infty} 4\pi r^{2} \left(\frac{AR^{6}}{r^{12}} - \frac{A}{r^{6}} \right) dr = \frac{4\pi}{9} \frac{A}{R^{3}}$$
(2.68)

This is in excellent agreement (within about 10%) of the empirical value of a. If we had used the Born-Green asymptotic form, we would have been quite wrong. Thus we conclude that this confirms the result (2.45) for argon and enables the equation of state to be calculated from first principles from the parameters in the force law (Woodhead-Galloway, Gaskell and March; in the course of publication).

Actually Longuet-Higgins and Widom used the results of machine calculations for $p_{hs}(\rho, T)$. If we are content with slightly less accuracy, we could use the Percus-Yevick result. Substituting in (2.43) at $\vec{k} = 0$ we find then for the equation of state, using (2.62) and (2.57),

$$\frac{p}{\rho k_{B}T} = (1 - \eta)^{-3} [1 + \eta + \eta^{2}]$$
(2.69)

This is not unique; however, if we use the virial expression for the pressure we get a rather similar result and the thermodynamic inconsistencies are not too serious in this case.

If we use this argument in a metal, $\tilde{c}_{hs}(0)$ is made <u>more</u> negative by adding $\tilde{c}_{\ell r}(0)$, whereas in fluid argon it is made <u>less</u> negative. A crude calculation in a metal shows that $\tilde{\phi}_{\ell r}(0)$ is derivable from the pseudopotential which, as Ziman has discussed, tends to $2/3 E_f$ as $k \to 0$. But $E_f \propto \rho^{\frac{3}{2}}$ from electron theory, and integrating this we get a term in the equation of state $\propto \rho^{\frac{5}{2}}$. This replaces the ρ^2 term in argon, the difference coming from the density dependence of the pair potential. Unfortunately, in a metal, we are not sure whether R, defined by $\phi(R) = 0$ for present purposes, is significantly density dependent. It seems likely that it is and this means a more complex situation in a liquid metal than in fluid argon.

2.10. Summary and comments on approximate theories

We summarize below a few conclusions about the relative merits of the approximate theories:

- i) For short-range forces, the Percus-Yevick method seems best. In particular, the equation of state for hard spheres which it predicts is in reasonable agreement with machine calculations.
- ii) The random phase approximation, while of value as we have seen for argon, is not directly applicable to fluids until the hard core is subtracted and treated separately.

- iii) There is some evidence, both pragmatic and fundamental, (for the latter, see remarks in Brout's book on 'Phase Transitions[8]) that the Born-Green theory is preferable for long-range forces.
- iv) For equilateral triangular configurations, Alder has shown that for hard spheres $\rho^{(3)} = \rho^3 [g(r)]^3$ to high accuracy by machine calculations.
 - v) It appears that the correct asymptotic result for c(r) is $c(r) \sim -\phi(r)/k_BT$, provided $h^2 < |c|$, the inequality defining the range of validity readily following from the Abe approximation. The condition is satisfied well away from the critical point.

One final comment seems called for. We began by asking how $\rho^{(3)}$ could be related to the two-body correlations. In retrospect, it seems that we should first have asked about the range of the forces! It seems clear that a relation between $\rho^{(3)}$ and $\rho^{(2)}$ which will be useful for long-range forces is not likely to be valid for short-range interactions. This probably means that it is going to be hard to find a single equation for relating structure and forces which will successfully describe both liquid argon and liquid lead.

3. FLUCTUATIONS, COMPRESSIBILITY AND STRUCTURE

We have seen that $g(r) \rightarrow 1$ at large r to O(1/N). This is troublesome only when we want to calculate accurately integrals of g(r) - 1 over the volume of the fluid. It turns out that the quantity $1 + \rho \int [g(r) - 1] d\vec{r}$, which through (1.9) is simply the long wave length limit of the structure factor, can be related to the isothermal compressibility κ_T .

3.1. Grand partition function

The procedure we shall use, to avoid the above-mentioned difficulty, is based on the grand partition function. As is well known, this is related to the configuration integral Z of the canonical ensemble rather directly. Precisely, let us define the partition function as

Q(N, Ω, T) =
$$\frac{1}{h^{3N}N!} (2\pi Mk_BT)^{\frac{3N}{2}} Z$$
 (3.1)

where we have now included the kinetic energy part of H, have put in the result that quantum mechanics divides the phase space for a single particle into cells of h^3 and have accounted for indistinguishability. This ensures a correct limiting transition from quantum mechanics. Then the grand partition function is given by

$$Q_{G} = \sum_{all N} e^{\frac{N\mu}{k_{B}T}} Q(N, \Omega, T)$$
 (3.2)

where μ is the chemical potential.

Obviously we have a weighted sum of the partition functions for a canonical ensemble, the individual terms corresponding to different

numbers of particles. This is the new point about the grand canonical ensemble: it relaxes the condition that we have a definite number of particles N.

We see from (3.2) that the probability that a system in the grand canonical ensemble does contain N atoms is given by

$$P_{N} = \frac{e^{\frac{N\mu}{k_{B}T}}}{Q_{G}}$$
(3.3)

Let $\rho^{(n)}(\vec{r_1}...\vec{r_n})d\vec{r_1}...d\vec{r_n}$ be the probability of observing molecules in $d\vec{r_1}...d\vec{r_n}$ at $\vec{r_1}...\vec{r_n}$, irrespective of N. Then evidently

$$\rho^{(n)} = \sum_{N \ge n} \rho_N^{(n)} P_N \qquad (3.4)$$

where the $\rho_N^{(n)}$ are the distribution functions in the canonical ensemble. Also

$$\iint \rho^{(n)}(\vec{r_1} \dots \vec{r_n}) d\vec{r_1} \dots d\vec{r_n} = \sum_{N \ge n} P_N \frac{N!}{(N-n)!}$$
(3.5)

Always defining averages with $\boldsymbol{P}_{\!\boldsymbol{N}}$ we may write

$$\int \dots \int \rho^{(n)} (\vec{r}_1 \dots \vec{r}_n) d\vec{r}_1 \dots d\vec{r}_n = \langle \frac{N!}{(N-n)!} \rangle$$
(3.6)

3.2. Long wave length limit of structure factor in terms of fluctuations

As important special cases of the normalization condition (3.6) we have

$$\iint \rho^{(2)}(\vec{r}_1 \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \langle N(N-1) \rangle$$
$$= \overline{N}^2 - \overline{N} \qquad (3.7)$$

Furthermore,

$$\int \rho^{(1)}(\vec{r}_1) d\vec{r_1} = \vec{N}$$

and therefore

$$\iint \rho^{(1)}(\vec{r_1})\rho^{(1)}(\vec{r_2})d\vec{r_1}d\vec{r_2} = (\overline{N})^2$$
(3.8)

Hence, by subtracting (3.8) from (3.7), and remembering the fluid properties $\rho^{(1)}(\mathbf{r}) = \text{constant density } \rho$, $\rho^{(2)} = \rho^{(2)}(|\vec{\mathbf{r}}_2 - \vec{\mathbf{r}}_1|)$, we find

$$\Omega \int \left[\rho^{(2)}(\mathbf{r}) - \rho^2\right] d\vec{\mathbf{r}} = \overline{N}^2 - (\overline{N})^2 - \overline{N}$$
(3.9)

Thus, we can express $\int [g(r) - 1] d\vec{r}$, as we desired, in terms of fluctuations, and, in particular, the difference between \overline{N}^2 and $(\overline{N})^2$. From (3.9), we find for the limit of the structure factor S(k) as $k \neq 0$

$$S(0) = 1 + \rho \int [g(\mathbf{r}) - 1] d\mathbf{\vec{r}} = 1 + \frac{\overline{N}^2 - (\overline{N})^2 - \overline{N}}{\rho \Omega}$$
$$= \frac{\overline{N}^2 - (\overline{N})^2}{\rho \Omega}$$
(3.10)

The final stage of the proof is to relate $\overline{N}^2 - (\overline{N})^2$ to the isothermal compressibility. We can do this by noting that

$$\overline{N}Q_{G^{\Xi}} \sum_{N} N e^{\frac{N\mu}{k_{B}T}} Q(N, \Omega, T)$$
(3.11)

We now differentiate this with respect to the chemical potential μ , at constant Ω and T. We then find

 $\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{\Omega T} Q_{G} + \overline{N} \sum_{N} \frac{N}{k_{B}T} e^{\frac{N\mu}{k_{B}T}} Q(N, \Omega, T)$ $= \sum_{N} N \frac{N}{k_{B}T} e^{\frac{N\mu}{k_{B}T}} Q(N, \Omega, T)$ (3.12)

 \mathbf{or}

$$\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{\Omega T} = \frac{1}{k_{B}T} \left[\overline{N}^{2} - (\overline{N})^{2}\right]$$
(3.13)

Thus, combining this result with (3.10) we find

$$S(0) = \frac{k_B T}{\rho \Omega} \left(\frac{\partial N}{\partial \mu} \right)_{\Omega T}$$
(3.14)

All that remains is to relate $(\partial \overline{N}/\partial \mu)_{\Omega,T}$ to $(\partial p/\partial \Omega)_{N,T}$, remembering that in thermodynamics $\overline{N} \leftrightarrow N$. The essential results we require to do

this is the Gibbs-Duhem relation

$$SdT - \Omega dp + Nd\mu = 0 \tag{3.15}$$

S being the entropy. This expresses the fact that μ is determined by p and T, and we cannot vary the three quantities independently. In a system at constant temperature we may therefore write

$$d\mu = \frac{\Omega}{N} dp \qquad (3.16)$$

 \mathbf{or}

$$\left(\frac{\partial\mu}{\partial\rho}\right)_{\rm T} = \frac{1}{\rho} \left(\frac{\partial p}{\partial\rho}\right)_{\rm T}$$
(3.17)

But

$$\left(\frac{\partial \mathbf{N}}{\partial \mu}\right)_{\Omega, \mathbf{T}} = \Omega \left(\frac{\partial \rho}{\partial \mu}\right)_{\mathbf{T}}$$
(3.18)

and hence

$$\left(\frac{\partial N}{\partial \mu}\right) = \Omega \rho \left(\frac{\partial \rho}{\partial p}\right)_{T}$$
(3.19)

The isothermal compressibility κ_T is defined by

$$\frac{1}{\kappa_{\rm T}} = -\Omega \left(\frac{\partial p}{\partial \Omega}\right)_{\rm T}$$
$$= \rho \left(\frac{\partial p}{\partial \rho}\right)_{\rm T}$$
(3.20)

Hence, using (3.14), (3.19) and (3.20) we have the desired result

$$S(0) = k_B T \rho \kappa_T \tag{3.21}$$

As we stressed earlier, both (2.30) and (3.21) will be highly relevant to our later discussion of critical phenomena. However, we have a further result for the specific heat at constant volume C_v , which we can derive from fluctuation theory. Again the application will be to the critical region.

3.3. Specific heat at constant volume

It will turn out that the specific heat at constant volume C_v is related to a more complex quantity than N- $\overline{N}.$ In fact, the fluctuation we require

is in Φ_N^2 , or the energy. Specifically, we shall calculate

 $\langle \Phi_N \Psi_N - \overline{\Phi}_N \overline{\Psi}_N \rangle$

where eventually we shall put Ψ_N = $\Phi_N, \quad \Phi_N$ and Ψ_N are both assumed to have the forms

$$\Phi_{N} = \sum_{i < j} \phi(\mathbf{r}_{ij}), \quad \Psi_{N} = \sum_{i < j} \psi(\mathbf{r}_{ij})$$
(3.22)

Working out $\Phi_N \Psi_N$ explicitly for N = 4 is instructive in verifying that the following terms come in:class (1) involving only two atoms ij and therefore the averages involving $\rho^{(2)}$ only, class (2) three atoms and the averages involving $\rho^{(3)}$ and finally class (3) depending only on $\rho^{(4)}$.

3.3.1. Fluctuations in $\langle \Phi_N \Psi_N \rangle$

- (1) Every one of $\frac{1}{2}N(N-1)$ pairs ij gives a term $\psi(r_{ij})\phi(r_{ij})$.
- (2) Every one of $\frac{1}{6}N(N-1)(N-2)$ triplets ijk gives 6 terms of type $\psi(\mathbf{r}_{ij})\phi(\mathbf{r}_{jk})$ (two each of the three possibilities with the three indices occurring twice)
- (3) Every one of $\frac{1}{24}$ N(N-1)(N-2)(N-3) quadruplets gives six terms of type $\psi(\mathbf{r}_{ii})\phi(\mathbf{r}_{ki})$.

Then we must average, and we find

$$\rho \langle \Phi_{\rm N} \Psi_{\rm N} \rangle = \frac{1}{2} \int d\vec{r}_2 \ \rho^{(2)}(\vec{r}_1 \vec{r}_2) \phi(r_{12}) + \iint d\vec{r}_2 d\vec{r}_3 \ \rho^{(3)}(\vec{r}_1 \vec{r}_2 \vec{r}_3) \phi(r_{12}) \psi(r_{23}) + \frac{1}{4} \iiint d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \left[\rho^{(4)}(\vec{r}_1 \vec{r}_2 \vec{r}_3 \vec{r}_4) \right] \phi(r_{12}) \psi(r_{34})$$
(3.23)

Finally we subtract $\langle \overline{\Phi}_N \overline{\Psi}_N \rangle$, and the last term becomes proportional to

$$\iiint \left[\rho^{(4)}(\vec{r}_1 \, \vec{r}_2 \, \vec{r}_3 \, \vec{r}_4) - \rho^{(2)}(r_{12}) \rho^{(2)}(r_{34}) \right] \phi(r_{12}) \psi(r_{34}) d\vec{r}_2 \, d\vec{r}_3 \, d\vec{r}_4 \tag{3.24}$$

This latter term will prove the crucial one in determining the form of C_v near the critical point, as we shall see explicitly in a later lecture.

4. LIQUID DYNAMICS AND TIME DEPENDENT CORRELATION FUNCTIONS

We shall introduce the van Hove correlation function in an intuitive way, and will later point out its intimate connection with neutron scattering. We argue purely classically at first. Suppose that we define G(r,t) as the average density of atoms at the point \vec{r} at time t, if an atom was at the

origin $\vec{r} = 0$ at time t = 0. Thus, it gives us the correlation in the positions of two atoms which may or may not be different at different times. This function can be expressed in the form

$$G(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{i, j=1}^{N} \delta(\vec{r} + r_i(0) - \vec{r}_j(t)) \rangle$$
 (4.1)

The average of the δ function involved in Eq.(4.1) is obviously the probability that at time t the jth atom will be at \vec{r} with respect to the position of the ith atom at time t = 0. We then sum this probability over j and average over i. G(r,t) is the space-time pair-correlation function.

The quantum mechanical generalization of Eq.(4.1) is in fact

$$G_{\text{quantum}}(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{i, j=1}^{N} \int d\vec{\mathbf{r}}' \, \delta(\vec{\mathbf{r}} + \vec{\mathbf{r}}_{2}(0) - \vec{\mathbf{r}}') \delta(\vec{\mathbf{r}}' - \vec{\mathbf{r}}_{j}(t)) \rangle \qquad (4.2)$$

where $\vec{r_i}(0)$ and $\vec{r_j}(t)$ are now Heisenberg operators which do not commute. If this failure to commute is ignored, it proves possible to integrate over $\vec{r'}$, and then Eq.(4.1) is regained.

4.1. Relation to density operator

An alternative and sometimes useful form for G(r, t) is obtained by introducing the density operator $\rho(\vec{r}, t)$ of the atoms at the point \vec{r} at the time t: (cf. Eq. (2.35))

$$\rho(\vec{r}t) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r_0}(t))_i$$
 (4.3)

If we employ this form in the definition (4.2) and change the origin by substituting $\vec{r}^{\dagger} = \vec{r}^{\dagger} - \vec{r}$, we find

$$G_{quantum}(\mathbf{r},t) = \frac{1}{N} \langle \int d\vec{r}^{n} \rho(\vec{r}^{n},0)\rho(\vec{r}^{n}-\vec{r},t) \rangle \qquad (4.4)$$

Thus, we can interpret $G(\vec{r}, t)$ as the space-time correlation of the density ρ .

If we now take explicit account of the homogeneity of the liquid, then the integrand in (4.4) is independent of \vec{r}^n and we find

$$G(\vec{r} - \vec{r'}, t - t') = \frac{1}{\rho} \left\langle \rho(\vec{r'}, t') \rho(\vec{r}, t) \right\rangle$$

$$(4.5)$$

At this point we follow van Hove, and take the diagonal terms i = j out of the sum over i and j in (4.2) when we obtain

$$G(r, t) = G_{s}(r, t) + G_{d}(r, t)$$
 (4.6)

where

$$G_{s}(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{i=1}^{N} \int d\vec{\mathbf{r}}^{i} \, \delta \left(\vec{\mathbf{r}} + \vec{\mathbf{r}}_{i}(0) - \vec{\mathbf{r}}^{i} \right) \delta \left(\vec{\mathbf{r}}^{i} - \vec{\mathbf{r}}_{i}(t) \right) \rangle \qquad (4.7)$$

and

$$G_{d}(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{i \neq j=1}^{N} \int d\vec{r}' \, \delta(\vec{r} + \vec{r}_{i}(0) - \vec{r}') \, \delta(\vec{r}' - \vec{r}_{j}(t)) \rangle_{0} \qquad (4.8)$$

By this separation, we can interpret G_s as the correlation function which tells us the probability that a particle which was at the origin at time t = 0, will be at \vec{r} at time t. The part G_d obviously refers to the analogous conditional probability of finding a different atom at \vec{r} at time t.

Let us now investigate the correlation functions at time t = 0. Going back to (4.2) and noting that $\vec{r}_i(0)$ and $\vec{r}_j(0)$ commute, we can integrate over $r_i^{"}$ (cf. remarks after (4.2)) and we find

$$G_{\text{quantum}}(\mathbf{r}, 0) = \frac{1}{N} \langle \sum_{i, j=1}^{N} \delta(\vec{r} + \vec{r}_{i}(0) - \vec{r}_{j}(0)) \rangle \qquad (4.9)$$

Splitting this according to (4.6), we find almost immediately

$$G_{s}(\vec{r}, 0) = \delta(\vec{r}) \tag{4.10}$$

$$G(\vec{r}, 0) = \delta(\vec{r}) + \rho g(r)$$
 (4.11)

where g(r) is given by

$$\rho g(\mathbf{r}) = \frac{1}{N} \sum_{i \neq j=1}^{N} \langle \delta(\vec{r} + \vec{r}_i - \vec{r}_j) \rangle \qquad (4.12)$$

the usual radial distribution function we have discussed earlier.

In the limit of long times, we can assume there is no correlation between positions of particles. Thus, in (4.2) we can replace the average of the product of the δ -functions by the product of the averages

$$\sum_{i, j=1}^{N} \langle \delta(\vec{r} + \vec{r}_{i}(0) - \vec{r}') \delta(\vec{r}' - \vec{r}_{j}(t)) \rangle$$

$$\approx \langle \sum_{i=1}^{N} \delta(\vec{r} + \vec{r}_{i}(0) - \vec{r}') \rangle \langle \sum_{j=1}^{N} \delta(\vec{r}' - \vec{r}_{j}(t)) \rangle \qquad (4.13)$$

Thus, for large \vec{r} or large t we may write

$$G_{\text{quantum}}(\mathbf{r}, t) = \frac{1}{N} \int d\vec{\mathbf{r}} \, \rho(\vec{\mathbf{r}} - \vec{\mathbf{r}}) \rho(\vec{\mathbf{r}}) \qquad (4.14)$$

which is simply the density-density correlation function. For systems with long-range order, $\rho(\mathbf{r})$ and $G(\mathbf{r},t)$ are periodic in space. For a fluid $\rho = N/\Omega$ where Ω is the volume, and therefore

$$G_{\text{quantum}}(\mathbf{r}, \infty) \approx \rho$$
 (4.15)

Similarly for the self-correlation function we can show that for a homogeneous system

$$G_{s}(r,\infty) = \frac{1}{\Omega}$$
(4.16)

which tends to zero as Ω tends to infinity. This is in marked contrast to the situation in which atoms are not free to move far from some 'lattice' sites. In this case, appropriate to solids when we neglect diffusion $G_s(r, \infty) \neq 0$.

For short times $G_s(\mathbf{r}, t)$ approximates to a δ function according to (4.10), while $G_d(\mathbf{r}, t)$ is approximately the pair correlation function $g(\mathbf{r})$. As $t \to \infty$, $G_s(\mathbf{r}, t) \to 0$ and $G_d(\mathbf{r}, t) \to \rho$, and these forms are shown schematically in Fig.9.



FIG. 9. Approximations of $G_{s}(\mathbf{r}, t)$ and $G_{d}(\mathbf{r}, t)$.

4.2. Van Hove correlation function

Having defined the time-dependent correlation function $G(\vec{r}, t)$ and having examined its general properties for short and for long times, we shall proceed to discuss two equivalent forms. Whereas $G(\vec{r}, t)$ is a sum of two parts G_s and G_d , the latter part being the time-dependent generalization of the radial distribution function g(r) [actually $G_d \rightarrow \rho g(r)$ as $t \rightarrow 0$], the desired generalization of the structure factor S(k) is obtained by taking a double Fourier transform of $G(\vec{r}, t)$.

Thus we write

$$S(\vec{k},\omega) = \frac{1}{2\pi} \iint dt \ d\vec{r} \ e^{\vec{i}(\vec{k}\cdot\vec{r}-\omega t)} G(r,t)$$
(4.17)

and

$$S_{s}(\vec{k},\omega) = \frac{1}{2\pi} \iint dt \, d\vec{r} \, e^{i\vec{k}\cdot\vec{r} - \omega t} G_{s}(r,t)$$
(4.18)

 $S(k, \omega)$ is directly related to neutron scattering from the fluid and gives the probability that there is a momentum transfer fik and an energy transfer fiw between the neutron and the fluid. The relation between the van Hove correlation function $S(k, \omega)$ and neutron scattering will be discussed in more detail by Professor Brockhouse. (Prof.Brockhouse's lectures are not published in these proceedings.)

4.3. Intermediate scattering function

Another tool which is often useful is the so-called intermediate scattering function, defined by

$$\mathbf{F}_{s}(\vec{k},t) = \int d\vec{r} \, e^{\vec{i} \, \vec{k} \cdot \vec{r}} \, \mathbf{G}_{s}(\vec{r},t) \qquad (4.19)$$

with a corresponding relation between $G(\vec{r}, t)$ and $F(\vec{k}, t)$.

If we substitute the definition of $G_s(\vec{r},t)$ into (4.19) and deal with the classical case only, we have

$$F_{s}(\mathbf{k}, t) = \int d\vec{\mathbf{r}} e^{i\vec{\mathbf{k}\cdot\mathbf{r}}} \frac{1}{N} \langle \sum_{i=1}^{N} \int d\vec{\mathbf{r}} \delta(\vec{\mathbf{r}} + \vec{\mathbf{r}}_{i}(0) - \vec{\mathbf{r}}) \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{i}(t)) \rangle$$

$$= \frac{1}{N} \langle \sum_{i=1}^{N} e^{-i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}_{i}(0) - \vec{\mathbf{r}}_{i}(t))} \rangle$$

$$= \langle e^{-i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}_{1}(0) - \vec{\mathbf{r}}_{1}(t))} \rangle \qquad (4.20)$$

If we choose the x axis along the direction of k then we may write

$$F_{s}(\vec{k},t) = \langle e^{-ik \{x_{1}(0)-x_{1}(t)\}} \rangle$$
 (4.21)

4.4. Moments of van Hove correlation function and short-time expansions

From the definitions it follows immediately that

$$\mathbf{F}_{s}(\vec{\mathbf{k}},t) = \int_{-\infty}^{\infty} \mathbf{S}_{s}(\vec{\mathbf{k}},\omega) e^{i\omega t} d\omega \qquad (4.22)$$

with a similar relation between F(k,t) and $S(k,\omega)$. Differentiating (4.22) twice with respect to t we find

$$\frac{\partial^2 \mathbf{F}_{\mathfrak{s}}(\vec{k},t)}{\partial t^2} = \int_{-\infty}^{\infty} (-)\omega^2 \mathbf{S}_{\mathfrak{s}}(\vec{k},\omega) e^{i\omega t} d\omega \qquad (4.23)$$

Hence we have for the second moment of $S_s(k, \omega)$:

$$\int_{-\infty}^{\infty} \omega^2 S_s(\vec{k}, \omega) d\omega = - \frac{\partial^2 F_s(\vec{k}, t)}{\partial t^2} \bigg|_{t=0}$$
(4.24)

Similarly, for the fourth moment we may write

$$\int_{-\infty}^{\infty} \omega^4 S_{s}(\vec{k}, \omega) d\omega = \frac{\partial^4 F_{s}(\vec{k}, t)}{\partial t^4} \bigg|_{t=0}$$
(4.25)

.

Thus, if the second and fourth time derivatives of $F_s(kt)$ can be found from (4.21), we have the desired expression for the moments.

To evaluate these derivatives, we find it convenient to develop the small t expansion of (4.21). Then, since

$$x_1(t) = x_1(0) + t \dot{x}_1(0) + \frac{t^2}{2!} \ddot{x}_1(0) + \dots$$
 (4.26)

we have

$$F_{s}(k,t) = \langle e^{ikt \dot{x}_{1}(0)} e^{\frac{i kt^{2}}{2!} \ddot{x}_{1}(0)} e^{\frac{i kt^{3}}{3!} \ddot{x}_{1}(0)} e^{\frac{i kt^{4}}{4!} x_{1}^{IV}(0)}$$
(4.27)

The coefficient of t^2 in the short-time expansion of (4.27) is clearly given by

$$\frac{ikt^{2}}{2!} \langle \bar{x}_{1}(0) \rangle - \frac{k^{2}t^{2}}{2!} \langle \{ \dot{x}_{1}(0) \}^{2} \rangle \qquad (4.28)$$

The first term clearly averages zero, while the second term gives for $\left.\partial^2 F_s/\partial t^2\right|_{t=0}$ the result

$$\frac{\partial^2 \mathbf{F}}{\partial t^2} \bigg|_{t=0} = -\mathbf{k}^2 \langle \{ \dot{\mathbf{x}}_1(0) \}^2 \rangle$$
(4.29)

But the thermal average of $\langle \{\dot{x}_1(0)^2 \rangle$ is given by

$$\frac{1}{2}M \langle {\dot{x}_1(0)}^2 \rangle = \frac{1}{2}k_BT$$
 (4.30)

and combining (4.24), (4.29) and (4.30) we find

$$\int_{-\infty}^{\infty} \omega^2 S_s(k,\omega) d\omega = \frac{k^2 k_B T}{M}$$
(4.31)

Actually, from the definition of F(kt) as

$$F(k,t) = \sum_{i} \langle e^{-i\vec{k} \cdot \{\vec{r}_{1}(0) - \vec{r}_{i}(t)\}} \rangle$$
 (4.32)

the distinct term $i \neq 1$ vanishes, since the velocities of two atoms taken at the same instant of time are uncorrelated. Hence

$$\int_{-\infty}^{\infty} \omega^2 S(\mathbf{k}, \omega) d\omega = \frac{\mathbf{k}^2 \mathbf{k}_B T}{M}$$
(4.33)

for classical fluids.

4.4.1. Fourth moment theorem

We now turn to extract the coefficient of t^4 in (4.27). After a straightforward calculation, we find the real part (the imaginary part is readily shown to average zero) as

$$\left[\frac{k^{4} \left< \left\{ \dot{\mathbf{x}}_{1}(0) \right\}^{4} \right>}{24} - \frac{k^{2}}{6} \left< \dot{\mathbf{x}}_{1}(0) \ddot{\mathbf{x}}_{1}(0) \right> - \frac{k^{2}}{8} \left< \left\{ \ddot{\mathbf{x}}_{1}(0) \right\}^{2} \right> \right]$$
(4.34)

In Appendix 3, we develop the consequences of the fact that for a fluid the various time dependent correlation functions must be independent of

the choice of the origin of time. In particular, it is shown there that

$$\langle \dot{x}_{1}(0) \, \ddot{x}_{1}(0) \rangle = - \langle \{ \, \ddot{x}_{1}(0) \}^{2} \rangle$$
 (4.35)

and hence from (4.37) it follows that

$$\frac{\partial^4 \mathbf{F}_s}{\partial t^4} \bigg|_{t=0} = k^4 \langle \{ \dot{\mathbf{x}}_1(0) \}^4 \rangle + k^2 \langle \{ \ddot{\mathbf{x}}_1(0) \}^2 \rangle$$
(4.36)

The first term can be immediately calculated to yield $3k^4(k_BT)^2/M^2$ while in the second we use the Newtonian equation of motion

$$M \ddot{x}_{1} = -\frac{\partial \Phi_{N}}{\partial x_{1}}$$
(4.37)

Carrying out the averaging with respect to exp $-\Phi_N/k_BT$, we note that

$$\frac{\partial}{\partial x_1} \left\{ e^{\frac{-\Phi_N}{k_B T}} \right\} = -\frac{1}{k_B T} \frac{\partial \Phi_N}{\partial x_1} e^{\frac{-\Phi_N}{k_B T}}$$
(4.38)

and using this to integrate by parts we obtain

$$\frac{\partial^{4} \mathbf{F}_{s}}{\partial t^{4}} \bigg|_{t=0} = \frac{3k^{4} (k_{B}T)^{2}}{M^{2}} + \frac{\rho k^{2} k_{B}T}{M^{2}} \int d\vec{r} g(r) \frac{\partial^{2} \phi}{\partial x^{2}}$$
(4.39)

Hence from (4.25) we have

$$\int_{-\infty}^{\infty} \omega^{4} S_{s}(\mathbf{k},\omega) d\omega = \frac{3k^{4}(\mathbf{k}_{B}T)^{2}}{M^{2}} + \frac{\rho k^{2} k_{B}T}{3M^{2}} \int d\vec{r} g(\mathbf{r}) \nabla^{2} \phi$$
$$= \frac{3k^{4}(\mathbf{k}_{B}T)^{2}}{M^{2}} + \frac{4\pi \rho k^{2} k_{B}T}{3M^{2}} \int g(\mathbf{r}) \left\{ \phi^{*}(\mathbf{r}) + \frac{2}{r} \phi^{*}(\mathbf{r}) \right\} r^{2} dr \quad (4.40)$$

A more lengthy calculation leads to the fourth moment for $S(k, \omega)$ as

$$\int_{-\infty}^{\infty} \omega^4 S(\mathbf{k}, \omega) d\omega = \frac{3\mathbf{k}^4 (\mathbf{k}_B T)^2}{M^2} + \frac{\rho \mathbf{k}^2 \mathbf{k}_B T}{M^2} \int d\mathbf{\vec{r}} g(\mathbf{r}) \left\{ 1 - \cos \mathbf{kx} \right\} \frac{\partial^2 \phi}{\partial \mathbf{x}^2} \qquad (4.41)$$

Thus, we can get the fourth moment in terms of the radial distribution function g(r) and the pair potential $\phi(r)$.

4.5. Asymptotic form of G(r, t) at large r and short times for van der Waals forces

Using these sum rules, plus the fact that

$$\int_{0}^{\infty} S(k, \omega) d\omega = S(k)$$
(4.42)

we can immediately expand

 $F(kt) = \int_{-\infty}^{\infty} e^{-i\omega t} S(k, \omega) d\omega \qquad (4.43)$

as

F(kt) = S(k) -
$$\frac{t^2 k^2 (k_B T)}{2M} + \frac{t^4 k^4 (k_B T)^2}{8M^2}$$

$$+\frac{\rho k^2 t^4 (k_B T)}{24 M^2} \int d\vec{r} g(r) \left[1 - \cos kx\right] \frac{\partial^2 \phi}{\partial x^2} + O(t^6) \qquad (4.44)$$

We can again employ the Fourier transform arguments we used in Part I for van der Waals forces to show that $\int d\vec{r} g(r) [1 - \cos kx] \partial^2 \phi / \partial^2 x^2$ has a term $-\pi^2 A k^5 / 12$ as the first odd power of k in its small k expansion. Actually the presence of this odd power of k is signalled by examining the coefficient of k^6 in the above integral. This involves $\int d\vec{r} g(r) x^6 \partial^2 \phi / \partial x^2$, and at large r the integrand (replacing $d\vec{r}$ by $r^2 dr$ for the dimensional argument) behaves as $r^8 \partial^2 \phi / \partial r^2 \rightarrow \text{constant}$. Hence the integral blows up and we must have missed out a term in the expansion.

 $F(kt) = \int d\vec{r} \, e^{i\vec{k}\cdot\vec{r}} G(\vec{r}t) \qquad (4.45)$

it is readily shown from the Lighthill theorem that the leading term in $G(\vec{rt})$ at large r is precisely

$$\frac{-70 \text{ At}^4}{\text{M}^2 r^{10}}$$
 (k_BT)

where, as usual, A is the strength of the van der Waals interaction. Should it prove desirable, the next term can also be calculated by this method for a Lennard-Jones (6-12) potential.

The non-analyticity arising from van der Waals interactions dominates the short-time dependence of G(rt) at large r.

5. ELEMENTARY TRANSPORT THEORY: PARTICULARLY SELF-DIFFUSION

The van Hove function $S(k, \omega)$ determines the scattering of neutrons by a fluid. In fact, as we shall see below, if we could make a first principles calculation of $S(k, \omega)$ from a pair potential $\phi(r)$, then we can also obtain exactly certain transport coefficients.

This is, at first sight, surprising, because older theories of viscosity have always proceeded by approximate calculations of the distribution function for the non-equilibrium situation. But $S(k,\omega)$ is determined by the equilibrium properties and that seems a great advantage. However, no exact calculation of $S(k,\omega)$ has proved possible so far for any realistic force law, and generally (see Sec.6) the methods of calculation available at present have to proceed via some kind of Boltzmann equation. Nevertheless, these results for transport coefficients are central in the fundamental theory. We shall give an elementary treatment in the text of one transport coefficient, the self-diffusion coefficient D. However, in order to give the reader an idea of how the general argument goes, a sketch of a much more sophisticated treatment, requiring, though, a good deal of advanced theoretical background, is given in Appendix 4.

5.1. Solution of diffusion equation for $G_s(rt)$

We can make contact with the macroscopic diffusion constant by arguing that the self correlation function $G_s(rt)$ must be related to the solution of the diffusion equation, for it represents the meanderings of a particle initially at the origin at time t = 0. Actually, this particle can exchange energy and momentum with its neighbours and we then fundamentally have only one conservation law for particle number. This is why the self-diffusion problem is much easier than when we have to deal with viscosity and heat conduction.

The diffusion equation should be obeyed by $G_s(rt)$ for times long compared with the collision time and, bearing this in mind for later purposes, we write

$$D\nabla^2 G_s(\mathbf{r}, t) = -\frac{\partial G_s}{\partial t}$$
(5.1)

As we have seen, we need a solution satisfying the condition

$$G_s(\mathbf{r}, 0) = \delta(\vec{\mathbf{r}}) \tag{5.2}$$

and such that, for the probabilistic interpretation of G

$$\int G_{s} d\vec{r} = 1, \text{ for all t}$$
 (5.3)

Actually, (5.1) has the form of the Bloch equation for the density matrix and since this will be useful for quantal fluids, we obtain the desired solution from that equation in Appendix 5. The result is

$$G_{s}(r,t) = \frac{1}{(4\pi D |t|)^{3/2}} e^{\left(\frac{-r^{2}}{4D |t|}\right)}$$
(5.4)

which is soon shown to satisfy (5.2) and (5.3)

From the results of Appendix 5 we can immediately extract the intermediate scattering function $F_s(kt)$, with the result

$$F_{s}(k,t) = e^{-k^{2}D|t|}$$
 (5.5)

From phenomenological theory, we expect the diffusion coefficient to be related to some mean square distance over a characteristic time and so we next calculate the mean square displacement $\langle r^2 \rangle$ as

$$\langle \mathbf{r}^2 \rangle = \int \mathbf{r}^2 \mathbf{G}_{\mathbf{s}} (\mathbf{r}, \mathbf{t}) \, \mathrm{d} \vec{\mathbf{r}} = 6 \mathrm{D} \mathbf{t}$$
 (5.6)

from (5.4). This result is valid for times large compared with collision times and we must expect that, for a $G_s(rt)$ correctly calculated from a force law, $\langle r^2 \rangle$ will be proportional to t, the slope yielding the diffusion constant. Machine calculations have been made for a number of cases and Fig. 10 shows typical results for two different potentials for liquid sodium. These potentials were of truncated oscillatory character and the marked differences between curves 1 and 2 show that the diffusion constant is sensitive to the pair potential.



FIG. 10. Machine calculations for two different potentials for liquid sodium. It illustrates sensitivity to the potential.

5.2. Diffusion constant as a limit of $S_s(k, \omega)$

We turn now to obtain an important expression for D in terms of $S_s(k,\omega).$ To do so, we recall that

$$S_{s}(k,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_{s}(k,t) e^{-i\omega t} dt \qquad (5.7)$$

and using (5.6) and (5.7) we find

$$S_{s}(k,\omega) = \frac{1}{\pi} \int_{0}^{\infty} e^{-k^{2}Dt} \cos \omega t dt$$
$$= \frac{Dk^{2}}{\pi [\omega^{2} + (Dk^{2})^{2}]}$$
(5.8)

The form of $S_s(k,\omega)$ as a function of ω is shown in Fig.11 and it may be seen that the total width at half maximum is determined by the diffusion constant D.



FIG. 11. Schematic form of $S_s(k,\omega)$ for diffusion.

We have already seen that the above theory can only work for long times or small ω and, in general, we expect macroscopic arguments to work in the long wave length or small k limit. While, therefore, we cannot trust (5.8) in general, it is perfectly proper for the limiting case of small k and ω . If we wish to obtain a non-zero limit as $k \rightarrow 0$ we must, from (5.8), consider $S_s(k,\omega)/k^2$, and in the limit we have

$$\lim_{k \to 0} \frac{S_s(k,\omega)}{k^2} = \frac{D}{\pi \omega^2}$$
(5.9)

In general, for a proper calculation of $S_s(k,\omega)$ the left-hand side of (5.9) will be a function of ω which will only become proportional to ω^2 as $\omega \to 0$. Thus, a general result for D may be written

$$D = \pi \lim_{\omega \to 0} \omega^2 \lim_{k \to 0} \frac{S_s(k, \omega)}{k^2}$$
(5.10)

So far, no precise use of this result for any realistic interaction has been made, but it clearly gives interesting information about the structure of $S_s(k,\omega)$ near the origin of the (k,ω) plane, which any approximate theory must yield to be at all acceptable. However, an alternative exact form for D in terms of the velocity correlation function proves more fruitful for calculating D.

5.3. Velocity correlation function

We have seen earlier that, for long times, the self-diffusion constant of a fluid is given by

$$D = \frac{\langle r^2 \rangle}{6t}$$

It is instructive to rewrite this result in terms of velocity \vec{v} rather than displacement. We have

$$\vec{\mathbf{r}} = \int_{0}^{t} \vec{\mathbf{v}}(\mathbf{s}) d\mathbf{s}$$
 (5.11)

and hence

$$\langle \mathbf{r}^2 \rangle = \int_{0}^{t} \int_{0}^{t} \langle \vec{\mathbf{v}}(\mathbf{s}_1) \cdot \vec{\mathbf{v}}(\mathbf{s}_2) \rangle \mathrm{ds}_1 \mathrm{ds}_2$$
 (5.12)

We have assumed that we can interchange the order of the operations of time integration and ensemble averaging. This is not always possible as we shall see later in a specific example.

We cannot expect the velocity correlation function to depend on the choice of the origin of time and we therefore write (5.12) in terms of $\tau = s_2 - s_1$. We then find

$$\langle \mathbf{r}^2 \rangle = \int_0^t \int_0^t \langle \vec{\mathbf{v}}(0) \cdot \vec{\mathbf{v}}(\mathbf{s}_2 - \mathbf{s}_1) \rangle d\mathbf{s}_1 d\mathbf{s}_2$$
 (5.13)

and, after changing the variable and some manipulation, we find

$$\langle \mathbf{r}^2 \rangle = 2t \int_0^t d\tau \langle \vec{\mathbf{v}}(0) \cdot \vec{\mathbf{v}}(\tau) \rangle \left[1 - \frac{\tau}{t} \right]$$
 (5.14)

Provided the velocity correlation function $\langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle$ decays sufficiently rapidly at large t, then in the limit as t becomes very large we find

$$D = \lim_{r \to \infty} \frac{\langle r^2 \rangle}{6t} = \frac{1}{3} \int_{0}^{\infty} dt \langle \vec{v}(0) \cdot \vec{v}(t) \rangle$$
(5.15)

This is the desired alternative exact expression for D.

5.4. Calculation of D for hard spheres

We have seen in a fluid like argon that some of the physical properties can be usefully discussed by using a hard sphere model. Following the

procedure we used in deriving the moment theorem, let us carry out a short time expansion of the velocity correlation function

$$\langle \vec{\mathbf{v}}(0) \cdot \vec{\mathbf{v}}(t) \rangle = \langle \mathbf{v}^2 \rangle + t \langle \frac{d}{dt} (\vec{\mathbf{v}}(0) \cdot \vec{\mathbf{v}}(t) \rangle_{t=0} + \frac{t^2}{2} \langle \frac{d^2}{dt^2} (\vec{\mathbf{v}}(0) \cdot \vec{\mathbf{v}}(t)) \rangle_{t=0} + \dots$$
(5.16)

In most cases, it can be shown that the odd powers of t have vanishing coefficients which, it turns out, is related to the fact that positions and velocities are uncorrelated in an equilibrium ensemble.

Unfortunately, when we take the limit of hard spheres, this is no longer true. The ensemble averaging has to be done <u>before</u> the time derivatives, because of the ill-defined properties of a single molecule when there is a pathological force law. The term in t remains and to make progress, we follow Longuet-Higgins and Pople [9] and write

$$\langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \langle v^2 \rangle e^{-\xi t}$$
 (5.17)

where we stress that this is specific to hard spheres. [Actually, we point out in Appendix 6 that this is precisely the form describing Brownian motion. It is usually rejected as unrealistic for liquids, because of the long range of the Fourier transform of the velocity correlation function leading to a divergent second moment. This divergence, however, exists for hard spheres and (5.17) seems a useful approximation in this case.] Substituting (5.17) in (5.15) we have immediately

$$D = \frac{1}{3} \frac{\langle v^2 \rangle}{\xi}$$
$$= \frac{k_B T}{M\xi}$$
(5.18)

The decay time ξ^{-1} of the velocity correlation function may be calculated by a kinetic argument, if we write it in the alternative form

$$\xi = -\lim_{\Delta t \to 0} \left\{ \frac{\langle \vec{v} \cdot \Delta \vec{v} \rangle}{\langle v^2 \rangle \Delta t} \right\}$$
(5.19)

where $\Delta \vec{v}$ is the vector increment in velocity of the molecule in the time interval Δt . The argument is given in detail in Appendix 7 and the final result for D is given by

$$D = \frac{R}{2} \left(\frac{\pi k_B T}{M} \right)^{\frac{1}{2}} \left[\frac{\rho}{\rho k_B T} - 1 \right]^{-1}$$
(5.20)
where the pressure p has entered because, through the virial result (1.21), it is related to the value of g(r) at the hard sphere diameter R. This result is probably valid over a wide density range. In particular, for low densities the square bracket in (5.20) may be replaced by the second virial coefficient, which is, in fact, $(16/3) \pi R^3$ for hard spheres. Then D becomes

$$D = \frac{3}{32R^2\rho} \left(\frac{k_BT}{\pi M}\right)^{\frac{1}{2}}$$
(5.21)

which is the result obtained earlier by Chapman and Enskog for a low density system.

5.5. Fourier transform of velocity correlation function

It is often illuminating to consider the Fourier transform of the velocity correlation function. We define this explicitly as

$$z(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle v_x(0) v_x(t) \rangle e^{-i\omega t} dt \qquad (5.22)$$

and we then have

$$\int_{-\infty}^{\infty} z(\omega) d\omega = \int_{-\infty}^{\infty} \langle v_{x}(0) v_{x}(t) \rangle \delta(t) dt$$
$$= \langle \{v_{x}(0)\}^{2} \rangle$$
$$= \frac{k_{B}T}{M}$$
(5.23)

It is also clear that $z(0) = D/\pi$.

Actually, for hard spheres, this is particularly interesting, because of the presence of an odd power of t in the short time expansion of the velocity correlation function. Substituting for the velocity correlation function assuming the Longuet-Higgins-Pople form (5.17) for hard spheres we find

$$z(\omega) = \frac{1}{\pi} \frac{k_B T}{M} \int_0^{\infty} e^{-\xi t} e^{-i\omega t} dt$$
$$= \frac{i}{\pi} \frac{k_B T}{M} \frac{\xi}{\xi^2 + \omega^2}$$
(5.24)

Thus, at large ω ,

$$z(\omega) \sim \frac{1}{\pi} \frac{k_{\rm B}T}{M} \frac{\xi}{\omega^2}$$
$$= \frac{1}{\pi} \left(\frac{k_{\rm B}T}{M}\right)^2 \frac{1}{D}$$
(5.25)

using (5.18). This slow fall-off of $z(\omega)$ is a consequence of the nonanalyticity of the velocity correlation function for hard spheres at the origin of time. z(0), on the other hand, from the above result for $z(\omega)$ is simply $(k_BT/\pi M\xi) = D/\pi$, as it must be.

Actually, we can make contact with experiment via $z(\omega)$ and results obtained for liquid sodium and liquid argon are shown in Fig.12. The hard sphere model is clearly inadequate, being far too long-range, as remarked above, and not exhibiting the structure found experimentally. Machine calculations have shown that the shape for argon comes from a van der Waals tail on a hard sphere potential and it is an interesting problem for the future to understand the initial dip in sodium in terms of the force law.



FIG. 12. Schematic form of Fourier transform of velocity correlation function. The dashed lines represent the result (5.24).

We may also remark that for a Debye solid, $z(\omega)$ is equal to the frequency spectrum and hence is zero at $\omega=0$, as it must be.

Some further discussion of transport is given in Appendix 4, but it is finally worth recording here that a result having a structure similar to (5.10) exists for viscosity. Thus

$$\left(\frac{4}{3}\eta + \zeta\right) = \frac{\pi}{k_{\rm B}T} \, \mathrm{M}^2 \rho \lim_{\omega \to 0} \, \omega^4 \lim_{k \to 0} \, \frac{\mathrm{S}(k,\omega)}{k^4} \tag{5.26}$$

where η is the shear viscosity and ξ the bulk viscosity.

6. COLLECTIVE MOTIONS AND $S(k,\omega)$

So far we have discussed mainly exact results for $S(k,\omega)$. However, it is clear that to calculate $S(k,\omega)$ from the pair potential we must make approximations, for after all, we have seen that we cannot as yet calculate S(k), which is the integral of $S(k,\omega)$ over ω . It is clearly of great interest to enquire whether we can approximately relate $S(k,\omega)$ to S(k) in a classical dense fluid.

Clearly, the time dependence of the correlation functions in a classical system must be determined by the Liouville equation for the phase space distribution function $\rho(\vec{r}_1 \dots \vec{r}_N; \vec{p}_1 \dots \vec{p}_N)$. This has the form

$$L\rho = i\frac{\partial\rho}{\partial t}$$
(6.1)

where explicitly, in a classical fluid, L is given by

$$L = -i \sum_{j} \frac{\vec{p}_{j}}{M} \cdot \frac{\partial}{\partial \vec{r}_{j}} - i \sum_{j \to} \vec{F}_{j} \cdot \frac{\partial}{\partial \vec{p}_{j}}$$
(6.2)

where \vec{F}_i is the total force on the j-th molecule.

Now suppose for a moment that we could calculate the eigenfunctions Ψ_i of the Liouville operator L, with their eigenvalues λ_i . Then in principle we can construct a solution of (6.1) as

$$\rho = \sum_{j} c_{j} e^{i\lambda_{j}t} \Psi_{j}$$
 (6.3)

Thus the problem is reduced to the calculation of the eigenfunctions. This is obviously impossible for a general force law and we follow Zwanzig [10] and employ the variational method. Thus, the requirement that

$$\frac{\langle \Psi^* L \Psi \rangle}{\langle \Psi^* \Psi \rangle} \tag{6.4}$$

is stationary with respect to small variations in Ψ and Ψ^* leads directly to the eigenvalue equations for Ψ and Ψ^* .

We must then decide on the form of trial function. Since, as we have said, our basic object is to get the time-dependent correlation function in terms of S(k) (or equivalently g(r)) we can only usefully allow $\Psi^*\Psi$ to contain two-body terms. Thus, Ψ itself must decompose into one-body terms to make progress and we write

$$\Psi = \sum_{j} \psi(\vec{r}_{j} \vec{p}_{j}) = \sum_{j} \psi(j)$$
(6.5)

where we have written j for \vec{r}_j ; \vec{p}_j .

Now it is very interesting that (6.5) already includes collective motions, for if it is applied to a crystal it yields an independent phonon description. This is satisfactory for there can be little doubt that, in a dense fluid, the phonons play a crucial role. The merit of this method is now that an Euler equation for $\psi(j)$ may be obtained in terms of the radial distribution function.

6.1. Euler equation for trial function.

Because we are dealing with identical molecules, we can immediately reduce $\left<\Psi^*\Psi\right>$ to the form

$$\langle \Psi^* \Psi \rangle = N \langle \psi^*(1) \psi(1) \rangle + N(N-1) \langle \psi^*(2) \psi(1) \rangle$$
 (6.6)

Introducing the single- and two-particle distribution functions f(1) and $f^{(2)}(1, 2)$ we have

$$\langle \Psi^{*} \Psi \rangle = N \int f(1) \psi^{*}(1) \psi(1) d\vec{r_{1}} d\vec{p}_{1} + N(N-1) \int f^{(2)}(1,2) \psi^{*}(2) \psi(1) d\vec{r_{1}} d\vec{p}_{1} d\vec{r}_{2} d\vec{p}_{2}$$
(6.7)

Similarly we have

$$\langle \Psi^{*}L\Psi \rangle = N \langle \Psi^{*}L\psi(1) \rangle$$
 (6.8)

and L acting on $\psi(1)$ gives

$$L\psi(1) = \frac{-ip_{i}}{M} \cdot \frac{\partial\psi(1)}{\partial\vec{r}_{1}} - i\vec{F}_{1} \cdot \frac{\partial\psi(1)}{\partial\vec{p}_{1}}$$
(6.9)

On integration by parts we find

$$\langle \Psi^* L \Psi \rangle = N \langle \psi^*(1) \left[\frac{-i\vec{p}_1}{M} \cdot \frac{\partial}{\partial \vec{r}_1} - i\vec{F}_1 \cdot \frac{\partial}{\partial \vec{p}_1} \right] \psi(1) \rangle$$
 (6.10)

We define the average force on a particular atom by

$$\langle \vec{F}_1, 1 \rangle = \int d(2) \dots d(N) f(1, 2 \dots N) \vec{F}_1 / f(1)$$
 (6.11)

and thus the quantity $\langle \Psi^* L \Psi \rangle$ becomes

$$N\int d(1) f(1) \psi^{*}(1) \left[\frac{-i\vec{p}_{1}}{M} \cdot \frac{\partial}{\partial \vec{r}_{1}} - i\langle \vec{F}_{1}, 1 \rangle \cdot \frac{\partial}{\partial \vec{p}_{1}} \right] \psi(1)$$
 (6.12)

Forming $\langle \Psi^* L \Psi \rangle / \langle \Psi^* \Psi \rangle$ and varying with respect to ψ^* , we find the eigenvalue equation for ψ as

$$\begin{bmatrix} -i\vec{p}_{1} \\ M \end{bmatrix} \cdot \frac{\partial}{\partial \vec{r}_{1}} - i \langle \vec{F}_{1}, 1 \rangle \cdot \frac{\partial}{\partial \vec{p}_{1}} \end{bmatrix} \psi(1)$$
$$= \lambda \left[\psi(1) + (N-1) \int d(2) \frac{f(1,2)}{f(1)} \psi(2) \right]$$
(6.13)

This is the fundamental equation of the present method.

6.2. Solution for fluid and connection with Vlasov equation

We note first that the one- and two-particle densities $P^{(1)}$ and $P^{(2)}$ discussed in Part I are given in the canonical ensemble by

$$P^{(1)}(\vec{r}_{1}) = f(1)/\phi_{B}(\vec{p}_{1})$$
(6.14)

$$P^{(2)}(\vec{r}_1 \vec{r}_2) = f(1, 2) / \phi_B(\vec{p}_1) \phi_B(\vec{p}_2)$$
 (6.15)

where ϕ_{B} is the Maxwell-Boltzmann distribution

$$\phi_{\rm B} = (2\pi \,\mathrm{Mk}_{\rm B}\mathrm{T})^{-\frac{3}{2}} \,\exp\left(\frac{-\mathrm{p}^2}{2\mathrm{Mk}_{\rm B}\mathrm{T}}\right) \tag{6.16}$$

In a fluid, the one-particle density $P^{(1)}$ is of course independent of position, $P^{(2)} \propto g(\vec{r}_1 \vec{r}_2)$ depends only on $|\vec{r}_1 - \vec{r}_2|$ and $\langle F_1, 1 \rangle$ vanishes, because of homogeneity. Hence the basic eigenvalue equation reduces to

$$\frac{-i\vec{p}_{1}}{M} \cdot \frac{\partial \psi}{\partial \vec{r}_{1}} = \lambda \psi + \lambda \rho \int d\vec{p}_{2} d\vec{r}_{2} \int \phi_{B}(\vec{p}_{2})g(|\vec{r}_{1} - \vec{r}_{2}|) \psi(r_{2}) dr_{2} \quad (6.17)$$

By Fourier transform, or noting that we can solve (6.17) using functions of the form

$$\psi(\vec{r}\vec{p}) = e^{i\vec{k}\cdot\vec{r}}\gamma(\vec{p}) \qquad (6.18)$$

where \vec{k} is an arbitrary vector, we find

$$(\vec{k} \cdot \vec{r}_1 | M) \gamma(\vec{p}_1) = \lambda \gamma(\vec{p}_1) + \lambda \rho \int d\vec{r}_2 g(\vec{r}_{12}) e^{i\vec{k} \cdot (\vec{r}_2 - \vec{r}_1)} \int d\vec{p}_2 \phi_B(\vec{p}_2) \gamma(\vec{p}_2)$$
(6.19)

To cast this into a recognizable form, we transform (using velocity \vec{v} rather than momentum \vec{p} for convenience) from $\gamma(\vec{v})$ to $\chi(\vec{v})$ defined by

$$\gamma(\vec{\mathbf{v}}) = \frac{\chi(\vec{\mathbf{v}})}{\phi_{\mathsf{B}}(\vec{\mathbf{v}})} - \frac{\widetilde{\mathbf{h}}(\mathbf{k})}{1 + \widetilde{\mathbf{h}}(\mathbf{k})} \int d\vec{\mathbf{v}}' \chi(\vec{\mathbf{v}}')$$
(6.20)

where we have replaced $g(r_{12})-1$ by its Fourier transform $\widetilde{h}(k)$. The quantity $\int d\vec{v'} \chi(\vec{v'})$ is simply the direct correlation function $\widetilde{c}(k)$ and if we use the identity

$$-\vec{k}\cdot\vec{v}\phi_{B} = k_{B}T\vec{k}\cdot\frac{\partial\phi_{B}}{\partial\vec{v}}$$
(6.21)

we finally obtain

$$\vec{k} \cdot \vec{v} \chi + k_B T \tilde{c}(k) k \cdot \frac{\partial \phi_B}{\partial \vec{v}} \int d\vec{v'} \chi(v') = \lambda \chi \qquad (6.22)$$

The essential achievement is then summarized by noting that this equation has exactly the form of the linearized Vlasov equation, widely used in plasma theory (see, for example, Montgomery and Tidman [11]) with $-k_BT$ $\tilde{c}(k)$ playing the part of an effective potential. This is an appealing result in the light of our earlier discussion of structure.

Actually, the Vlasov equation is a Boltzmann equation with however, no collision term, but including instead a self-consistent treatment of the intermolecular (effective) potential. Then, viewed as a kinetic equation, it can be used to calculate a distribution function in \vec{r} and \vec{v} which, when integrated over \vec{v} will give us G(r,t) or, by Fourier transforming, S(k, ω). The achievement of this calculation is that it determines S(k, ω) in terms of S(k). Though the treatment is primitive we summarize the essential argument, due to Nelkin and Ranganathan [12], in Appendix 8, starting out from the Vlasov equation in customary Boltzmann equation form. We find that S(k, ω) is given by

$$S(k, \omega) = \frac{2\pi^{\frac{1}{2}}}{k\left(\frac{2k_{B}T}{M}\right)^{\frac{1}{2}}} \frac{e^{-x}}{\left[S^{-1}(k) + 2\tilde{c}(k)x^{2}e^{-x}\int_{0}^{x}e^{-t^{2}}dt\right]^{2} + \left[\tilde{c}(k)x\pi^{\frac{1}{2}}e^{-x}\right]^{2}}$$

where

$$x = \frac{\omega}{k} \sqrt{\frac{M}{2k_BT}}$$
 (6.23)

This expression, inserting S(k) and $\tilde{c}(k)$ from experiment or, say, for hard spheres from Percus-Yevick theory, has the correct general features, as shown schematically in Fig.13. The side peaks show the sound propagation and have finite breadth. It is clearly too early to say whether this method can be made fully quantitative but it represents a promising start on the problem.



FIG. 13. Schematic form of $S(k, \omega)$ against ω as calculated from the solution of the Vlasov equation.

7. LIQUID-GAS CRITICAL POINT

So far, we have been concerned mainly with liquids in the region of the triple point, where the liquid and solid densities are comparable. However, we shall turn briefly to discuss the region near the critical point, where liquid and gas densities become comparable. Though the arguments we gave earlier relating c(r) to $\phi(r)$ break down here, since the required inequality $h^2 < |c|$ is violated, the direct correlation function still plays a central role. We shall first discuss a phenomenological approach and later deal with the nature of the correlation functions.

7.1. Phenomenology

The most obvious definition of the critical point is that point at which the isotherm has a point of inflexion satisfying

$$\left(\frac{\partial \mathbf{p}}{\partial \rho}\right)_{\mathrm{T}} = 0, \left(\frac{\partial^2 \mathbf{p}}{\partial \rho^2}\right)_{\mathrm{T}} = 0$$
 (7.1)

Actually, another definition sometimes given involves the specific heat at constant volume C_v , for from thermodynamics we can show that

$$\frac{-1}{C_{v}} \left(\frac{\partial p}{\partial V}\right)_{T} \ge 0$$
(7.2)

the equality being satisfied at the critical point. We shall be concerned with the behaviour of c_v at the critical point later.

From (7.1) it immediately follows that the isothermal compressibility K_T and therefore S(0), diverge at the critical point. Usually, the form of K_T is taken as

$$K_{T} = (T - T_{c})^{-\gamma}$$
 (7.3)

measured at the critical density ρ_c , and for insulating liquids $\gamma \sim 1.1$. As we shall see below, this is near to the value of a van der Waals fluid. Also, we have that the difference between liquid and gas densities is given by

$$\rho_{1ig} - \rho_{gas} = (T - T_c)^{\beta}$$
 (7.4)

 β takes the values 0.35±0.02 for insulating fluids from the available data.

To understand these forms, let us start from the van der Waals equation of state. We shall see, in fact, that the predictions of this equation are valid whenever we can make a Taylor expansion of the equation of state round the critical point.

The considerations of the van der Waals equation are elementary and we shall only note that, rewriting

$$\frac{p}{k_BT} = \frac{\rho}{1-b\rho} - \frac{a\rho^2}{k_BT}$$
(7.5)

in terms of the reduced quantities $p^* = p/p_c$, etc., we find, using condition (7.1) to determine p_c , ρ_c and T_c ,

$$\frac{p^*}{T^*} = \frac{8\rho^*}{3-\rho^*} - \frac{3\rho^{*2}}{T^*}$$
(7.6)

We can now find the critical exponents by expanding about the critical point and then, with $\Delta p = p - p_c$, etc., we find

$$\Delta p = a_1 \Delta T + b_1 \Delta T \Delta \rho + d(\Delta \rho)^3 + \dots$$
(7.7)

Though a_1 , b_1 and d can be determined, of course, from the van der Waals equation of state, the exponents γ and β of (7.3) and (7.4) do <u>not</u> depend on them, but only on the gross assumption that we can Taylor expand the equation of state round the critical point.

Now it follows from (7.7) that

$$b_1 \Delta T + d(\Delta \rho)^2 \sim \frac{\Delta p}{\Delta \rho} - \frac{a \Delta T}{\Delta \rho}$$
 (7.8)

and both quantities on the right-hand side $\rightarrow 0$ as $T \rightarrow T_c$. Hence $\Delta \rho \propto (\Delta T)^{\frac{1}{2}}$, and $\beta = \frac{1}{2}$ in this theory. This is in conflict with the experimental value $\beta = 0.35 \pm 0.02$ referred to above. However, for liquid metals, where the forces are longer range there is tentative evidence that $\beta \sim 0.45$. This would be as one would expect, for a van der Waals theory is correct as the range of the forces becomes very great.

The conclusion seems to be that β depends on the range of the forces and the above Taylor expansion does not work for insulating fluids.

We can immediately calculate ($\partial p / \partial \rho$)_T from (7.7) and we find

$$\left(\frac{\partial p}{\partial \rho}\right)_{\rm T} \sim b_1 \Delta T + 3d(\Delta \rho)^2$$
 (7.9)

But since we have shown that $b_1 \Delta T + d(\Delta \rho)^2 \rightarrow 0$ at $T \rightarrow T_c$ we may write, at the critical density ρ_{g_c} ,

$$K_{T} = \frac{1}{\rho} \left(\frac{\partial p}{\partial \rho} \right)_{T} = \frac{\text{constant}}{\Delta T}$$
(7.10)

giving the exponent $\gamma = 1$ in reasonable agreement with experiment.

We turn next to enquire how the correlation functions behave in the neighbourhood of the critical point.

7.2. Ornstein-Zernike theory

The old argument of Ornstein and Zernike as to the form of h(r) near T_c went essentially as follows. From the definition of c(r) we have

$$h(\mathbf{r}) = c(\mathbf{r}) + \rho \int c(|\vec{\mathbf{r}} \cdot \vec{\mathbf{r}}')| h(\mathbf{r}') d\vec{\mathbf{r}'}$$
(7.11)

and we expand $h(\mathbf{r}')$ in a Taylor series about the point $\vec{\mathbf{r}}$. The first term $h(\mathbf{r})$ gives a contribution $h(\mathbf{r})\rho \int c(\mathbf{r})d\vec{\mathbf{r}}$ to the convolution in (7.11), the term involving grad h integrates to zero, while the term in $|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|^2$ evidently gives a contribution

constant
$$\nabla^2 h \int cr^2 d\vec{r}$$
 (7.12)

We then find, since there is no reason why $\int cr^2 d\vec{r}$ should vanish, that, provided c(r) is short range compared with h(r),

$$\nabla^{2} h = \text{const} \left[1 - \rho \int c(\mathbf{r}) d\vec{\mathbf{r}} \right] h$$
$$= \text{const} \left[1 - \tilde{c}(0) \right] h \qquad (7.13)$$

But, in fact $S(0) = [1 - \tilde{c}(0)]^{-1}$, and hence at the critical point, if we write

$$\nabla^2 h = q^2 h \tag{7.14}$$

 $q \rightarrow 0$. The solution of (7.14) decaying at infinity is evidently

h = const.
$$\frac{e^{-qr}}{r}$$
 (7.15)

and hence, at T_c

$$h = \frac{const}{r}$$
(7.16)

But

$$S(0) = 1 + \rho \int h(r) d\vec{r}$$
 (7.17)

and it is clear that S(0) then diverges because of the r^1 correlations. Obviously from (7.15)

$$\widetilde{h}(k) = \frac{\text{const}}{k^2 + q^2}$$
(7.18)

and hence, S(k) $\sim 1/k^2$ at small k as $T \longrightarrow T_c$.

This argument is perhaps not particularly convincing, though it is internally consistent because it is readily verified that c(r) is indeed short range compared with h(r), from (7.15). However, a recent important paper by Choy and Mayer [13] has obtained essentially the same result from the force equation (1.25), by arguing about the form of the three-body correlation function near T_c . Their lengthy argument, to which the reader is referred, leads to a factorization of $\rho^{(\ell+m)}(\ell+m)$ into ρ^{ℓ} and ρ^{m} , the result being

$$\rho^{(\ell+m)}(\ell+m) - \rho^{(\ell)}(\ell)\rho^{(m)}(m)$$

$$= \left[\frac{\partial \rho^{(\ell)}(\ell)}{\partial \rho}\right]_{\beta} \left[\frac{\partial \rho^{(m)}(m)}{\partial \rho}\right]_{\beta} (\ell m)^{-1} \sum_{\gamma=1}^{\ell} \sum_{k=\ell+1}^{\ell(\ell+m)} h(r_{\gamma k}): \beta = \frac{1}{k_{\beta}T}$$
(7.19)

If we use the special case

$$\rho^{(3)}(\vec{r}_{1}\vec{r}_{2}\vec{r}_{3}) - \rho \rho^{(2)}(r_{12})$$

$$= \frac{1}{2}\rho^{2} \left(\frac{\partial\rho^{(2)}(r_{12})}{\partial\rho}\right)_{\beta} \left[h(r_{13}) + h(r_{23})\right]$$
(7.20)

we regain the Ornstein-Zernike result from the force equation.

7.3. Specific heat at constant volume

Finally, we note that an interesting result for C_v can be obtained by combining our fluctuation result (3.24) with (7.19). Then it proves possible, near the critical point, to rewrite C_v entirely in terms of thermodynamic quantities (compare Choy and Mayer, 1967; Botch and Fixman [14]) and the following result is obtained

$$C_{v} \sim \frac{1}{2} \left\{ \beta \frac{\partial^{2}(p\beta)}{\partial \rho \partial \beta} \right\}^{2} \left(\frac{\pi D^{3} \rho}{\frac{\partial (p\beta)}{\partial \rho}} \right)^{\frac{1}{2}}$$
(7.21)

where D is given by

$$4\pi\rho \ \mathrm{Dq}^{-2} = \mathrm{S}(0)$$
 (7.22)

 q^{-1} being the range of the Ornstein-Zernike result (7.15) for h(r).

It then follows that if S(0) diverges as (T - $T_{\rm c}$) $^{\gamma}$, we may write, for the specific heat,

$$C_v \sim (T - T_c)^{\frac{1}{2}(3\gamma - 4)}$$
 (7.23)

It will be seen that unless $\gamma \leq 4/3$, C_v would tend to zero at T_c which is clearly non-physical. With the van der Waals value $\gamma = 1$ we find a divergence given by

 $C_{y} \simeq (T - T_{c})^{-\frac{1}{2}}$ (7.24)

This is an interesting result and further work, both experimental and theoretical, is called for to substantiate it or otherwise.

A much more sophisticated discussion of critical phenomena is given by Dr. Thomas. However, we refer the interested reader to an important paper by Tisza (1951) for a deeper discussion of the critical point.

8. QUANTAL FLUIDS

We shall conclude the course with a brief discussion of the quantal fluids and mainly helium four in its ground state. We shall see that the same methods we have employed for classical fluids have a good deal of relevance.

The theory of Landau was based on the idea of well-defined elementary excitations which were phonon-like for small \vec{k} and of a more complicated (roton) character at larger k. This description was made precise by Feynman whose work we focus on first.

As shown in Appendix 9, we can express the Hamiltonian of a nonviscous compressible fluid approximately in the form

$$H = \frac{1}{2} \sum_{k} \frac{M}{Nk^{2}} \left[\dot{\rho}_{k} \dot{\rho}_{k}^{*} + \omega_{k}^{2} \rho_{k} \dot{\rho}_{k}^{*} \right]$$
(8.1)

where the $\rho_{\vec{k}}$ are the density fluctuations we introduced earlier and $\omega_k = ck$, where c is the velocity of sound. Thus, we have reduced the problem to independent oscillators. Now as we have seen the structure factor S(k) is essentially the expectation value of $N^{-1} \rho_{\vec{k}} \rho_{-\vec{k}}$ and since the average values of kinetic and potential energies are equal, from the virial theorem, for a harmonic oscillator, we may write

$$\frac{M}{N}c^{2}\langle\rho_{k},\rho_{k}^{*}\rangle = \langle E_{k}\rangle$$
(8.2)

where $\langle E_k \rangle$ is the average energy of the oscillator representing sound of wave number k. When T = 0°K, all the oscillators are in their ground states and hence

$$\left\langle \mathbf{E}_{\mathbf{k}} \right\rangle = \frac{1}{2} \, \mathbf{\hat{h}} \, \boldsymbol{\omega}_{\mathbf{k}} = \frac{1}{2} \, \mathbf{\hat{h}} \mathbf{ck} \tag{8.3}$$

It then follows from (8.2) and (8.3) that

$$S(k) = \frac{\langle E_k \rangle}{Mc^2} = \frac{\hbar k}{2Mc}$$
(8.4)

This result has been shown by Gavoret and Nozières [15] to be exact for sufficiently small k. Actually, using Lighthill's theorem (2.22) again, we obtain the exact asymptotic form of h(r) as

$$h(\mathbf{r}) = \frac{-\hbar}{2\pi^2 p M c \mathbf{r}^4}$$
(8.5)

The above result for the ground state structure factor is readily generalized to elevated temperatures for we then have that the probability of finding the oscillator representing phonons of wave number \vec{k} in its n-th excited state is proportional to exp(- E_n/k_BT) and then it follows straightforwardly that

$$S(k) = \frac{\hbar k}{2mc} \operatorname{coth} \frac{1}{2}\beta\hbar ck$$
$$\Rightarrow (\beta M c^{2})^{-1} + \frac{\beta\hbar^{2}}{12M} k^{2} + \dots \qquad (8.6)$$

Here $\beta = (k_B T)^{-1}$ and as $k \rightarrow 0$ we find

$$S(0) = \rho_0 k_B T K_T \qquad (8.7)$$

which is the result of fluctuation theory again. It should be noted from (2.5) that the term linear in k has disappeared from the expansion (8.5) valid at elevated temperatures.

8.1. Form of $S(k, \omega)$ for ground state of ⁴He

Since the above model is one of independent phonons, we expect that $S(k,\omega)$ will show a δ function behaviour and we may write

$$S(k,\omega) = S(k)\delta(\omega - ck)$$
(8.8)

which satisfies $\int S(k,\omega)d\omega = S(k)$, as it must. Earlier, we derived moment theorems in classical theory and the quantum mechanical first-moment theorem which we state below includes the classical second-moment result,

when combined with the requirement of detailed balance, namely,

$$S(k,\omega) = e^{-\beta h \omega} S(k,-\omega)$$
(8.9)

The moment theorem is then

$$\int_{0}^{\infty} \omega S(k, \omega) d\omega = \frac{\hbar k^2}{2M}$$
(8.10)

and substituting into (8.9) we regain the result (8.4) for S(k).

However, the above argument can now be generalized away from the long-wave limit if we assume that elementary excitations with a more general dispersion relation $\omega = \omega(\mathbf{k})$ exist.

8.2. Use of structure data to determine $\omega(k)$ and form of ground state wave function

Ideally we, of course, wish to calculate g(r), S(k), etc., from first principles given only the interaction $\phi(r)$. However, in the absence of such calculations we can gain insight into the problem using the measured structure factor S(k). First we shall get an approximation to $\omega(k)$ from S(k) and secondly we shall consider the ground state many-body wave function.

To get $\omega(k)$, we simply generalize (8.8) away from small k by writing

$$S(k, \omega) = S(k) \delta(\omega - \omega(k))$$
(8.11)

when we find from (8.10)

$$\omega(\mathbf{k}) = \frac{\hbar k^2}{2MS(\mathbf{k})}$$
(8.12)

Using S(k) having the form shown in Fig.14, we find all the features of the Landau excitation spectrum, though the results are not quantitative.

However, we can go further, and obtain the ground state wave function if we assume for the boson fluid that

$$\Psi(\vec{r}_1 \dots \vec{r}_N) = \prod_{i < j} e^{\frac{1}{2}u(r_{ij})}$$
(8.13)

If we form $\Psi^* \Psi$ and hence find the distribution functions, it can be seen that there is a complete analogy with classical statistical mechanics, and the approximate theories of structure we discussed earlier are immediately applicable, with $-\phi(\mathbf{r})/k_BT$ in the classical theory replaced by $u(\mathbf{r})$. In particular at large \mathbf{r} , since $c(\mathbf{r}) \sim -\phi(\mathbf{r})/k_BT$ we have that $u(\mathbf{r})$

behaves as c(r) asymptotically. But we have

$$\widetilde{c}(k) = \frac{S(k) - 1}{S(k)} \rightarrow \frac{-1}{S(k)} \text{ as } k \rightarrow 0$$
$$= \frac{-2Mc}{\hbar k} \text{ at small } k$$
(8.14)

Hence by Fourier transform

$$c(r) \sim u(r) \sim -\frac{Mc}{\pi^2 \rho \hbar} r^{-2}$$
 (8.15)

The correlations are seen then, in the wave function (8.13), to be of very long range.



FIG. 14. Experimental structure factor for ⁴He at 1.06° K (points). Line through origin represents Feynman result 8.4. Full line is Percus-Yevick solution for hard spheres (diameter of hard spheres is 2.6Å, η of Eq. (2.58) is 0.20).



FIG. 15. Two-body correlation function u(r) in wave function (8.13) ξ = 1 is the Abe approximation.
 u₀ is simply lng(r).
 u₁ is the first step in iterative solution of the Born-Green equation using u₀ as the starting point. Other curves are for ξ < 1.

If we use the experimental S(k) we can in principle obtain u(r) for all r. Thus, using the Abe approximation (2.31), which reads in this case

$$u(r) - \ln g(r) = h(r) - c(r)$$
 (8.16)

we can find u(r) from the experimental data. The result, first obtained by Wu and Feenberg [16] is shown in Fig.15. The function becomes strongly negative inside the core, as is to be expected. Actually (8.16) can be written explicitly in terms of S(k) as

$$u(r) = \ln g(r) - \frac{1}{8\pi^{3}\rho} \int \frac{[S(k) - 1]^{2}}{1 + \xi[S(k) - 1]} e^{\vec{k}\cdot\vec{r}} d\vec{k}$$
(8.17)

with $\xi = 1$. The factor ξ was introduced by Wu and Feenberg to facilitate comparison with their numerical solution of the Born-Green equation, also shown in Fig.15. Actually, the introduction of $\xi \neq 1$ spoils the asymptotic result (8.15) however.

The conclusion is that the approximate theories lead to two-particle correlation functions u(r) in fair agreement with one another. These can then be used to calculate the ground state energy, since it is readily verified for the wave function (8.13) that the mean kinetic energy $\langle T \rangle$ is given by

$$\langle T \rangle = \frac{N\rho\hbar^2}{8M} \int g'(\mathbf{r})u'(\mathbf{r})d\vec{\mathbf{r}}$$
 (8.18)

and the mean potential energy (cf. eq. (1.18)) is

$$\langle \Phi \rangle = \frac{N\rho}{2} \int g(\mathbf{r})\phi(\mathbf{r})d\vec{\mathbf{r}}$$
 (8.19)

In this way, Wu and Feenberg obtained reasonably satisfactory results for the ground state energy and we can conclude that we have a very useful approximation now available to the true ground state wave function for ⁴He. For further discussion of this problem, the reader should refer to very recent work by Chester and Reatto [17].

8.3. Preliminary remarks on the structure of 3 He

Much less work has been done on the structure of 3 He. We want only to emphasize here that 3 He is a Fermi liquid and we expect the sharp Fermi surface to affect the structure.

To illustrate this, we use the pair function g(r) for free fermions derived in Appendix 5 to write

$$g(r) = \left[1 - \frac{q}{2} \left\{\frac{j_{1}(k_{f}r)}{k_{f}r}\right\}^{2}\right]$$
(8.20)

which is, of course, the 'Fermi hole', with

$$j_1(x) = \frac{\sin x - x \cos x}{x^2}$$
(8.21)

and $k_{\rm f}$ the Fermi wave number. We see immediately from (8.20) and (8.21) that at large r

$$h(r) \sim \frac{\cos^2 k_f r}{r^4} \tag{8.22}$$

We rewrite this as

$$h(r) \sim \frac{1 + \cos 2k_f r}{r^4}$$
 (8.23)

and we recognize two distinct contributions in (8.23), one $(1/r^4)$ from small k, and the other from the point $2k_f$. This is quite explicitly demonstrated if we calculate the structure factor from (8.20), for we find

$$S(k) = \frac{3}{4} \left(\frac{k}{k_f}\right) - \frac{1}{16} \left(\frac{k}{2k_f}\right)^3 \text{ for } k \leq 2k_f$$

$$= 1 \qquad \qquad \text{for } k > 2k_f \qquad (8.24)$$

The discontinuity in S''(k) at $2k_f$ is responsible for the term $(\cos 2k_f r)/r^4$ in (8.23) while the term linear in k in (8.24) leads to the term $1/r^4$ with the velocity of sound c in the Feynman theory of ⁴He replaced by essentially the Fermi velocity.

Needless to say, (8.24) is a bad approximation for ³He because of the neglect of the hard core. But all the evidence we have (particularly the success of Fermi liquid theory) points to the fact that in interacting fluid ³He the Fermi surface is still sharp. We expect then the non-analyticity at $2k_f$ to remain and the structure factor in ³He to oscillate out to much larger distances than in ⁴He. It will be of considerable interest to see if an X-ray experiment on ³He can reveal the pathology at $2k_f$, but clearly high accuracy will be required.

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Rushbrooke's form of the Born-Green equation

We wish to show here how to go from Eq.(2.4) to the form (2.5). The argument is due to Rushbrooke [19]. Write

$$G(\vec{t}) = g(t) \frac{\partial \phi(t)}{\partial t} \frac{t_z}{t}$$
(A1.1)

and consider the integral

$$J = \int h(r_{23})G(\vec{t})d\vec{r}_3 \qquad (A1.2)$$

To make progress in getting J, consider a function $\epsilon(t)$ given by

.

$$\epsilon(t) = \int_{a}^{t} g(x) \frac{\partial \phi(x)}{\partial x} dx \qquad (A1,3)$$

Then

$$\frac{\partial \epsilon}{\partial t} = g(t) \frac{\partial \phi(t)}{\partial t}$$

and multiplying both sides by $\partial t/\partial t_z \equiv t_z^{}/t$ we find

$$\frac{\partial \epsilon}{\partial t_z} = G(\vec{t}) \tag{A1.4}$$

Defining Fourier transforms by

$$\widetilde{G}(k) = \rho \int G(\vec{t}) e^{i\vec{k}\cdot\vec{t}} d\vec{t}$$
 etc (A1.5)

we find from (A1.4)

$$\widetilde{G}(k) = -ik_z \widetilde{\epsilon}(k)$$
 (A1.6)

Now

$$h(\mathbf{r}) = \frac{1}{(2\pi)^{3}\rho} \int \widetilde{h}(\mathbf{k}) e^{-i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}} d\vec{\mathbf{k}}$$
(A1.7)

and hence from (A1.2) we have

•

$$J = \frac{1}{(2\pi)^3 \rho} \int \tilde{h}(k) e^{-i\vec{k} \cdot (\vec{r_3} - \vec{r_2})} G(\vec{t}) d\vec{k} d\vec{r_3}$$
(A1.8)

After some manipulation and use of (A1.6) we obtain

$$J = \frac{-i}{(2\pi)^3 \rho^2} \int d\vec{k} \, \tilde{h}(k) k_z \, \tilde{\epsilon}(k) e^{ik_z s}$$
(A1.9)

where $s = |\vec{r}_2 - \vec{r}_1|$ and hence

$$J = \frac{-1}{(2\pi)^3 \rho^2} \frac{d}{ds} \int d\vec{k} \ \tilde{h}(k) \tilde{\epsilon}(k) e^{i\vec{k}\cdot\vec{s}}$$
(A1.10)

Hence we have

$$\ln g(s) + \frac{\phi(s)}{k_B T} = \frac{1}{(2\pi)^3 k_B T \rho} \int d\vec{k} \ \tilde{h}(k) \tilde{\epsilon} \ (k) e^{i\vec{k}\cdot\vec{s}} + \text{constant}$$
(A1.11)

Now reverse the Fourier transform argument and put E(t) = (-1/k_BT) ε (t). We then find

$$\ln g(s) + \frac{\phi(s)}{k_B T} = \frac{\rho}{k_B T} \int E(|\vec{r} - \vec{s}|)h(r)d\vec{r} + \text{constant} \qquad (A1.12)$$

The requirement that the left-hand side shall tend to zero as $r \to \infty$ shows that we can choose the constant in (A1.12) as zero if we put $a = \infty$ in (A1.3). Hence we have the desired results (2.5) and (2.6).

APPENDIX 2

Exact relation between radial distribution function and equation of state for hard spheres

Suppose that the configurational partition function for N hard spheres, each of volume v, in a liquid of volume Ω is $Z(\Omega,v)$. Then, from a purely dimensional argument we find that if we expand the volumes of the liquid and the spheres by the same scale factor λ , then

$$Z(\lambda\Omega, \lambda v) = \lambda^{N} Z(\Omega, v)$$
 (A2.1)

Then by Euler's theorem we find

$$\Omega \frac{\partial Z}{\partial \Omega} + v \frac{\partial Z}{\partial v} = NZ$$
 (A2.2)

$$\mathbf{or}$$

$$\frac{\partial \ln Z}{\partial \Omega} + \frac{\partial \ln Z}{\partial \ln v} = N$$
 (A2.3)

But, quite generally we have

$$\frac{p\Omega}{k_{B}T} = \frac{\partial \ln Z}{\partial \ln \Omega}$$
(A2.4)

and hence

 $\frac{\partial \ln Z}{\partial \ln v} = N - \frac{p\Omega}{k_B T}$ (A2.5)

Arguing along lines proposed by Longuet-Higgins and Pople (1956), we now suppose the hard spheres, in some randomly chosen nonoverlapping configuration, to increase in volume from v to v+dv. The chance that this expansion causes no two spheres to overlap is

$$\frac{Z(\Omega, v + dv)}{Z(\Omega, v)}$$

We may write this, by Taylor's theorem, in the form

$$1 + \frac{\mathrm{d}v}{\mathrm{v}} \frac{\partial \ln Z}{\partial \ln \mathrm{v}} = 1 + \frac{\mathrm{d}v}{\mathrm{v}} \left[\mathrm{N} - \frac{\mathrm{p}\Omega}{\mathrm{k_B T}} \right]$$
(A2.6)

But the chance that two of the expanded spheres do overlap is $2g_0\Omega \ dR$, where dR is the increase in radius and $g_0 \equiv g(k)$. Thus,

$$1 - 2g_0 \Omega dR = 1 - \frac{dv}{v} \left(\frac{p\Omega}{k_B T} - N \right)$$
 (A2.7)

or

$$g_0 = \frac{3}{2R} \left(\frac{p}{k_B T} - \frac{N}{\Omega} \right)$$
 (A2.8)

This is an exact result.

APPENDIX 3

Relations between time-dependent correlation functions

The choice of the origin of time cannot affect time-dependent correlation functions in a fluid and therefore we may write

$$\langle x^{(n)}(0)x^{(m)}(t) \rangle = \langle x^{(n)}(\tau)x^{(m)}(t+\tau) \rangle$$
 (A3.1)

where $x^{(n)}$ denotes the nth derivative. Taylor expanding the right-hand side we then find

$$\langle x^{(n)}(0)x^{(m)}(t) \rangle = \langle x^{(n)}(0)x^{(m)}(t) \rangle$$

$$+\tau \langle x^{(n)}(0)x^{(m+1)}(t) + x^{(n+1)}(0)x^{(m)}(t) \rangle + O(\tau^{2})$$
 (A3.2)

Thus we must have

$$\langle x^{(n)}(0)x^{(m+1)}(t) \rangle = -\langle x^{(n+1)}(0)x^{(m)}(t) \rangle$$
 (A3.3)

Putting n = 1 and m = 2 we find

$$\langle \dot{\mathbf{x}}(0) \, \ddot{\mathbf{x}}(t) \rangle = - \langle \ddot{\mathbf{x}}(0) \, \ddot{\mathbf{x}}(t) \rangle$$
 (A3.4)

and Eq.(4.35) is a special case of this result. It is worth noting the general results

$$\langle \dot{x}(0) x^{(2m)}(0) \rangle = 0$$
 (A3.5)

and

$$\langle \dot{\mathbf{x}}(0) \mathbf{x}^{(2m+1)}(0) \rangle = (-1)^{m} \langle \{\mathbf{x}^{(m+1)}(0)\}^{2} \rangle$$
 (A3.6)

APPENDIX 4

Sketch of derivation of correlation function expressions for the transport coefficients²

As with our discussion of self-diffusion, we begin with the macroscopic equations, which are the equations of hydrodynamics in linearized form.

A4.1. Hydrodynamic equations in k space

Let $\rho(\vec{r}, t)$ be the average density with \vec{g} and \vec{E} as the corresponding momentum and energy density. Then since $\vec{g} = M\rho\vec{v}$, where \vec{v} is the velocity we have

(i) Equation of continuity

$$-\frac{\operatorname{div}\vec{g}}{M} = \frac{\partial \overline{\rho}(\vec{r}t)}{\partial t}$$
(A4.1)

² Study of this Appendix is <u>not</u> required for the understanding of the rest of the course. The material in it is 'highbrow' compared with the other lectures, and the purpose of this sketch is to try to expose the main features of the argument. We follow very closely the work of Felderhof and Oppenheim [20].

(ii) Navier-Stokes equation

$$\frac{\partial}{\partial t} \operatorname{div} \overline{\overline{g}} (\overline{r} t) = -\left(\frac{\partial p}{\partial \rho_0}\right)_{E_0} \nabla^2 \overline{\rho} + \frac{\left[\frac{4}{3} \eta + \zeta\right]}{\rho_0 M} \nabla^2 \operatorname{div} \overline{\overline{g}} - \left(\frac{\partial p}{\partial E_0}\right)_{\rho_0} \nabla^2 \overline{E}$$
(A4.2)

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where the subscript zero denotes equilibrium values and η and ζ are, respectively, the shear and bulk viscosities:

(iii) Energy density equation

$$\frac{\partial}{\partial t} \overrightarrow{E} (\overrightarrow{r} t) = K \left(\frac{\partial T}{\partial \rho_0} \right)_{E_0} \nabla^2 \overrightarrow{\rho} \cdot \frac{E_0 + p}{\rho_0 M} \operatorname{div} \overline{\overline{g}} + K \left(\frac{\partial T}{\partial E_0} \right)_{\rho_0} \nabla^2 \overline{E}$$
(A4.3)

where K is the thermal conductivity.

If we separate \vec{g} into two parts d and \vec{c} defined by

$$d = \operatorname{div} \vec{g}(\vec{r}), \quad c(\vec{r}) = \operatorname{curl} \vec{g}$$
 (A4.4)

and go into \vec{k} space then Eqs (A4.1-3) become

$$\frac{\partial \rho_{\vec{k}}}{\partial t} = -\frac{\vec{d}_{\vec{k}}}{M}$$
(A4.5)

١

$$\frac{\partial \vec{d}_{k}}{\partial t} = k^{2} \left(\frac{\partial p}{\partial \rho_{0}} \right)_{E_{0}} \vec{\rho}_{k} - \frac{k^{2} \left(\frac{4}{3} \eta + \zeta \right)}{\rho_{0} M} \vec{d}_{k} + k^{2} \left(\frac{\partial p}{\partial E_{0}} \right)_{\rho_{0}} \vec{E}_{k}$$
(A4.6)

and

$$\frac{\partial \overline{E}_{\vec{k}}}{\partial t} = -k^2 K \left(\frac{\partial T}{\partial \rho_0}\right) \overline{\rho}_{\vec{k}} - \frac{E_0 + p}{\rho_0 M} \overline{d}_{\vec{k}} - k^2 K \left(\frac{\partial T}{\partial E_0}\right)_{\rho_0} \overline{E}_{\vec{k}}$$
(A4.7)

where the subscript k denotes the Fourier components of the appropriate variable.

These equations may be summarized as the matrix equation

$$\frac{\partial}{\partial t} \begin{pmatrix} \widetilde{\rho}_{k} \\ \widetilde{d}_{k} \\ \widetilde{E}_{k} \end{pmatrix} = - \begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{bmatrix} \begin{pmatrix} \widetilde{\rho}_{k} \\ \widetilde{d}_{k} \\ \widetilde{E}_{k} \end{pmatrix}$$
(A4.8)

From the continuity equation (A4.5) we see immediately that the matrix $\vec{\tilde{M}}$ is such that

$$M_{11} = 0, M_{12} = M^{-1}, M_{13} = 0$$
 (A4.9)

The only other feature we wish to stress is that, from (A4.7), $M_{32} \rightarrow \text{constant}$ as $\vec{k} \rightarrow 0$, whereas all other coefficients in the last two rows of \vec{M} tend to zero as k^2 in the long wavelength limit.

If we could calculate \vec{M} from microscopic equations, then clearly we have expressions for the transport coefficients. The resulting correlation function expressions appear to stem from the works of Kirkwood [21] and Green [22], though we follow Kubo's ideas in this presentation.

We notice that c has disappeared from the equations, and the easiest transport coefficient to calculate after D is η which, essentially, can be got from a macroscopic diffusion-like equation (cf. Eq.(A4.40)).

A4.2. Solution for perturbed distribution function

Without the necessity of enquiring into the physical mechanism, we suppose some 'forces' are switched on, which couple to a particular dynamical variable, A_{α} say. It is only the 'response' of the system to a weak force which will concern us. The details of the 'probe' used are therefore not involved at all in the final results.

Let us denote the phase space co-ordinates by \dot{X} and then we write the Hamiltonian in the presence of the 'force' as

$$H_{total} = H(\vec{X}) - \int_{\Omega} A_{\alpha}(\vec{X}, \vec{r}) F_{\alpha}(\vec{r}t) d\vec{r}$$
 (A4.10)

We proceed to calculate the change in the distribution function f to first order in F from the Liouville equation (see Eq.(6.1)). Assuming that at $t = -\infty$ the forces vanish and that the system is described by a canonical ensemble (with $\rho = \rho_{enull}$), we find

$$\Delta \rho \left(\vec{X}, t \right) \equiv \rho \left(\vec{X} t \right) - \rho_{\text{equil}} \left(\vec{X} \right)$$
$$= \int_{\Omega} \int_{-\infty}^{t} e^{-iL(t-t')} \left[\rho_{\text{equil}} \left(\vec{X} \right), A_{\alpha} \left(X, \vec{r'} \right) \right] F_{\alpha} \left(\vec{r'} t' \right) dr' dt'$$
(A4.11)

where L is the Liouville operator L=i{m,], the symbol [,] denoting Poisson brackets.

We now Fourier transform and define

Å

$$A_{\alpha}(\vec{k},\omega) = \int_{-\infty}^{\infty} \langle A_{\alpha \vec{k}}(\vec{X}) \rangle_{\Delta} e^{i\omega t} dt \qquad (A4.12)$$

and

$$F_{\beta}(\vec{k},\omega) = \int_{-\infty}^{\infty} dt \int d\vec{r} F_{\beta}(\vec{r},t) e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$$
(A4.13)

where $\langle \rangle_{\Delta}$ denotes an average over the ensemble $\Delta \rho(\vec{x}t)$ then the result for the first order change in the observables is

$$A_{\alpha}(\vec{k},\omega) = \sum_{\beta} \chi_{\alpha\beta}(\vec{k},\omega)F_{\beta}(\vec{k},\omega) \qquad (A4.14)$$

where $\chi_{\alpha e}(\vec{k}, \omega)$, which is generally called the susceptibility, is given by

$$\chi_{\alpha\beta}(\vec{k},\omega) = \int_{0}^{\infty} e^{i\omega t} dt \int \phi_{\alpha\beta}(\vec{r},t) e^{-i\vec{k}\cdot\vec{r}} d\vec{r} \qquad (A4.15)$$

The quantity ϕ is defined in terms of the observables by

$$\phi_{\alpha\beta}(\vec{r} - \vec{r}', t - t') = \langle [A_{\beta}(\vec{X}(t'); \vec{r}'), A_{\alpha}(\vec{X}(t); \vec{r})] \rangle \qquad (A4.16)$$

Taking the Fourier transform of $\phi_{\alpha\beta}$, say $\tilde{\phi}$, defined by

$$\tilde{\phi}_{\alpha\beta}(\vec{k},t) = \int \phi_{\alpha\beta}(\vec{r},t) e^{i\vec{k}\cdot\vec{r}} d\vec{r} \qquad (A4.17)$$

then it is easy to show that for a canonical ensemble at temperature T

$$\widetilde{\phi}_{\alpha\beta}(\vec{k},t) = \frac{-1}{k_{B}T\Omega} \left\langle \dot{A}_{\alpha k}(\vec{X}(t)) A_{\beta,-\vec{k}}(\vec{X}) \right\rangle, \ \vec{k} \neq 0$$
(A4.18)

Hence, it may be shown that the susceptibility $\boldsymbol{\chi}$ at zero frequency is given by

$$\chi_{\alpha\beta}(\vec{k}, 0) = \frac{1}{k_{B}T\Omega} \langle A_{\alpha k} (X) A_{\beta, -k} (X) \rangle, \ k \neq 0$$
 (A4.19)

A4.3. Connection with macroscopic equations

This response theory is, of course, microscopic, representing a first-order perturbation solution of the Liouville equation.

We wish now to make contact with the hydrodynamic equations. As a starting point, take the time dependence of the 'forces' to be

$$F_{\alpha}(\vec{r}, t) = F_{\alpha}(\vec{r})e^{-i\omega_{0}t} \quad \text{for } t \leq 0$$

$$= 0 \quad \text{for } t > 0 \quad (A4.20)$$

where ω_0 has a positive imaginary part. Then we find immediately from (4.14) that

$$A_{\alpha}(\vec{k},\omega) = \sum_{\beta} \frac{\chi_{\alpha\beta}(\vec{k}\omega)F_{\beta}(\vec{k})}{i(\omega-\omega_{0})}$$
(A4.21)

From (A4.12), it follows that

$$\langle A_{\alpha \vec{k}}(\vec{x}) \rangle_{\Delta, t=0} = \sum_{\beta} \chi_{\alpha \beta}(\vec{k} \omega_0) F_{\beta}(\vec{k})$$
 (A4.22)

Let us define the quantity $\sigma_{\alpha\beta}(\vec{k}\omega)$ by ³

$$\sigma_{\alpha\beta}(\vec{k},\omega) = \frac{\chi_{\alpha\beta}(\vec{k},\omega) - \chi_{\alpha\beta}(\vec{k},0)}{i\omega}$$
(A4.23)

Then the behaviour for t>0 is described by

$$A_{\alpha}(\vec{k},\omega) = \sum_{\beta} \frac{\chi_{\alpha\beta}(\vec{k},\omega) - \chi_{\alpha\beta}(\vec{k},\omega_{0})}{i(\omega - \omega_{0})} F_{\beta}(\vec{k})$$
(A4.24)

and then, from (A4.23), it follows that the right-hand side of (A4.24) tends to $\sum_{\beta} \sigma_{\alpha\beta}(\vec{k},\omega)F_{\beta}(\vec{k})$ as $\omega_0 \neq 0$.

The essential point to stress is that the 'forces' can now be eliminated between (A4.22) and (A4.24). We then find

$$[A_{\alpha}(\vec{k},\omega)]_{+} = \sum_{\gamma} \frac{\chi_{\alpha\beta}(\vec{k},\omega) - \chi_{\alpha\beta}(\vec{k},\omega_{0})}{i(\omega - \omega_{0})} \chi_{\beta\gamma}^{-1}(\vec{k},\omega_{0}) \langle A_{\gamma\vec{k}}(\vec{X}) \rangle_{\Delta,\tau=0}$$
(A4.25)

At this stage we connect directly with macroscopic theory by supposing that the variables $A_{\alpha}(\vec{X}(t); \vec{r})$ satisfy (see Eq.(A4.8)):

$$\frac{\partial \overline{A_{\alpha \vec{k}}}(\vec{x}(t))}{\partial t} = -\sum_{\beta} M_{\alpha \beta}(\vec{k}) \overline{A_{\beta \vec{k}}}(\vec{x}(t))$$
(A4.26)

If we solve this as an initial value problem, we find

$$\overline{A_{\alpha \vec{k}}(\vec{X}(t))} = \sum_{\beta} \left\{ \exp\left[-M(\vec{k})t\right] \right\}_{\alpha \beta} \overline{A_{\beta \vec{k}}(\vec{X})}$$
(A4.27)

where the exponential operator is defined by its series expansion.

³ More generally, it is the Fourier transform of the relaxation function $\phi_{\alpha,\beta}(kt)$.

If we assume that macroscopic and microscopic results can be compared, then we find from (A4.25) and (A4.27)

$$\sum_{\beta} \frac{\chi_{\alpha\beta}(\vec{k},\omega) - \chi_{\alpha\beta}(\vec{k},\omega_0)}{i(\omega - \omega_0)} \chi_{\beta\gamma}^{-1}(\vec{k},\omega_0)$$
$$= \left(\frac{1}{-i\omega + M(\vec{k})}\right)_{\alpha\gamma}$$
(A4.28)

Let $\omega_0 \rightarrow 0$ when we find the solution as

$$\chi_{\alpha\beta}(\vec{k},\omega) \approx \sum_{\gamma} \left[\frac{M(\vec{k})}{-i\omega + M(\vec{k})} \right]_{\alpha\gamma} \chi_{\alpha\beta}(\vec{k},0)$$
(A4.29)

To pass to macroscopic theory, we need only consider the small \vec{k} behaviour of \vec{M} . When $M(\vec{k})$ has the form

$$M(\vec{k}) = k^2 N(\vec{k})$$
 (A4.30)

where $N(\vec{k}) = N(0)$ as $\vec{k} \rightarrow 0$ (see remarks after (A4.9)), then we find the matrix N(0) as

$$\lim_{\omega \to 0} \lim_{\omega \to 0} -\frac{i\omega}{k^2} \chi_{\alpha\beta}(k,\omega) = \sum_{\gamma} \{N(0)\}_{\alpha\gamma} \lim_{k \to 0} \chi_{\gamma\beta}(\vec{k},0) \qquad (A4.31)$$

However, (A4.30) is not quite general enough for the hydrodynamics equations because not all the elements of the matrix a satisfy (A4.30) as $k \rightarrow 0$, as we have seen.

A4.4. Shear viscosity

As remarked earlier, \vec{c} is not coupled with the other physical variables, and we can therefore find an expression for the shear viscosity rather readily.

We have, as defined earlier

$$d_{\vec{k}} = \sum_{j} i\vec{k} \cdot \vec{p}_{j} \exp(-i\vec{k} \cdot \vec{r}_{j})$$

$$(A4.32)$$

$$c_{\vec{k}} = \sum_{j} i\vec{k} \times \vec{p}_{j} \exp(-i\vec{k} \cdot \vec{r}_{j})$$

From isotropy arguments we can write

$$\sigma_{g_i g_j}(\vec{k}, \omega) = \left(\delta_{ij} - \frac{k_i k_j}{k^2}\right) \sigma_t(k^2 \omega) + \frac{k_i k_j}{k^2} \sigma_\ell(k^2 \omega)$$
(A4.33)

where i and j refer to Cartesian components and where σ_t and σ_ℓ are defined by this equation. There is a similar result for $\chi_{g_ig_j}$, and we also have, from (A4.19) the result

 $\chi_{t}(k^{2}0) = \chi_{\ell}(k^{2}0) = \rho_{0} M$ (A4.34)

where $\rho_0 = N/\Omega$. It follows that

$$\sigma_{\mathbf{c}_{i}\sigma_{j}}(\vec{\mathbf{k}},\omega) = (\mathbf{k}^{2}\delta_{ij} - \mathbf{k}_{i}\mathbf{k}_{j})\sigma_{t}(\mathbf{k}^{2}\omega) \qquad (A4.35)$$

$$\sigma_{dd}(\vec{k},\omega) = k^2 \sigma_{\ell}(k^2 \omega) \tag{A4.36}$$

with similar expressions for $\boldsymbol{\chi}$

$$\mathbb{M}_{c_i c_j}(\vec{k}) = \lambda(k^2) \delta_{ij} \qquad (A4.37)$$

follows, where λ is defined by this equation. It is related to σ_t by

$$\sigma_{t}(k^{2}, \omega) = \frac{\rho_{0}M}{-i\omega + \lambda(k^{2})}$$
(A4.38)

Since $c_{\vec{k}}$ becomes an integral of the motion as $\vec{k} \rightarrow 0$, the first term in the expansion of $\lambda(k^2)$ in powers of k^2 must vanish and we can write

$$\lambda(k^2) = \frac{\eta}{\rho_0 M} k^2 + \dots$$
 (A4.39)

where this defines η . Using only the first term of this expansion, we find the macroscopic equation for $\overline{\vec{c}}$ as

$$\rho_0 M \frac{\partial \vec{c}}{\partial t} = \eta \nabla^2 \vec{c}$$
 (A4.40)

We find then, the correlation function expression for the shear viscosity as

$$\eta = \lim_{\omega \to 0} \lim_{k \to 0} \frac{\omega^2}{k^2} \operatorname{Re} \sigma_t(\vec{k}, \omega)$$
 (A4.41)

This can be transformed into

$$\eta = \frac{1}{\mathbf{k}_{B}T} \int_{0}^{\infty} \langle \tau_{xy}(\vec{\mathbf{r}},t) \tau_{xy}(00) \rangle d\vec{\mathbf{r}} dt \qquad (A4.42)$$

where $\tau_{xy}\,$ is an off-diagonal element of the stress tensor, but we shall not go into further details here.

A4.5. Other hydrodynamic equations

We wish finally to sketch the derivation of the other hydrodynamic equations for the observables $\bar{\rho}$, \bar{d} and \bar{E} , using arguments similar to those used above for the shear viscosity.

From the definitions of the density fluctuations $\rho_{\vec{k}}$ and of $d_{\vec{k}}$ some relations follow between the elements of the susceptibility matrix $\chi(k,\omega)$. Thus, from Hamilton's equations we find

$$M\dot{\rho}_{\downarrow} = -d_{\downarrow} \qquad (A4.43)$$

and hence for the variables $\rho_{\vec{k}}$, $d_{\vec{k}}$ and $E_{\vec{k}}$ the matrix $\chi(\vec{k},\omega)$ takes the following form

$$\chi(\vec{k},\omega) = \begin{bmatrix} \chi_{\rho\rho}(\vec{k},\omega) & -i\omega M\chi_{\rho\rho}(\vec{k},\omega) & \chi_{\rho E}(\vec{k},\omega) \\ i\omega M\chi_{\rho\rho}(\vec{k},\omega) & k^{2}\rho_{0}M + \omega^{2}M^{2}\chi_{\rho\rho}(\vec{k},\omega) & i\omega M\chi_{\rho E}(\vec{k},\omega) \\ \chi_{\rho E}(\vec{k},\omega) & -i\omega M\chi_{\rho E}(\vec{k},\omega) & \chi_{EE}(\vec{k},\omega) \end{bmatrix} (A4.44)$$

where use has been made of symmetry relations, of the fact that for reasons of isotropy $\chi_{\rho\rho}(\vec{k},\omega)$ and $\chi_{\rho E}(\vec{k},\omega)$ can only depend on the scalar k^2 and on the vanishing of the correlation functions as the time interval tends to infinity.

Now we have that

$$\chi_{\alpha\beta}(\vec{k},\omega) = \sum_{\gamma} \left(\frac{\vec{M}(\vec{k})}{-i\omega + \vec{M}(\vec{k})} \right)_{\alpha\gamma} \chi_{\alpha\beta}(\vec{k},0)$$
(A4.45)

for small k and ω and any element of $\vec{\chi}(k,\omega)$ must have the form

$$\chi_{\alpha\beta}(\vec{k},\omega) = \frac{q_2\omega^2 + q_1\omega + q_0}{(\omega - \nu_1)(\omega - \nu_2)(\omega - \nu_3)}$$
(A4.46)

where the \vec{k} dependence of the q's and ν 's is implicit. Thus we can write more explicitly

$$\chi_{\rho\rho}(\vec{k},\omega) = \frac{a_1\omega + ia_0}{(\omega - \nu_1)(\omega - \nu_2)(\omega - \nu_3)}$$

$$\chi_{\rho E}(\vec{k},\omega) = \frac{b_1 \omega + i b_0}{(\omega - \nu_1)(\omega - \nu_2)(\omega - \nu_3)}$$
(A4.47)

$$\chi_{\text{EE}}(\vec{\mathbf{k}},\omega) = \frac{ih_2\omega^2 + h_1\omega - ih_0}{(\omega - \nu_1)(\omega - \nu_2)(\omega - \nu_3)}$$

where $a_1 = -\rho_0 k^2/M$ and the coefficients $a_0 \dots h_2$ are real. After some calculation, we obtain the matrix \vec{M} in the form

$$M(\vec{k}) = \begin{bmatrix} 0 & M^{-1} & 0 \\ M\frac{a_1h_0 - b_0b_1}{a_1h_2} & \frac{b_1^2 - a_1h_1}{a_1h_2} & M\frac{a_0b_1 - a_1b_0}{a_1h_2} \\ \frac{-b_0}{a_1} & \frac{b_1}{Ma_1} & \frac{a_0}{a_1} \end{bmatrix}$$
(A4.48)

It is easily verified that the matrix -iM has the eigenvalues $\nu_1 \nu_2 \nu_3$. The first line of this yields the continuity equation (A4.1). The second and third lines contain the coefficients of the equations for div \vec{g} and \vec{E} respectively.

In order to determine the lowest powers of k^2 in the series expansions of these coefficients, we invoke the fact that $\rho_{\vec{k}}$, $d_{\vec{k}}$ and E_k become integrals of the motion as $\vec{k} \neq 0$.

Then it can be shown that the matrix \vec{M} takes the form for small k

$$\mathbf{M}(\vec{\mathbf{k}}) \doteq \begin{bmatrix} 0 & \mathbf{M}^{-1} & 0 \\ \mathbf{k}^{2} \mathbf{M}_{21} & \mathbf{k}^{2} \mathbf{M}_{22} & \mathbf{k}^{2} \mathbf{M}_{23} \\ \mathbf{k}^{2} \mathbf{M}_{31} & \mathbf{M}_{32} & \mathbf{M}_{33} \end{bmatrix}$$
(A4.49)

just as required from the macroscopic equations, as discussed following (A4.9).

The last step involves showing that although the coefficients M_{21} , M_{22} etc. in (A4.49) are rather complicated when written in terms of a_0 , b_0 , h_0 etc., they may be expressed in terms of small (k, ω) limits of $\sigma_{\alpha\beta}$, just as with the shear viscosity η in (A4.41). For example, the thermal conductivity K may be written as

$$K = \frac{1}{T} \lim_{\omega \to 0} \lim_{k \to 0} \frac{\omega^2}{k^2} \operatorname{Re} \sigma_{EE}(\vec{k}, \omega)$$
 (A4.50)

or in terms to the total energy current $\vec{J}^{E}(t)$,

$$K = \frac{1}{k_{B}T^{2}\Omega} \int_{0}^{\infty} \langle J_{x}^{E}(t) J_{x}^{E}(0) \rangle dt \qquad (A4.51)$$

Thus it proves possible to derive the linearized equations of hydrodynamics, together with correlation function expressions for the transport coefficients, in a rather fundamental way. Unfortunately, any exact calculations from such formal expressions are, at present, beyond the power of man, but this represents a worthwhile goal in the theory of liquids.

APPENDIX 5

Density matrices and two-body correlation function for free fermions

If we have a single-particle Schrödinger equation with eigenvalues E_i and eigenfunctions ψ_i then the canonical or Bloch density matrix C defined by

$$C(\vec{r}, \vec{r}_{0}, \beta) = \sum_{all \ i} \psi_{i}^{*}(\vec{r})\psi_{i}(\vec{r}_{0})e^{-\beta E_{i}}; \qquad \beta = \frac{1}{k_{B}T}$$
(A5.1)

is such that the Hamiltonian $H_{\vec{r}}$ acting on $C(\vec{r}, \vec{r}_0, \beta)$ yields $\sum_i E_i \psi_i^*(\vec{r}) \psi_i(\vec{r}_0) e^{-\beta E_i}$. This is clearly the same as $-\partial C/\partial \beta$ and hence C

satisfies the Bloch equation

$$H_{\vec{r}}C = -\frac{\partial C}{\partial \beta}$$
 (A5.2)

It is now clear that for free particles, with $H_r = -\frac{1}{2}\nabla_{\vec{r}}^2$, this is identical with the diffusion Eq.(5.1) provided we replace $\beta/2$ by Dt. Also, as $\beta \rightarrow 0$, it follows from (A5.1) that

$$C(\vec{r}, \vec{r_{0}}, 0) = \sum_{i} \psi_{i}^{*}(\vec{r})\psi_{i}(\vec{r}_{0})$$
$$= \delta(\vec{r} - \vec{r_{0}})$$
(A5.3)

which is the completeness theorem for eigenfunctions. Thus, the required boundary condition (5.2) is also obeyed.

Hence, putting $\psi_i \equiv (1/\Omega^{\frac{1}{2}}) \exp i\vec{k} \cdot \vec{r}$, $E = k^2/2$ in (A5.1) and integrating over \vec{k} we find

$$C(\vec{r}, \vec{r}_{0}, \beta) = \frac{1}{8\pi^{3}} \int e^{-i\vec{k}\cdot\vec{r}-\vec{r}_{0}} e^{-\frac{\beta k^{2}}{2}} d\vec{k}$$
$$= \frac{1}{(2\pi\beta)^{3/2}} e^{-\frac{|\vec{r}-\vec{r}_{0}|^{2}}{2\beta}}$$
(A5.4)

Replacing $\beta/2$ by Dt leads immediately to (5.4) as required.

The Dirac density matrix

$$\rho(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{0}, E) = \sum_{i}^{E} \psi_{i}^{*}(\vec{\mathbf{r}}) \psi_{i}(\vec{\mathbf{r}}_{0})$$
 (A5.5)

is readily shown to be related to C by

$$C(\vec{r}, \vec{r_0}, \beta) = \beta \int_0^\infty \rho(\vec{r}, \vec{r_0}, E) e^{-\beta E} dE \qquad (A5.6)$$

and hence, from (A5.6) and (A5.5), or by direct calculation, we find

$$\rho(\vec{r}, \vec{r}_{0}, E) = \frac{k_{f}^{3}}{\pi^{2}} \frac{j_{1}(k_{f} | \vec{r} - \vec{r}_{0} |)}{k_{f} | \vec{r} - \vec{r}_{0} |}$$
(A5.7)

where E_f is the Fermi energy and k_f the Fermi wave number. For a determinant of plane waves, we can immediately construct the two-particle density matrix and we find on the diagonal

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$$\rho_{2}(\vec{r}, \vec{r}_{0}) = \rho^{2} - \frac{1}{2} \left[\rho(\vec{r}, \vec{r}_{0}) \right]^{2}$$

$$= \rho^{2} \left[1 - \frac{9}{2} \left\{ \frac{j_{1}(k_{f} | \vec{r} - \vec{r}_{0} |)}{k_{f} | \vec{r} - \vec{r}_{0} |} \right\}^{2} \right]$$

$$= \rho^{2} g(| \vec{r} - \vec{r}_{0} |) \qquad (A5.8)$$

where g(r) is the 'Fermi hole'. This is the result required in subsection 8.3.

APPENDIX 6

Velocity correlation function for Brownian motion and other cases

It is obvious that by neutron scattering we can gain some knowledge of individual atomic motion, unlike the information we can get from the study of bulk properties. A single atom moves, of course, in a very complex path and we expect to describe its motion by statistical considerations.

A model which is sometimes valuable is that used for Brownian motion. Here, for a heavy particle suspended in a fluid, we write

$$M\vec{\vec{r}} + M\zeta\vec{\vec{r}} = \vec{F}(t)$$
 (A6.1)

The term $M\zeta \dot{\vec{r}}$ is a frictional or damping term and $\vec{F}(t)$ is a rapidly varying stochastic force. For the velocity correlation function one obtains

$$\langle \vec{\mathbf{v}}(0) \cdot \vec{\mathbf{v}}(t) \rangle = \frac{3}{\beta M} \mathbf{e}^{-\zeta t}, \quad t > 0$$
 (A 6.2)

The friction constant $\,\zeta\,$ is related to the macroscopic self-diffusion constant through

$$D = \frac{1}{3} \int_{0}^{\infty} \langle \vec{v}(0) \cdot \vec{v}(t) \rangle dt = \frac{1}{M\zeta\beta}$$
(A6.3)

This is the result we shall use in obtaining the self-diffusion constant for hard spheres at high density below.

Limits of validity:

We can say that while (A6.1) proves to give an adequate description of Brownian motion, it is not known whether it can describe the motion of a single atom.

When we use Langevin's equation (A6.1) the assumptions are implicit that the correlated force is proportional to the velocity of the particle and that the fluctuating force varies much more rapidly than the correlated one. This will be valid for a heavy particle moving in a medium of light atoms.

It is of interest that (A6.2) can be obtained, quite properly, by studying the motion of a single heavy atom bound in a harmonic lattice (Rubin [23,24]). On the other hand, for equal masses, assuming only nearest neighbour interactions.

$$\langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \frac{3}{M\beta} J_0(\omega_0 t),$$
 (A6.4)

where J_0 is the zero order Bessel function.

For a large mass, Rubin showed that the same correlation functions are obtained as are given by Langevin's equation for a harmonic oscillator

$$M\vec{\dot{r}} + M\zeta\vec{\dot{r}} + M\omega_0^2\vec{r} = \vec{F}(t)$$
 (A6.5)

where $M\omega_0^2 \vec{r}$ is the harmonic restoring force. The velocity correlation function is in this case

$$\langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \frac{3}{M\beta} \left(\cos \omega_1 t - \frac{\zeta}{2\omega_1} \sin \omega_1 t \right) e^{-\frac{\zeta t}{2}}$$
 (A6.6)

where $\omega_1^2 = \omega_0^2 - \zeta^2 / 4$.

Connection with Liouville's equation

Sjölander has shown that one can get an approximate single-particle equation from Liouville's equation: namely

$$\dot{\vec{v}}(t) + \frac{\beta}{3M} \int_{0}^{t} \langle \vec{K}(t) \cdot \vec{K}(t') \rangle \vec{v}(t') dt' = \frac{1}{M} \vec{F}(t) \qquad (A \, 6 \, . \, 7)$$

where $\langle \vec{K}(t) \cdot \vec{K}(t') \rangle$ is the correlation function for the actual force on the atom and is related to the friction constant ζ by

$$\zeta = \frac{\beta}{3M} \int_{0}^{\infty} \langle \vec{K}(0) \cdot \vec{K}(t) \rangle dt \qquad (A \ 6 \ . \ 8)$$

 \overline{F} is a stochastic force which does <u>not</u> depend on the co-ordinates of the particle being considered.

If the velocity varies slowly over the relaxation time for the forcecorrelation function, then we regain the Langevin equation (A6.1) with the friction term (A6.8).

APPENDIX 7

Decay time of velocity correlation function for hard spheres

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If \vec{p}_1 and \vec{p}_2 are the momenta of two colliding molecules, then the momentum gained by sphere 1 will be

$$\Delta \vec{p}_1 = -(\vec{p}_1 \cdot \vec{l} - \vec{p}_2 \cdot \vec{l})\vec{l} \qquad (A7.1)$$

where \vec{l} is the unit vector in the direction 1 2. Consequently

$$-\vec{p}_{1} \cdot \Delta \vec{p}_{1} = (p_{1} - p_{2})p_{1}$$
 (A7.2)

where p_1 and p_2 are the components of $\vec{p_1}$ and $\vec{p_2}$ in the direction \vec{l} . The probability of sphere 1 experiencing such a collision per unit time is

$$\psi(p_1 - p_2)\phi(p_2)dp_2/M$$
 (A7.3)

where ψ is the chance of another molecule being within unit short distance of the first molecule and $\phi(p)$ is the Maxwell velocity distribution

$$\phi(\mathbf{p}) = (2\pi \,\mathrm{Mk}_{\mathrm{B}}\mathrm{T})^{-\frac{1}{2}} \exp\left[\frac{-\mathbf{p}^{2}}{2\mathrm{Mk}_{\mathrm{B}}\mathrm{T}}\right] \tag{A7.4}$$

 ψ is clearly related to ${\bf g}_0$, the value of ${\bf g}({\bf r})$ at the hard sphere diameter ${\bf R}$ by

$$\psi = \frac{2g_0}{N/\Omega} = \frac{3}{R} \left(\frac{p}{\rho k_B T} - 1 \right)$$
 (A7.5)

We now multiply $\vec{p_1} \cdot \vec{\Delta p_1}$ by $\phi(p_1)dp_1$, and integrate over p_1 and p_2 $(p_1 - p_2 > 0)$, when we obtain

$$-\lim_{\Delta t \to 0} \frac{\langle \vec{p}_1 \cdot \Delta \vec{p}_1 \rangle}{\Delta t}$$
$$= \frac{\psi}{M} \int_{p_1 - p_2 > 0} \int \phi(p_1) \phi(p) (p_1 - p_2)^2 p_1 dp_1 dp_2 \qquad (A7.6)$$

Using sum and difference variables we can perform the integration, when we find the result

$$-\lim_{\Delta t \to 0} \frac{\langle \vec{p}_1 \cdot \Delta \vec{p}_1 \rangle}{\Delta t} = 2\psi \left(\frac{m}{\pi}\right)^{\frac{1}{2}} (k_B T)^{3/2}$$
 (A7.7)

Thus we obtain finally the result (5.20).

APPENDIX 8

Solution of linearized Vlasov equation for $S(k, \omega)$

We now change direction slightly and work from the Vlasov equation, having justified (to some extent) replacing the interaction by the direct

correlation function. The Vlasov equation, which resembles the Boltzmann equation, but which has no collision term in it, reads (see, for example, Montgomery and Tidman [11], Eq.(5.3))

$$\frac{\partial F}{\partial t} + v \cdot \frac{\partial F}{\partial \vec{r}} = \frac{\rho}{M} \int d\vec{r}_2 \, d\vec{v}_2 \, \frac{\partial \phi_{12}}{\partial \vec{r}} F(\vec{r}_2, \vec{v}_2, t) \cdot \frac{\partial F}{\partial \vec{v}}$$
(A8.1)

for the single-particle function $F(\vec{r,v,t})$ in the phase space, where $\phi_{12} = \phi(|\vec{x} - \vec{x}_2|)$. Linearizing this by writing

$$F(\vec{r}, \vec{v}, t) = \phi_{B}(v) + f(\vec{r}, \vec{v}, t)$$
 (A8.2)

we find

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} = \frac{\rho}{M} \frac{\partial}{\partial \vec{v}} \phi_{B}(v) \int d\vec{r}_{2} d\vec{v}_{2} \frac{\partial \phi_{12}}{\partial \vec{r}} f(\vec{x}_{2}, \vec{v}_{2}, t)$$
$$= \frac{-\rho}{k_{B}T} \phi_{B}(v) \vec{v} \int d\vec{r}_{2} \frac{\partial \phi_{12}}{\partial \vec{x}} z(x_{2}, t)$$
(A8.3)

where

$$z(x_2, t) = \int f(\vec{x}_2, \vec{v}_2, t) d\vec{v}_2$$
 (A8.4)

Taking the transform of this we find

$$(i\omega - i\vec{K} \cdot \vec{v}) f(\vec{K}, \vec{v}, \omega) - \frac{\phi_{B}(v)}{k_{B}T} i\vec{k} \cdot \vec{v} \rho \phi(K) z (\vec{K}, \omega) = f(\vec{K}, \vec{v}, 0)$$
(A8.5)

where $f(\vec{K}, \vec{v}, 0)$ is the appropriate initial condition. We put

$$f(\vec{K}, \vec{v}, 0) = \phi_{B}(\vec{v})S(K)$$
 (A8.6)

Taking the z axis as the direction of \vec{K} and replacing the interaction by the direct correlation function, we have

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$$f(\vec{K}, \vec{v}, \omega) = \frac{S(K)\phi_{B}(v)}{i\omega - iK_{z}v_{z}} - \frac{iK_{z}\vec{c}(k) z(K\omega)\phi_{B}(v)v_{z}}{i\omega - iK_{z}v_{z}}$$
(A8.7)

 $S(k,\omega)$ is given by the Fourier transform of G(rt) which, in turn is related to the integral over velocities of (\vec{r}, \vec{v}, t) . This, from (8.4), is

simply $z(\vec{r}, t)$ and we find then

$$Z(\mathbf{k},\omega) = \frac{S(\mathbf{K})\int (\mathbf{i}\omega - \mathbf{i}\mathbf{K}\,\mathbf{v}_{z})^{-1} \phi_{B}(\mathbf{v}) \left(\frac{2\mathbf{k}_{B}\,T}{m}\right)^{\frac{3}{2}} d\vec{\mathbf{v}}}{1 + \tilde{\mathbf{c}}(\mathbf{K})\int (\mathbf{i}\omega - \mathbf{i}\mathbf{K}\mathbf{v}_{z})^{-1} \phi_{B}(\mathbf{v})}$$

$$\times \mathbf{i}\mathbf{K}\mathbf{v}_{z} d\mathbf{v} \left(\frac{2\mathbf{k}_{B}\,T}{m}\right)^{\frac{3}{2}}$$
(A8.8)

Taking the real part of $z(k, \omega)$ we then find the result (6.22).

APPENDIX 9

Phonon Hamiltonian for fluid

In dealing with the irrotational motion of a non-viscous fluid, we shall find it convenient to use the velocity potential ϕ , the density ρ and the pressure p as variables. Let the equilibrium state be defined by values ρ_0 and p_0 of the density and pressure.

We now use as a starting point for describing the fluid the Bernoulli equation $% \left({{{\left[{{{\left[{{{\left[{{{\left[{{{c}}} \right]}} \right]_{i}} \right]_{i}}}}}} \right]_{i}}} \right)$

$$\dot{\phi} = \frac{1}{2} (\text{grad } \phi)^2 + U \qquad (A9.1)$$

where U is the quantity $\int_{P_0}^{P} \frac{dp}{\rho}$ together with the equation of continuity

$$\dot{\rho} = \operatorname{div} \left(\rho \operatorname{grad} \phi \right)$$
 (A9.2)

An equivalent description can be obtained by starting from a Lagrangian density given by

$$L = \rho \left[\dot{\phi} - \frac{1}{2} (\text{grad } \dot{\phi})^2 - W \right]$$
$$= \rho \dot{\phi} - E_k - E_p$$
(A9.3)

Here, E_k is the kinetic energy density and E_p = ρ W is the potential

density. W is given by $\int_{\rho_0}^{\rho} \frac{p - p_0}{\rho^2} d\rho.$

We see that

L =
$$\rho$$
 (U - W) = $\rho^2 \frac{dW}{d\rho}$ = p - p₀, (A9.4)

using the explicit expressions given above for U and W. The Lagrangian density is seen then to be the deviation of the pressure from its equilibrium value.

 ρ is the generalized momentum corresponding to the 'co-ordinate' ϕ , and hence we can construct the Hamiltonian density as

$$H = \rho \dot{\phi} - L$$
$$= \frac{1}{2} \rho (grad \phi)^{2} + \rho W \qquad (A9.5)$$
$$= E_{k} + E_{p}$$

In quantum theory, this expression becomes

$$H = \frac{1}{2} \operatorname{grad} \phi \cdot \rho \operatorname{grad} \phi + \rho W$$
 (A9.6)

We now write the equation of state as

$$p = f(\rho) = p_0 + f'(\rho_0)(\rho - \rho_0) + \frac{1}{2} f''(\rho_0)(\rho - \rho_0)^2 + \dots$$
(A9.7)

The velocity of sound c is given by

$$c^2 = \frac{dp}{d\rho} = f'$$
 (A9.8)

and in particular $c_0^2 = f'(\rho_0)$

Now we expand U and W in Taylor series around ρ_0 and we find

$$U = \frac{c_0^2}{\rho^2} (\rho - \rho_0) + \frac{1}{2} \left(\frac{d}{d\rho} \left\{ \frac{c^2}{\rho} \right\} \right)_0 (\rho - \rho_0)^2$$

$$\rho W = \frac{1}{2!} \frac{c_0^2}{\rho_0} (\rho - \rho_0)^2 + \dots$$
(A9.9)

and

Hence, for the leading terms H' in the Hamiltonian we have

H' =
$$\frac{1}{2} \rho_0 (\text{grad } \phi)^2 + \frac{1}{2} \frac{c_0^2}{\rho_0} (\rho - \rho_0)^2$$
 (A9.10)
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At this stage we make a Fourier analysis of ϕ and use the density fluctuations $\vec{\rho_k}$ instead of ρ . Thus

 $\phi(\vec{\mathbf{r}}) = \Omega^{-\frac{1}{2}} \sum_{\vec{k}} q_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}}$ (A9.11)

and

$$\rho(\vec{\mathbf{r}}) = \rho_0 + \Omega^{-\frac{1}{2}} \sum_{\vec{\mathbf{k}}} \rho_{\vec{\mathbf{k}}} e^{-i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}}$$
(A9.12)

Since
$$\phi$$
 and ρ are real we have

$$\mathbf{q}_{\vec{k}} = \mathbf{q}_{\vec{k}}^*$$
, $\rho_{\vec{k}} = \rho_{\vec{k}}^*$ (A9.13)

where the star denotes the Hermitian conjugate.

The operators ϕ and ρ satisfy the relations

$$[\phi(\vec{r}), \phi(\vec{r'})] = [\rho(\vec{r}), \rho(\vec{r'})] = 0$$
 (A9.14)

and

$$[\rho \vec{\mathbf{r}}, \phi \vec{\mathbf{r}}] = \frac{\hbar}{i} \delta \vec{\mathbf{r}} \vec{\mathbf{r}}$$
(A9.15)

These relations yield

$$[q_{\vec{k}}, q_{\vec{k}'}] = [\rho_{\vec{k}}, \rho_{\vec{k}'}] = 0$$
(A9.16)

$$\begin{bmatrix} \rho_{\rightarrow}, q_{\rightarrow} \end{bmatrix} = \frac{\hbar}{i} \delta_{kk}$$
(A9.17)

Thus we find

$$H' = \frac{1}{2} \sum_{k} \left[\rho_0 k^2 q_{\overrightarrow{k}} q_{\overrightarrow{k}} + \left(\frac{c_0^2}{\rho_0} \right) \rho_{\overrightarrow{k}} \rho_{\overrightarrow{k}} \right]$$
(A9.18)

If we introduce $a_{\vec{k}}$ and $a_{\vec{k}}^*$ by

$$q_{\vec{k}} = \sqrt{\frac{c_0 \hbar}{2\rho_0 k}} (a_{\vec{k}} + a_{\vec{k}}^*), \ \rho_{\vec{k}} = \sqrt{\frac{\rho_0 k \hbar}{2c_0}} i(a_{\vec{k}}^* - a_{\vec{k}})$$

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these obey

$$[a_{\overrightarrow{k}}, a_{\overrightarrow{k}}] = [a_{\overrightarrow{k}}^{\ast}, a_{\overrightarrow{k}}^{\ast}] = 0$$
 (A9.19)

and

$$[a_{\vec{k}}, a_{\vec{k}'}^*] = \delta_{\vec{k}} \cdot \vec{k}.$$
(A9.20)

H^I then becomes

$$H' = \frac{1}{2}\hbar \sum_{\vec{k}} \left[c_0 k \left(a_{\vec{k}}^* a_{\vec{k}} + a_{\vec{k}} a_{\vec{k}}^* \right) \right] \frac{1}{2}\hbar \sum_{\vec{k}} c_0 k \left[2N_k + 1 \right]$$
(A9.21)

where the quantities $2N_k$, positive integers or zero, represent the number of phonons in state k. Thus, to this approximation, we have a system of non-interacting phonons.

Using (A9.2), we find to the same order of accuracy that

$$\dot{\rho} = \rho_0 \Omega^{-\frac{1}{2}} \sum_{\vec{k}} q_{\vec{k}} (-\vec{k}^2) e^{\vec{i}\vec{k}\cdot\vec{r}}$$
(A9.22)

and

$$\dot{\rho} = \Omega^{-\frac{1}{2}} \sum_{\vec{k}} \dot{\rho}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$
(A9.23)

Thus we obtain

$$\dot{\rho}_{\vec{k}} = -k^2 \rho_0 q_{\vec{k}}$$
(A9.24)

and from (A9.18) we have the result for the energy density

$$H' = \frac{1}{2} \sum_{\overrightarrow{k}} \frac{1}{\rho_0 k^2} \left[\dot{\rho}_{\overrightarrow{k}} \dot{\rho}_{\overrightarrow{k}}^* + \omega_k^2 \rho_{\overrightarrow{k}} \rho_{\overrightarrow{k}}^* \right]$$
(A9.25)

The desired result (8.1) follows when we write the total energy as

$$H = \Omega H' = \frac{1}{2} \sum_{\vec{k}} \frac{1}{Nk^2} \left[\dot{\rho}_{\vec{k}} \dot{\rho}_{\vec{k}}^* + \omega_{\vec{k}}^2 \rho_{\vec{k}} \dot{\rho}_{\vec{k}}^* \right]$$
(A9.26)

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Abstract

1. Introduction. 2. Dynamics of a molecule. 3. Symmetry operations. 4. Symmetry operations and waves in infinite lattices. 5. Elastic theory. 6. Classical eigenoscillations and quantum states of a finite lattice. 7. Lattice Green's functions. 8. Models for potentials and coupling parameters.

1. INTRODUCTION

In this contribution we shall give an introduction into lattice dynamics. Starting point is the existence of a potential ϕ which depends on the coordinates of the atoms or ions forming the lattice. This is the adiabatic approximation introduced by Born and Oppenheimer wher ϕ is given by the energy of the electronic ground state where the nuclear co-ordinates are to be regarded as fixed parameters. We shall throughout remain within the frame of the "harmonic approximation" which only takes account of quadratic terms in the displacements from the static equilibrium conditions. Anharmonic effects are not discussed. Section 2 deals with the dynamics of an arbitrary molecule. The effects of translational and rotational invariance are discussed, and the procedure of resolving the equation of motion into oscillator motions is treated in a general way. A simple proof is given of the fact that a purely harmonic theory for threedimensional arrangements is not consistent. In section 3, the influence of molecular symmetries is discussed in detail. The lattice symmetries are discussed in section 4 for an infinite lattice. It is shown there how harmonic motions can be derived easily by employing the lattice translational symmetry. Only simple cubic Bravais lattices are discussed in detail. The reduction of coupling matrices for near neighbours, and the lattice waves in symmetrical directions are treated extensively, including dispersion curves and sound waves for small frequencies. The Brillouin zone is introduced. Section 5 deals with theory of elasticity, its derivation from lattice theory, and the calculation of elastic moduli from lattice data. In section 6, a finite crystal is treated by introducing a periodic boundary condition, and the quantum theory of the crystal is shortly discussed. The lattice and elastic spectra and the thermal energy are treated. Finally, as a simple example the scattering cross-sections for X-ray scattering are derived including the Debye-Waller factor and one-phonon crosssection. In section 7, lattice Green's functions are introduced. As a simple application the dynamical behaviour of an isotopic defect is treated. Section 8 contains a brief review of the methods used to obtain coupling matrices and dispersion curves. References to review articles and books are given at the end.

2. DYNAMICS OF A MOLECULE

The atoms of the molecule will be labelled by the superscripts m, n etc. (m, n:1,2,..., N for an N-atomic molecule), the masses will be denoted by M^m , and the atomic positions by $\vec{r}^{m} = (x_1^m)$, where the three spatial indices i can be 1, 2, 3, or x, y, z (Fig. 1). The molecular dynamics is mainly determined by the potential energy $\phi(..\vec{r}^m..)$. If, for the sake of simplicity, we assume the external forces to vanish then ϕ must be invariant under translations and rotations including improper rotations such as reflections and inversion. If we denote these operations by O:

$$\overrightarrow{Or} = \overrightarrow{t} + \overrightarrow{\Omega r} = (t_i + \sum_k \overrightarrow{\Omega}_{ik} x_k)$$

where \vec{t} is the translation and Ω the matrix representing the rotation about an axis through the origin, we have

$$O\phi = \phi (..O^{-1} \vec{r}^{m}..) = \phi (..\vec{r}^{m}..)$$

$$O^{-1} \vec{r} = -\vec{t} + \Omega^{-1} \vec{r}$$
(2.1)

These two invariances correspond to homogeneity and isotropy of space; both together also guarantee rotational invariance for arbitrary rotational axes.



FIG.1. Atomic positions in a molecule: Oactual positions \vec{r}^m , O equilibrium positions \vec{k}^m , displacements from equilibrium: $\vec{u}^m = \vec{r}^m \cdot \vec{k}^m$.

In classical dynamics the minimum of ϕ determines the equilibrium positions \vec{R}^{m} . They are not unique because $\phi \vec{R}^{m}$ are equivalent equilibrium positions. Starting from one set of positions \vec{R}^{m} we describe the molecular state by the displacements \vec{u}^{m} from equilibrium

$$\vec{r}^{m}(t) = \vec{R}^{m} + \vec{u}^{m}(t)$$
 (2.2)

where t is the time.

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In most cases it is sufficient to focus attention on small displacements. Consequently, we can expand ϕ in powers of the displacements and keep only the low-order terms in an approximate treatment:

 $\phi(..\vec{R}^{m} + \vec{u}^{m}...) = \phi(...\vec{R}^{m}...) +$ classical equilibrium energy + $\frac{1}{2}\sum_{m,i}\sum_{n,k} \phi_{ik}^{mn} u_{i}^{m} u_{k}^{n} +$ harmonic approximation (2.3) + $\frac{1}{3!}\sum_{m,i}\sum_{n,k}\sum_{p,l} \phi_{ikl}^{mnp} u_{i}^{m} u_{k}^{n} u_{l}^{p} +$ anharmonic terms

where

$$\phi_{ik}^{mn} = \frac{\partial^2 \phi(\vec{R}^1, \dots, \vec{R}^N)}{\partial X_{ik}^m} = \phi_{ki}^{nm}, \text{ etc.} \qquad (2.3a)$$

The first-order term vanishes because one starts from the minimum of ϕ . The second-order term determines the dynamics of small oscillations.





This term alone is most widely used and called the harmonic approximation because it is equivalent to a set of 3N independent harmonic oscillators with various frequencies. The higher-order, anharmonic, terms destroy the independence and lead to interactions between the harmonic modes (frequency shift, damping, temperature dependence).

In the equation of motion in the harmonic approximation

$$\mathbf{M}^{\mathbf{m}}\ddot{\mathbf{u}}_{i}^{\mathbf{m}} = -\frac{\partial \phi}{\partial \mathbf{u}_{i}^{\mathbf{m}}} = -\sum_{\mathbf{n},\mathbf{k}} \phi_{i\mathbf{k}}^{\mathbf{m}\mathbf{n}} \mathbf{u}_{\mathbf{k}}^{\mathbf{n}}$$
(2.4)

the coupling parameters (c.p.'s) of second order, ϕ_{ik}^{mn} , play the decisive role. Their meaning is obvious: $-\phi_{ik}^{mn}$ is the force on atom m in the i direction if atom n only is displaced by unit distance in the k direction while all other atoms remain in their equilibrium positions (or vice versa, depending on the symmetry in m, i; n, k according to Eq.(2.3a)) (see (Fig. 2)). With respect to the spatial indices i, k the quantity ϕ^{mn} is a three-dimensional matrix, not necessarily symmetrical except for ϕ^{mm} .

Besides the symmetries (2.3a) the c.p.'s must obey additive relations which guarantee the invariances (2.1). These can be obtained already from infinitesimal translations (t_i infinitesimal) and proper rotations ($\Omega_{ik} = \delta_{ik} + \omega_{ik}$ with infinitesimal, anti-symmetrical $\omega_{ik} = -\omega_{ki}$, $\Omega = 1 + \omega$, $\Omega^{-1} = 1 - \omega$). The most important relations can be derived easily from the equation of motion. If the molecule in equilibrium as a whole is displaced ($\vec{u}^n = \vec{t}$) or rotated ($\vec{u}^n = \omega \vec{R}^n$) no forces can arise and the right-hand side of Eq.(2.4) must vanish. Consequently, from translational invariance, we have

$$\sum_{n} \phi_{ik}^{mn} = 0 = \sum_{n} \phi_{ki}^{nm} = 0, \text{ for all } m, k, i \qquad (2.5)$$

(equivalent to the conservation of total momentum, $\sum_{m} M^{m} \dot{\vec{u}}^{m}$, in Eq.(2.4)), and from rotational invariance

$$\sum_{n,k,l} \phi_{ik}^{mn} \omega_{kl} X_l^n \approx 0 \text{ or } \sum_{n} \phi_{ik}^{mn} X_l^n, \text{ symmetrical in } kl$$
 (2.6)

(equivalent to the conservation of total angular momentum, $\sum_{m} M^{m} \vec{r}^{m} \times \vec{r}^{m}$

 $\cong \sum_{m} \mathbf{M}^{m} \vec{\mathbf{R}}^{m} \times \dot{\vec{u}}^{m}, \text{ in (2.4).}$

The most general conditions (see Ref. [4]) are obtained from

$$O\phi = \phi(... O^{-1} \vec{r}^{m}...) = \phi(... \vec{R}^{m} + \vec{u}^{m} - \vec{t} - \omega(\vec{R}^{m} + \vec{u}^{m})) = \phi(... \vec{R}^{m} + \vec{u}^{m}...)$$

if we again expand about equilibrium, keep only linear terms in \vec{t} and ω for infinitesimal changes and compare terms with equal powers in \vec{u} . Translational invariance connects only c.p.'s of the same order, e.g., for the third-order c.p.'s:

$$\sum_{p} \phi_{ikl}^{mnp} = 0 \qquad (2.5a)$$

whereas rotational invariance connects orders different by 1 through the term $\omega \vec{u}^{m}$. Equation (2.6) is actually a relation between c.p.'s of first and second order where the first-order terms vanish because we start from equilibrium. As an example, we may use the rotational connection between second- and third-order coefficients:

$$\phi_{ik}^{mn}\delta_{jl} + \phi_{li}^{mn}\delta_{jk} + \sum_{p}\phi_{lki}^{mnp}X_{j}^{p}$$
, symmetrical in i, j. (2.6a)

In a purely harmonic theory where all c.p.'s except those of second order would vanish Eq.(2.6a)

$$\phi_{ik}^{mn} \delta_{il} + \phi_{li}^{mn} \delta_{ik} = \phi_{ik}^{mn} \delta_{il} + \phi_{lj}^{mn} \delta_{ik}$$

leads to

$$\phi_{ik}^{mn} = \widehat{\phi}^{mn} \delta_{ik}, \ \widehat{\phi}^{mn} = \widehat{\phi}^{nm}$$

which can easily be derived by considering all combinations of i, k, j, l. Consequently, Eq. (2.6) reads now

$$\sum_{n} \hat{\phi}^{mn} X_{1}^{n} \delta_{ik} = \sum_{n} \hat{\phi}^{mn} X_{k}^{n} \delta_{i1}$$
(2.6b)

which implies that

$$\sum_{n} \hat{\phi}^{mn} X_{1}^{n} = 0 \text{ for } 1 = 1, 2, 3 \qquad (2.6c)$$

which can again be shown by considering all sets 1, i, k (for instance

l,i,k = 1,2,2 gives $\sum_{n} \hat{\phi}^{mn} X_{1}^{n} = \sum_{n} \hat{\phi}^{mn} X_{2}^{n} \delta_{12} = 0$. It is now easy to de-

monstrate that the equilibrium configuration of such a purely harmonic theory cannot be stable. By stable equilibrium we understand that the potential energy is a real minimum for small deviations \vec{u} except for small translations and proper rotations. If we now consider a small

homogeneous deformation, $u_i^m = \sum_{s}^{n} d_{is} X_s^m$, the energy above equilibrium

$$\frac{1}{2} \sum_{m,i} \sum_{n,k} \phi_{ik}^{mn} u_i^m u_k^n = \frac{1}{2} \sum_{m,n,s,t} \hat{\phi}^{mn} d_{is} X_s^m d_{it} X_t^n$$

vanishes because of Eq.(2.6c) for all homogeneous deformations, e.g. homogeneous compression or shear¹, whereas it should only disappear for small rotations, i.e., $d_{is} = \omega_{is}$. This fact, then, shows that a purely harmonic theory is unphysical, and that always anharmonic terms should be considered for stable molecular equilibrium configurations. The above argument does not apply to one-dimensional crystals with one-dimensional displacements, e.g. a linear chain connected by harmonic springs is a purely harmonic model for displacements parallel to the chain. In such cases, the rotational invariance does not come into play.

¹ By choosing d = -1 the molecule would be even reduced to a point at the origin without any change in potential energy.

Consequently, in any physical spatial configuration third-order terms are necessary to maintain rotational invariance. If we consider any close-packed arrangement with an interaction $\varphi(r)$ between next neighbour pairs only, the equilibrium distance 1 is given by $\varphi'(1) = 0$, the second-order c.p.'s are proportional to $\varphi''(1)$ and the third-order c.p.'s contain terms $\varphi''(1)/1$ and $\varphi'''(1)$. The contributions proportional to $\varphi''/1$ would satisfy Eq.(2.6a). Here φ^{m} would "induce" fourth-order terms proportional to $\varphi^{m}/1$ whereas the genuine fourth-order terms would be proportional to $\varphi^{m}(1)$. As a rule, the induced terms are small as compared to the genuine contributions, e.g. $|\varphi''(1)/1| \ll |\varphi^{m}(1)|$. Both terms together give the anharmonicity which can be treated as a perturbation except for special cases, e.g. He crystals, which we are not going to discuss.

The dynamical structure of the harmonic theory is rather easy to resolve. In the most general case, which is considered here, it is convenient to introduce other displacements

$$\vec{v}^{m} = \left\{\frac{M^{m}}{M}\right\}^{1/2} \vec{u}^{m}$$
 with the average mass $M = \frac{1}{N} \sum_{m} M^{m}$ (2.7)

where now

$$M \ddot{v}_{i}^{m} = -\sum_{n,k} \frac{M \phi_{ik}^{mn}}{(M^{m} M^{n})^{1/2}} v_{k}^{n} = -\sum_{n,k} D_{ik}^{mn} v_{k}^{n}$$
(2.7a)

If all masses were equal, such as in an elemental crystal, then $\vec{v} = \vec{u}$ and $D = \phi$. To simplify notation we replace the two indices m, i by one index I running from 1 to 3N. The simplest solution of the equation of motion

$$M\ddot{v}_{I} = -\sum_{K} D_{IK} \dot{v}_{K}, \quad D_{IK} = D_{KI}$$
(2.8)

are eigenoscillations where all displacements oscillate with the same frequency

$$v_{I} = w_{I} e^{-i\omega t}$$
, and² therefore $M\omega^{2}w_{I} = \sum_{K} D_{IK}w_{K}$ (2.8a)

There are 3N independent solutions w_I^A (A = 1 ... 3N) of the symmetrical eigenvalue problem (2.8a) with 3N eigenvalues $M\omega_A^2 = \lambda_A$. The "eigenvectors" w_I^A can be chosen real and such that



the eigenvectors are mutually perpendicular unit vectors in 3N-dimensional space the eigenvectors are independent and form a complete basis

² It is convenient to use a complex representation. We could as well use sin ωt or $\cos \omega t$ instead of exp(- $i\omega t$).

Then, v_I can be expressed in terms of the eigenvectors and the corresponding real amplitudes v^A , the so-called normal co-ordinates:

$$v_{I}(t) = \sum_{A} v^{A}(t) w_{I}^{A}, \quad v^{A}(t) = \sum_{I} v_{I}(t) w_{I}^{A}$$
 (2.9a)

The kinetic energy E_{kin} and the potential energy of the harmonic approximation ϕ_h are separated in the normal co-ordinates:

$$E_{kin} = \sum_{m,i} \frac{M^{m}}{2} (\dot{u}_{i}^{m})^{2} = \sum_{I} \frac{M}{2} \dot{v}_{I}^{2} = \sum_{A} \frac{M}{2} (\dot{v}^{A})^{2}$$
(2.10)
$$\phi_{h} = \frac{1}{2} \sum_{\substack{m,i \\ n,k}} \phi_{ik}^{mn} u_{i}^{m} u_{k}^{n} = \frac{M}{2} \sum_{IK} D_{IK} v_{I} v_{K} = \sum_{A} \frac{M}{2} \omega_{A}^{2} (v^{A})^{2}$$

The equation of motion becomes

$$M \ddot{v}^{A} = -M \omega_{A}^{2} v^{A} \qquad (2.10a)$$

and the Hamiltonian is given by

H =
$$\sum_{A} \left\{ \frac{(\pi A)^2}{2M} + \frac{M\omega_A^2}{2} (v^A)^2 \right\}$$
 (2.10b)

where π^A = M \dot{v}_A is the canonical momentum conjugate to the normal co-ordinate $v_A.$

The mechanics of the system is completely solved once the eigenvectors w_{1}^{A} and the frequencies ω_{A} are known. For example, if $v_{I}(0)$

and
$$\dot{v}_{I}$$
 (0) are given for t = 0 we obtain first $v^{A}(0) = \sum_{I} v_{I}(0) w_{I}^{A}$

and
$$\dot{\mathbf{v}}^{A}(0) = \sum_{I} \dot{\mathbf{v}}_{I}(0) \mathbf{w}_{I}^{A}$$
. Then from (2.10a) we have $\mathbf{v}^{A}(t) = \mathbf{v}^{A}(0) \cos \omega_{A} t$
+ $\dot{\mathbf{v}}^{A}(0) (\sin \omega_{A} t) / \omega_{A}$ and $\mathbf{v}_{I}(t) = \sum_{A} \mathbf{v}^{A}(t) \mathbf{w}_{I}^{A}$.

Stability of the molecule means now that all eigenvalues $M\omega_A^2$ must be positive³, except for 6 eigenvalues corresponding to possible translational and rotational motions in the most general case. Usually, for giant molecules such as small crystals translations and rotations are excluded, for example, by regarding three atoms on the surface as fixed. The

³ This is not the case in crystals such as He where the harmonic theory would lead to partly negative eigenvalues.

distribution of frequencies $\omega_A > 0$ is, in such cases, very dense and the spectrum⁴ $Z(\omega)$ of frequencies

$$Z(\omega) = \sum_{A} \delta(\omega - \omega_{A}) \text{ with } \int_{\omega \ge 0} Z(\omega) d\omega = 3N - 6 \cong 3N$$
 (2.11)

can be replaced by a smooth function of ω . The quantum theory of such a harmonic molecule is, of course, quite easy. Each term in Eq.(2.10b) corresponds to one linear harmonic oscillator wher π^A and v^A become conjugate operators, $[\pi^A, v^{A'}] = -i\hbar \delta_{AA'}$ are the commutation relations, and the quantum mechanical state $\psi_{n_0} \dots n_{A \dots}$ is given by the quantum numbers, $n_A = 0$, 1,2,3... of the various oscillators. Its energy E is

E...
$$n_A$$
... = $\sum_A \hbar \omega_A (n_A + 1/2)$.

3. SYMMETRY OPERATIONS

In many cases, we can find symmetry operations Ω , including improper rotations, which leave the equilibrium structure invariant. This means that with $\Omega \vec{R}^m = \vec{R}^{(m)} = \vec{R}^{\Omega(m)}$ the transformed vector $\vec{R}^{\Omega(m)}$ is an equivalent equilibrium position for all m. By this transformation the equilibrium structure is maintained. The simplest example is a diatomic molecule (Fig. 3) where the inversion, $\Omega = I = -1$, or the reflection at the y-z plane or 180° rotations about the y and z axis and all rotations about the x axis would be symmetry operations of this kind if we consider equal atoms. For unlike atoms only rotations about the x axis and reflections on planes through the x axis would be symmetry operations.



FIG.3. Diatomic molecule, equilibrium distance a, inversion symmetry about the origin.

Since ϕ (..., $\Omega \vec{r}^{m}$...) = ϕ (..., \vec{r}^{m} ...) for arbitrary rotations we have

$$\phi(\ldots,\vec{R}^{m}+\vec{u}^{m}\ldots)=\phi(\ldots,\vec{R}^{\Omega(m)}+\Omega\vec{u}^{m}\ldots) \qquad (3.1)$$

Expansion on the left-hand side up to second-order terms is the usual harmonic approximation. Expansion on the right-hand side is an expan-

⁴ By definition $\int_{\omega_1}^{\omega_2} Z(\omega) d\omega$ is the number of states with frequencies lying between ω_1 and $\omega_2 > \omega_1$.

sion about equivalent equilibrium positions $\mathbb{R}^{\Omega(m)}$ with rotated displacements $\Omega \vec{u}^{m}$. Both expansions must agree

$$\frac{1}{2} \sum_{\substack{m,n\\i,k}} \phi_{ik}^{mn} u_i^m u_k^n = \frac{1}{2} \sum_{\substack{m,n\\i',k}} \phi_{i'}^{\Omega(m)\Omega(n)} \Omega_{i'i} \Omega_{k'k} u_i^m u_k^n$$
(3.2)

for arbitrary displacement \vec{u} ; therefore

$$\phi_{ik}^{mn} = \sum_{i'k'} \phi_{i'}^{\Omega(m)} \phi_{k'}^{\Omega(n)} \Omega_{i'i} \Omega_{k'k}$$
(3.2a)

or, in matrix form

٩

 $\phi^{mn} = \Omega' \phi^{\Omega(m)\Omega(n)} \Omega, \quad \phi^{\Omega(m)\Omega(n)} = \Omega \phi^{mn} \Omega'$

where Ω' is the transposed matrix, $(\Omega')_{ik} = \Omega_{ki}$ and $\Omega'\Omega = 1$ for rotations. Equation (3.2a) can be used in two different ways. First, we consider operations where $\Omega(m) = m$, e.g. rotations about the x axis in Fig.3. Then Eq.(3.2a) relates only elements of one c.p. matrix which are now restricted for reasons of symmetry. Having found the admitted form of ϕ^{mn} we can then switch to other operations where $\Omega(m) \neq m$ and calculate $\phi^{\Omega(m)\Omega(n)}$ from equivalent ϕ^{mn} . In the simple example of Fig.3 we obtain in this way

-> m

$$(m = -1, +1, R^{m} = m (\frac{a}{2}, 0, 0))$$
from rotations
about the x axis⁵:

$$\phi^{mn} = \begin{pmatrix} \phi_{11}^{mn} & 0 & 0 \\ 0 & \phi_{22}^{mn} & \phi_{23}^{mn} \\ 0 & -\phi_{23}^{mn} & \phi_{22}^{mn} \end{pmatrix}$$
(3.3)
from reflection at
the x-y plane:

$$\phi^{-1-1} = \phi^{1-1}, \phi^{-1-1} = \phi^{1-1}$$
(3.3b)
from general translational
invariance:

$$\phi^{-1-1} + \phi^{-1-1} = 0$$
(3.3c)

$$(Eq. 2.5)$$
(3.3c)

 $\Omega = 1 + \omega, \ \omega = \left\{ \begin{array}{c} 0 & 0 \\ 0 & -0 \\ 0 - \theta \end{array} \right\} \text{ from Eq. (3.2a): } \omega \phi^{\text{mn}} = \phi^{\text{mn}} \omega$

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from general rotational invariance: $\phi_{22}^{1-1} = \phi_{22}^{1-1} \xrightarrow{(3.3c)} \phi_{22}^{mn} = 0$ (3.3d) (Eq.2.6)

Only one term $\phi_{1\,1}^{1\,1} = -f = \phi_{1\,1}^{-1-1} = -\phi_{1\,1}^{-1\,1} = -\phi_{1\,1}^{1-1}$ is left and the equation of motion

$$M \ddot{u}_{x}^{-1} = -f(u_{x}^{-1} - u_{x}^{1}), \qquad M \ddot{u}_{x}^{1} = -f(u_{x}^{1} - u_{x}^{-1})$$
$$M \ddot{u}_{y}^{-1} \quad \text{or } + 1 = 0$$

corresponds just to a simple harmonic spring with spring constant f.



FIG.4. Determination of ϕ_{in}^{-11} .

The conditions (3.3, 3.3a) can be demonstrated quite transparently in a more pedestrian way. Consider the situation of Fig.4 where atom 1 is displaced in z direction and the force $-\phi^{-1\,1}\,\vec{u}^{\dagger}$ is indicated. If we rotate the system through 180° about the x axis displacement and force are as shown in Fig.4. But, since then $\vec{u}^{\dagger} \rightarrow -\vec{u}^{\dagger}$ the force should have changed its sign. This is only consistent if the force has no x component, $\phi_{xz}^{-1\,1} = 0$. Using the same argument for the reflection at the x-y plane it follows that $\phi_{yz}^{-1\,1} = 0$. Therefore, only the $\phi_{zz}^{-1\,1}$ component of $\phi_{zz}^{-1\,1}$ remains. The same can be shown for $\phi_{yy}^{-1\,1}$. By rotating through 90° we can show that $\phi_{zz}^{-1\,1} = \phi_{yy}^{-1\,1}$.

Of course, if we start with a potential which is invariant under translations and rotations the symmetries of the c. p. 's must be obtained naturally. For the simple diatomic molecule we must have $\phi(\vec{r}^{i}, \vec{r}^{-1}) = \phi(|\vec{r}^{1} - \vec{r}^{-1}|)$. Starting with the configuration of Fig. 3 the expansion of ϕ becomes (equilibrium condition: $\phi'(a) = 0$)

$$\phi = \phi(a) + \frac{1}{2} \phi''(a) (u_x^1 - u_x^{-1})^2 + \dots$$

and with $\phi''(a) = f$, the harmonic potential is $\phi_h = \frac{1}{2} f(u_x^1 - u_x^{-1})^2$ which leads immediately to the above equation of motion. Another simple case is

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that of central, two-body potentials where ϕ is a sum over invariant two-body potentials:

$$= \frac{1}{2} \sum_{m,n} \phi^{mn} (|\mathbf{r}^m - \mathbf{r}^n|) \text{ with } \phi^{mm} = 0, \ \phi^{mn} = \phi^{nm}$$

where all the invariance relations can be checked.

The invariances (3, 2) have still another meaning. The equation of motion

$$\mathbf{M}^{\mathbf{m}} \mathbf{\dot{\vec{u}}}^{\mathbf{m}} = -\sum_{\mathbf{n}} \phi^{\mathbf{m}\mathbf{n}} \mathbf{\vec{u}}^{\mathbf{n}}$$

can as well be written as

$$\mathbf{M}^{\Omega}(\mathbf{m}) \, \mathbf{\ddot{u}}^{\Omega}(\mathbf{m}) = -\sum_{\mathbf{n}} \boldsymbol{\phi}^{\Omega}(\mathbf{m}) \, \Omega(\mathbf{n}) \, \mathbf{\vec{u}}^{\Omega}(\mathbf{n})$$

because this is just another notation for the same equation; further $M^{\Omega(m)} = M^m$ since $\Omega(m)$ and m are equivalent positions. Applying Eq.(3.2a) we get

$$\mathbf{M}^{\mathbf{m}} \Omega \mathbf{i} \mathbf{\vec{u}}^{\Omega(\mathbf{m})} = -\sum_{\mathbf{n}} \phi^{\mathbf{m}\mathbf{n}} \Omega \mathbf{i} \mathbf{\vec{u}}^{\Omega(\mathbf{n})}$$

or, in other words, if \vec{u}^m is a solution to the equation of motion so is

$$\Omega^{\dagger}\vec{u}^{\Omega(m)} = \Omega\{\vec{u}^{m}\} \text{ or } \Omega\vec{u}^{\Omega^{-1}(m)} = \Omega^{-1}\{\vec{u}^{m}\}$$

(with Ω also $\Omega' = \Omega^{-1}$ is a symmetry operation). This means simply that from one dynamically possible displacement pattern another admitted pattern is obtained by applying a symmetry operation (Fig. 5). Naturally, this is true in general, not only in the harmonic theory. For the same

reason, if
$$\vec{u}^m$$
 is an eigenvector of ϕ^{mn} , i.e. $\sum_{n} \phi^{mn} \vec{u}^n = \lambda \vec{u}^m$, then

 $\Omega^{\dagger}\vec{u}^{\Omega(m)}$ or $\Omega\vec{u}^{\Omega'(m)}$ are also eigenvectors with the same eigenvalue λ , so are linear combinations. The operation Ω is linear in the 3N-dimensional displacement space and the above considerations imply that the matrix D_{IK} or ϕ_{IK} commutes with Ω_{IK} . Therefore, we may require that the eigenvectors of ϕ be also eigenvectors of Ω . Sometimes, this makes it easier to find the eigenvectors and from them the eigenvalues by symmetry considerations. In the simple diatomic molecule with the inversion $\Omega = I = -1$ as symmetry operation I { \vec{u}^{m} } = $-\vec{u}^{-m}$, one obtains from one eigenstate \vec{u}^{m} another $-\vec{u}^{\cdot m}$ and by combination $\vec{u}^{m} \pm \vec{u}^{-m}$ which are eigenstates of I:I { $\vec{u}^{m} \mp \vec{u}^{-m}$ }. In this way, the eigenstates of the diatomic



FIG.6. Eigenstates of ${m n \atop i k}$ for the diatomic molecule; spring constant f; a) proper oscillation, $M_{\omega}^2 = 2f$; b, c) small rotations $M_{\omega}^2 = 0$, symmetrical against inversion; d, e, f) small translations $M_{\omega}^2 = 0$, antisymmetrical against inversion; eigenstates according to Eq. (2.9).

	а	b	с	d	e	f
$u_{\mathbf{X}}^{1}$	1	0	0	1 ·	0	0
u	0	1	0	0	1	0
√2 .u _Z ⁻¹	0	0	1	0	0	1
u _x ⁻¹ .	-1	0	0	1	0	0
uyi	0	-1	0	0	1	0
u _z -1	0	0	-1	0	Q	1

molecule can be easily determined. They are shown in Fig.6. They are chosen such that the eigenstates are also eigenstates of all the symmetry operations of the molecule mentioned above which all commute.

4. SYMMETRY OPERATIONS AND WAVES IN INFINITE LATTICES

The simplest lattices are Bravais lattices which contain only equal atoms. They are described by three non-coplanar basic vectors $\vec{a}^{(i)}$ which define the atomic equilibrium positions

$$\vec{R}^{m_1m_2m_3} = \vec{R}^{\vec{m}} = \sum_k \vec{a}^{(k)} m_k = A \vec{m}$$

$$X_i^m = \sum_k a_i^{(k)} m_k = \sum_k A_{ik} m_k$$
(4.1)

The atomic positions are now labelled by a vector \vec{m} rather than a simple index m. Simple examples for Bravais lattices of cubic symmetry are

simple cubic lattice (sc): A = a
$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
, V_c = a³ (Fig. 7a)
body-centred cubic lattice (bcc): A = $\frac{a}{2} \begin{pmatrix} 1 & 1-1 \\ -1 & 1 & 1 \\ 1-1 & 1 \end{pmatrix}$, V_c = $\frac{a^3}{2}$ (Fig. 7b)

face-centred cubic lattice (fcc):
$$A = \frac{a}{2} \begin{pmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix}$$
, $V_c = \frac{a^3}{4}$ (Fig. 7c)

Here a is the length of the elementary cube edge and V_c is the volume of the elementary cell (the volume per atom) which is given by the three basic vectors. The harmonic and anharmonic expansions can be expressed as in Eq.(2.3) where the sum over $m \rightarrow \vec{m}$, $n \rightarrow \vec{n}$ is now an infinite sum. The symmetry relation (2.3a) holds by virtue of the expansion because only the symmetrical part of $\phi_{1k}^{\vec{mn}}$ enters into the summation. The c.p.'s can no longer be determined by derivatives of ϕ because ϕ itself becomes infinite but, for example, the harmonic part remains finite if the displacements $\vec{u}^{\vec{m}}$ are restricted to finite \vec{m} . The invariance relations (2.5, 2.6) remain unchanged, and the symmetry arguments of section 3 can be applied as well.







FIG.7. Cubic Lattices: a is the cubic-lattice distance, the $a^{(5)}$ are the basic vectors; a) simple cubic lattice; b) body-centred cubic lattice; c) face-centred cubic lattice.

For an infinite lattice we have an additive and most important symmetry operation by which the lattice is transferred into itself. This is the lattice translation \vec{t} where the translation is given by any integer multiple of basic vectors $\vec{t}(\vec{h}) = A\vec{h}$. Obviously, the lattice is restored by these lattice translations and in analogy to the discussion leading to Eq. (3.2a) we obtain $\vec{t}(\vec{h}) \{\vec{u}\cdot\vec{m}\} = \vec{u}\cdot\vec{m}+\vec{h}, \vec{t}(\vec{h})(\vec{m}) = (\vec{m}+\vec{h})$

$$\phi_{i}^{\vec{m}+\vec{h}\vec{n}+\vec{h}} = \phi_{ik}^{\vec{m}\vec{n}}, \text{ for any integer } \vec{h}$$
(4.2)

and analogously for c.p.'s of other orders. If we go back to the definition of the c.p.'s as a force displacement pattern such as in Fig. 4 Eq.(4.2) is almost trivial because this pattern can be shifted by one or more basic

vectors without change. This symmetry shows further that if $\vec{u}^{\,\vec{n}}$ is eigenvector of $\phi^{\,\vec{n}\vec{n}}_{\,ik}$, so is

$$\vec{t}(\vec{h}) \{\vec{u}\vec{n}\} = \vec{u}\vec{n} + \vec{h}$$
(4.2a)

with the same eigenvalue, which means that by shifting a displacement pattern its property of being an eigenvector of ϕ_h remains unchanged.

For c.p.'s of first order, $\phi_1^{\overrightarrow{m}}$, lattice translational symmetry requires

$$\phi_{i}^{\vec{m}+\vec{h}} = \phi_{i}^{\vec{m}}$$
, independent of \vec{m} (4.3)

Another important symmetry of Bravais lattices is the inversion with its centre in an arbitrary lattice point \vec{Ap} . This means for inversion about the origin that

$$\phi^{-\overrightarrow{m}}_{i k} \stackrel{\overrightarrow{n}}{=} \phi^{\overrightarrow{mn}}_{i k}, \qquad -\phi^{-\overrightarrow{m}}_{i} = \phi^{\overrightarrow{m}}_{i}, \text{ etc.} \qquad (4.4)$$

Equations (4.4) and (4.3) imply that the first-order c.p.'s vanish $(\vec{h} = -2\vec{m} \text{ in Eq.}(4.3))$. Consequently, the equilibrium parameters of the lattice cannot be determined by requiring the first-order expansion term to vanish. The equilibrium can be determined by minimizing the potential energy per atom, e.g. for central potentials the energy ϵ_{at} per atom is given by

$$\epsilon_{at} = \frac{1}{2} \sum_{\vec{n} \ (\neq \vec{m})} \varphi(|A(\vec{m} - \vec{n})|) = \frac{1}{2} \sum_{\vec{h} \ (\neq 0)} \varphi(|A\vec{h}|)$$

and by minimizing ϵ_{at} the parameters A are given except for rotations. Since the symmetry relations will certainly also hold in the interior of a finite crystal, for short-range forces this means that the equilibrium conditions of a finite crystal are "surface" conditions. For the secondorder c. p. 's relations (4.4) and (4.2) combined require that

$$\phi_{ik}^{\vec{m}\vec{n}} = \phi_{ik}^{(\vec{m}-\vec{n})} = \phi_{ik}^{(\vec{n}-\vec{m})}$$
(4.5)

According to Eq.(2.3a) $\phi^{\vec{m}\vec{n}}$ must be a symmetrical matrix.

Equation (4.2a) allows us to find immediately harmonic solutions of the equation of motion by employing displacements which are eigenvectors of $\vec{t}(\vec{h})$, namely ⁶

$$\vec{u}^{\vec{n}}(t) = \vec{e} e^{i(\vec{q}\cdot\vec{An}-\omega t)} , \vec{t}(\vec{h})\{\vec{u}^{\vec{n}}\} = \vec{u}^{\vec{n}+\vec{h}} = e^{i\vec{q}\cdot\vec{Ah}} \vec{u}^{\vec{n}}$$
(4.6)

⁶The three translations $\vec{t}^{(1)}$ with $\vec{h} = (1, 0, 0)$, $\vec{t}^{(2)}$ with $\vec{h} = (0, 1, 0)$ and $\vec{t}^{(3)}$ with $\vec{h} = (0, 0, 1)$ are translations by the three basic vectors $\vec{a}^{(1)}$. If $\vec{u} \cdot \vec{m}$ is an eigenvector of the three commuting translations, $\vec{t}^{(1)}\vec{u} \cdot \vec{m} = \vec{u} \cdot \vec{m}^{+1}(1, 0, 0) = \lambda \vec{u} \cdot \vec{m}$ and analogously for $t^{(2)}$, $t^{(3)}$ we have $\vec{u} \cdot \vec{m} = \lambda_1^{m_1} \lambda_2^{m_2} \lambda_3^{m_3} \vec{u}^0$. Physically reasonable solutions are such that the amplitudes remain finite for all m; therefore the λ_1 must have an absolute value of 1 and $\vec{u} \cdot \vec{m} \sim \vec{u}^0 \exp(i\sum_k \varphi_k m_k) \sim \vec{e} \cdot e^{i\vec{q} \cdot \vec{A} \cdot \vec{m}}$ with $\varphi_k = \sum_i q_i A_{ik}$ and $\vec{u}^0 \sim \vec{e}$.

with an eigenvalue $\exp(i\vec{q}\cdot\vec{Ah})$ and with a yet unspecified "polarization" vector \vec{e} . We can easily see that expression (4.6) is a solution of the equation of motion if \vec{e} and ω are determined from

$$M \omega^{2} \vec{e} = \vec{\phi}^{\vec{q}} \vec{e}$$
$$\det |\vec{\phi}^{\vec{q}} - M \omega^{2}| = 0$$
$$M \omega^{2} = \lambda (\vec{q}, \sigma), \quad \sigma = 1, 2, 3$$
$$\vec{e} \rightarrow \vec{e} (\vec{q}, \sigma) \qquad (4.7)$$

where $\widetilde{\phi}^{\vec{q}}$ is the three-dimensional matrix

$$\widetilde{\phi}^{\vec{q}} = \sum_{\vec{h}} \phi^{\vec{(h)}} \cdot e^{-i\vec{q}\cdot\vec{A}\vec{h}} = \sum_{\vec{h}} \phi^{\vec{(h)}} \cos\vec{q}\cdot\vec{A}\vec{h}$$

$$= \sum_{\vec{h}} \phi^{\vec{(h)}} \{\cos(\vec{q}\cdot\vec{A}\vec{h}) - 1\} = -2 \sum_{\vec{h}} \phi^{\vec{(h)}} \sin^2\left(\frac{\vec{q}\cdot\vec{A}\vec{h}}{2}\right)$$

$$\left(\sum_{\vec{h}} \phi^{\vec{m}\vec{n}} = \sum_{\vec{h}} \phi^{\vec{(h)}} = 0 \text{ according to Eq.}(2.5)\right).$$
The solutions (4.6)

$$\vec{u}^{\vec{n}} = \vec{e}(\vec{q}, \sigma) \exp[i(\vec{q} \cdot \vec{R}^{n} - \omega(\vec{q}, \sigma) t)]$$
(4.8)

are travelling lattice waves with three possible, mutually perpendicular, polarization vectors $\vec{e}(\vec{q},\sigma)$ for given \vec{q} which are the eigenvectors of $\vec{\phi}\vec{q}$. The wave vector is \vec{q} , the "wavelength" $2\pi/q$. From Eq.(4.7a) we see that $\vec{\phi}\vec{q} = \vec{\phi}^{-\vec{q}}$. Consequently, waves with $\pm \vec{q}$ are degenerate and standing waves such as $\vec{u}^{\vec{n}} = \vec{e}(\vec{q},\sigma) \cos \vec{q} \cdot \vec{R}^{\vec{n}} \cos \omega(\vec{q},\sigma)$ t also are eigenvibrations.

Therefore, the lattice translational symmetry enormously simplifies the calculation of harmonic motions in an infinite lattice. For Bravais lattices, only an equation of third order has to be solved. For particular symmetric directions of \vec{q} the polarizations can be obtained directly, e.g. for \vec{q} pointing into the (1, 0, 0), (1, 1, 1), and $(1, \phi, 0)$ directions of the abovementioned cubic lattices. Let us discuss the (1, 0, 0) direction in detail. Symmetry operations⁷ Ω which leave \vec{q} invariant are 90° degree rotations about the x axis and reflections on the x-y and x-z planes. We know from section 3 that with $\vec{u}^{\vec{n}}$ also $\Omega'\{\vec{u}^{\vec{n}}\} = \Omega \vec{u}^{\Omega'(\vec{m})}$ is a solution. Since obviously $\vec{q} \cdot \vec{R}^{\vec{n}} \Rightarrow \vec{q} \cdot \vec{R} \ \Omega'(\vec{m}) = \vec{q} \cdot \Omega' \ \vec{R}^{\vec{n}} = \vec{R}^{\vec{n}} \Omega \cdot \vec{q} = \vec{q} \cdot \vec{R}^{\vec{n}}$, the phase of expression (4.8) is invariant and with \vec{e} also $\Omega \vec{e}$ is a polarization vector belonging to the same eigenvalue of $\vec{\phi} \ \vec{q}$. If \vec{e} has a component parallel to \vec{q} and if Ω represents

⁷ There are 48 symmetry operations: $\Omega(X, Y, Z) = (\pm X_i, \pm X_k, \pm X_l)$, $i \neq k \neq 1$, co-ordinate axes parallel to cube edges, origin in one of the cube corners, cube centres or face centres.

a 180° rotation, with \vec{e} also $\Omega \vec{e}$ and $\vec{e} + \Omega \vec{e} \sim \vec{q}$ are eigenvectors (Fig. 8b). Therefore, one eigenvector can be chosen longitudinal, i.e. parallel to $\vec{q}, \vec{e} \rightarrow \vec{e}_1$, $M \omega_1^2 = (\vec{e}_1, \tilde{\phi} \vec{q} \vec{e}_1)$ if \vec{e}_1 is normalized. The remaining two eigenvectors must be orthogonal to \vec{e}_1 and in the y-z plane, i.e., transverse. Figure 8c shows an assumed \vec{e}_1 and an equivalent polarization rotated through 90°. They form a complete basis for vectors normal to \vec{q} . Therefore, any $\vec{q} \perp \vec{q}$ is an eigenvector to the same eigenvalue $M \omega_1^2$ and the problem is two-fold degenerate. The reasoning for \vec{q} in the (1,1,0) and (1,1,1) direction is analogous; the results are summarized in Table I. With symmetry operations which do not leave \vec{q} invariant we can then produce equivalent lattice waves with $\Omega \vec{q}$. For the inversion, in particular, we find $\vec{e}(-\vec{q}, \sigma) \sim \vec{e}(\vec{q}, \sigma)$.



FIG.8. Polarizations for $\vec{q} = q(100)$; a) so lattice with $\vec{q} = q(100)$; b) rotation Ω by 180° about x axis: with \vec{e} , $\Omega \vec{e}$ and $\Omega \vec{e} + \vec{e} \sim \vec{q}$ as polarization vectors; c) rotation Ω by 90° about x axis: all polarizations $\vec{e}_{1} \perp \vec{q}$ are equivalent.

\overrightarrow{q}	$\vec{e}(\vec{q},\sigma)$	Mw? sc	Mw ² , bcc	$M\omega^2$, fcc
q(100)	d ⊤d	$4f_1 \sin^2 \frac{q_2}{2}$ $4f_2 \sin^2 \frac{q_2}{2}$	$16\frac{f_{1}+2f_{2}}{3}\sin^{2}\frac{q_{a}}{4}$	$8(f_1 + f_2) \sin^2 \frac{q_a}{4}$ $4(f_1 + f_2 + 2f_3) \sin^2 \frac{q_a}{4}$
<u>q</u> √3(111)	и q тq	$4(f_1 + 2f_2) \sin^2 \frac{q_a}{2\sqrt{3}}$	$4f_{1}\sin^{2}\frac{\sqrt{3}qa}{4} + 4\frac{f_{1} + 8f_{2}}{3}\sin^{2}\frac{qa}{4\sqrt{3}}$ $4f_{2}\sin^{2}\frac{\sqrt{3}qa}{4} + 4\frac{4f_{1} + 5f_{2}}{3}\sin^{2}\frac{qa}{4\sqrt{3}}$	$(8f_{1} + 4f_{3}) \sin^{2} \frac{qa}{2\sqrt{3}}$ $(2f_{1} + 6f_{2} + 4f_{3}) \sin^{2} \frac{qa}{2\sqrt{3}}$
$\frac{q}{\sqrt{2}}(110)$	" q (1 - 10) (001)	$4(f_1 + f_2)\sin^2\frac{qa}{2\sqrt{2}}$ $8f_2\sin^2\frac{qa}{2\sqrt{2}}$	$8 \frac{2f_1 + f_2}{3} \sin^2 \frac{qa}{2\sqrt{2}}$ $8 f_2 \sin^2 \frac{qa}{2\sqrt{2}}$ $8 \frac{f_1 + 2f_2}{3} \sin^2 \frac{qa}{2\sqrt{2}}$	$4f_{1} \sin^{2} \frac{qa}{2\sqrt{2}} + 4(f_{1} + f_{2} + 2f_{3}) \sin^{2} \frac{qa}{4\sqrt{2}}$ $4f_{2} \sin^{2} \frac{qa}{2\sqrt{2}} + 4(f_{1} + f_{2} + 2f_{3}) \sin^{2} \frac{qa}{4\sqrt{2}}$ $4f_{3} \sin^{2} \frac{qa}{2\sqrt{2}} + 8(f_{1} + f_{2}) \sin^{2} \frac{qa}{4\sqrt{2}}$

TABLE I. VALUES OF $M\omega^2$ FOR DIFFERENT LATTICE TYPES AND DIRECTIONS

The symmetry operations (3.2) restrict the number of independent c.p.'s in the symmetrical matrices $\phi_{ik}^{(\vec{h})}$. In general, $\phi_{ik}^{(\vec{h})}$ can be represented by its three mutually perpendicular and normalized eigenvectors $\vec{P}^{(s)}$ and corresponding eigenvalues π_s :

$$\phi^{(\vec{h})} \overrightarrow{P}^{(s)} = \pi_{s} \overrightarrow{P}^{(s)}, \quad \phi^{(\vec{h})}_{ik} = \sum_{s=1}^{3} \pi_{s} P_{i}^{(s)} P_{k}^{(s)}$$

$$\sum_{i} P_{i}^{(s)} P_{i}^{(s')} = \delta_{ss}, \quad \sum_{s} P_{i}^{(s)} P_{k}^{(s)} = \delta_{ik}$$

$$(4.9)$$

with

By the relations (3.2) the eigenvectors and ratios of the eigenvalues can be partly determined. To see this, we shall discuss this question again for $\vec{h} = (1, 0, 0)$ in the s.c. lattice. The possible symmetry operations which leave \vec{h} invariant have been given above when discussing $\vec{e}(\vec{q} || (1, 0, 0))$.



FIG.9. Force displacement pattern for $\phi_{iz}^{(100)}$ a) arbitrary force; b) force compatible with lattice symmetry.

The result is

$$\phi \stackrel{(1,0,0)}{ik} = \begin{pmatrix} \pi_1 & 0 & 0 \\ 0 & \pi_2 & 0 \\ 0 & 0 & \pi_2 \end{pmatrix} = (\pi_1 - \pi_2) \underbrace{\hat{X}_1^{\vec{h}} \hat{X}_k^{\vec{h}}}_{h_1 h_k} + \pi_2 \delta_{ik} \text{ for } h = (1,0,0) \quad (4.10)$$

where $\hat{\mathbf{R}}^{\vec{\mathbf{n}}} = \mathbf{\vec{R}}^{\vec{\mathbf{n}}} / |\mathbf{\vec{R}}^{\vec{\mathbf{n}}}|$ ($= \mathbf{\vec{n}}$) is the unit vector in the $\mathbf{\vec{R}}^{\vec{\mathbf{n}}}$ direction. It shows that $\mathbf{\vec{R}}^{\vec{\mathbf{n}}}$ is an eigenvector with an eigenvalue π_1 , and all vectors normal to $\mathbf{\vec{R}}^{\vec{\mathbf{n}}}$ are eigenvectors with an eigenvalue π_2 exactly as in $\vec{\mathbf{e}}(\vec{\mathbf{q}})$, and for the same reasons. Also this fact is obvious from a force displacement pattern (Fig. 9a) where only $\vec{\mathbf{u}}^{(\mathbf{n})} \neq 0$. If $\vec{\mathbf{u}}^{(\mathbf{n})}$ points in the z direction and a rotation through 180° about the x axis is carried out, which is an allowed operation, the rotated force must equal to the negative of the original force. Consequently, $\phi_{\mathbf{v}_2}^{\mathbf{v}_2} = 0$. By reflection at the xy plane it is shown

that also $\phi(\vec{n}) = 0$. Therefore, $\phi(\vec{n})$ has only a $\phi(\vec{n})$ component, π_3 . Analogously we can show that $\phi(\vec{n})$ and $\phi(\vec{n})$ also have only diagonal components π_2 and π_1 . By rotating the pattern in Fig. 8b through 90° it is shown that $\pi_2 = \pi_3$. By applying a rotation through 90° about the y axis we can relate $\phi(^{0,0,1})$ to $\phi(^{1,0,0})$ etc., e.g.

$$\phi^{(0,0,1)} = \begin{pmatrix} \pi_2 & 0 & 0 \\ 0 & \pi_2 & 0 \\ 0 & 0 & \pi_1 \end{pmatrix}$$

Representation (4.10) is valid for all equivalent sites, $|\vec{h}| = 1$. Only two independent c.p.'s remain. The parameter π_1 , represents a normal harmonic spring parallel to x with a spring constant - π_1 , the parameter π_2 represents a leaf spring which is isotropic about the (1,0,0) axis. For central forces $\pi_2 = 0$. Therefore, π_2 gives an indication for many-body forces. For the third nearest neighbours, $\vec{h} = (1,1,1)$ $\vec{R}\vec{h} = (1,1,1)/\sqrt{3}$, the physical situation is the same. Equation (4.10) holds also for $\vec{h} = (1,1,1)$, naturally with other values of $\pi_{1,2}$ and the matrix has the form

$$\phi_{ik}^{(1,1,1)} = \frac{1}{3} \begin{pmatrix} \pi_1 + 2\pi_2 & \pi_1 - \pi_2 & \pi_1 - \pi_2 \\ \pi_1 - \pi_2 & \pi_1 + 2\pi_2 & \pi_1 - \pi_2 \\ \pi_1 - \pi_2 & \pi_1 - \pi_2 & \pi_1 + 2\pi_2 \end{pmatrix}$$

$$= (\pi_1 - \pi_2) \frac{h_i h_k}{3} + \pi_2 \delta_{ik}, \text{ for } \vec{h} = (1 \ 1 \ 1)$$

$$(4.11)$$

For $\vec{h} = (1, 1, 0)$ we obtain the eigenvectors $\vec{P}^{(1)} = \vec{h}/\sqrt{2}$, $\vec{P}^{(3)} = (0, 0, 1)$ and $P^{(2)} = (1, -1, 0)/\sqrt{2}$ and, in general, three different eigenvalues. Here the leaf spring is anisotropic, its stiffness is different in the $\vec{P}^{(2)}$ and $\vec{P}^{(3)}$ directions. The eigenvectors can be given in a more general form. The first eigenvector belonging to the normal spring is proportional to \vec{h} , i.e. the simple spring connects the two atoms 0 and \vec{h} . Another eigenvector is that of the basic vectors $a^{(s)}$ which is perpendicular to h. It can be represented by

$$P_i^{(3)} = (1 - h_i^2)$$
 (4.12)

which is valid for any of the twelve equivalent vectors \vec{h} , $\vec{h} = (1, 1, 0)$, (-1, 1, 0), (0, 1, 1) etc. An invariant representation is given by

$$\vec{P}^{(3)} = \sum_{s=1}^{3} \vec{a}^{(s)} (\vec{h} \cdot \vec{a}^{(s+1)}) (\vec{h} \cdot \vec{a}^{(s+2)})$$
(4.12a)

where

$$\overrightarrow{a}(s+3) = \overrightarrow{a}(s)$$

The matrix is given by

$$\phi_{ik}^{(\vec{h})} = (\pi_1 - \pi_2) h_i h_k / 2 + (\pi_3 - \pi_2) P_i^{(3)} P_k^{(3)} + \pi_2 \delta_{ik}$$
(4.13)

for all \vec{h} equivalent to (110) and

$$\phi_{ik}^{(1\ 1\ 0)} = \begin{pmatrix} \frac{\pi_1 + \pi_2}{2} & \frac{\pi_1 - \pi_2}{2} & 0\\ \frac{\pi_1 - \pi_2}{2} & \frac{\pi_1 + \pi_2}{2} & 0\\ 0 & 0 & \pi_3 \end{pmatrix}$$
(4.13a)

for \vec{h} = (110). For \vec{h} = 0 all cubic symmetry operations can be used and we obtain

$$\phi_{ik}^{(000)} = \pi_1 \delta_{ik} \tag{4.14}$$

If \vec{q} is parallel to one of the above symmetrical directions \vec{h} the eigenvectors and the structure of the matrices $\vec{\phi}^{\vec{q}}$ and $\phi \vec{m}$ are the same. Further, the form of the c.p. matrices connecting atoms along (100), (111), and (110) directions is the same for all three cubic lattices of Fig. 7 because the corresponding symmetry operations are identical. The results are given by Fig. 10.

To illustrate the results obtained above we shall calculate the eigenvalues for nearest-neighbour interactions. The simplest case is the linear lattice (Fig. 11), X^m = ma with m= 0, ±1, ±2..., displacements u^m in the x direction. Nearest-neighbour interaction means that besides $\phi^{(0)}$ only $\phi^{(h=\pm 1)}$ = -f are different from zero. This represents a situation where neighbouring atoms are connected by harmonic springs with a spring constant f. In this case, the polarization need not be determined and we have (Fig. 11):

$$M \omega^{2}(q) = \tilde{\phi}^{q} = -2 \sum_{h} \phi^{(h)} \sin^{2} \frac{qah}{2} = 4f \sin^{2} \frac{qa}{2} \qquad (4.15)$$

$$\omega(q) = \left(\frac{4f}{M}\right)^{1/2} \sin qa/2 = \omega_{\max} \sin \frac{qa}{2} \qquad (4.15a)$$

 \mathbf{or}

The $\omega(q)$ curve is called the dispersion curve.

In the simple cubic lattice in (4.7a) for nearest-neighbour interaction only the six matrices $\phi(\vec{h})$ with $|\vec{h}| = 1$ corresponding to the six nearest



FIG.10. c.p. matrices, eigenvectors and eigenvalues for near neighbours of the sc lattice.



FIG.11. Dispersion curve of a linear crystal with nearest-neighbour interaction.

neighbours of $\vec{h} = 0$ along the cube edges enter. We give only the quantities $\tilde{\phi}_{11}^{\vec{q}}$ and $\tilde{\phi}_{12}^{\vec{q}}$, the other elements follow by cyclic permutation

$$\phi_{i+1, k+1}^{(q_s)} = \phi_{ik}^{(q_{s+1})}, s+3 \text{ equivalent to s.}$$
(4.16)

The matrices have the form (4.10), and we obtain with $\pi_s = -f_s$:

$$\widetilde{\phi}_{11}^{\vec{q}} = 4 \left\{ f_1 \sin^2 \frac{q_1 a}{2} + f_2 \left[\sin^2 \frac{q_2 a}{2} + \sin^2 \frac{q_3 a}{2} \right] \right\}$$
(4.17)
$$\widetilde{\phi}_{12}^{\vec{q}} = 0$$

This is a rather degenerate case. The eigenvectors are the three basic vectors $\mathbf{a}^{(i)}$ independent of $\vec{q} : \vec{e}(\vec{q},\sigma) = \vec{a}^{(\sigma)}$, and the eigenfrequencies are given by the diagonal elements. Naturally, the eigenvectors and their degeneracies in the three symmetrical directions which are determined by lattice symmetry must be compatible with (4.17) as can be seen in Table I.

In the body-centred cubic lattice eight nearest neighbours with $\vec{R}^{\vec{h}} = a/2 \vec{h}, \vec{h} = (111), \text{ etc.}, |\vec{h}| = 3 \text{ have to be taken into account.}$ The c.p. matrices have the form (4.11) and $\vec{\phi}^{\vec{q}}$ becomes

$$\widetilde{\phi}_{11}^{\vec{q}} = 2 \frac{f_1 + 2f_2}{3} \sum_{|h| = 3} \sin^2 \frac{\vec{q} \cdot \vec{h}}{4} a$$

$$\widetilde{\phi}_{12}^{\vec{q}} = 4 \frac{f_1 - f_2}{3} \left\{ \sin^2 \frac{a}{4} (q_1 + q_2 + q_3) + \sin^2 \frac{a}{4} (q_1 + q_2 - q_3) - \sin^2 \frac{a}{4} (q_1 - q_2 - q_3) \right\}$$

$$(4.18)$$

The eigenvalues for symmetrical directions are given in Table I.

In the face-centred cubic lattice one has twelve nearest neighbours with $\vec{R}\vec{h} = a/2\vec{h}$, $\vec{h} = (110)$, etc., |h| = 2. The matrices have the form (4.13) and from

$$\widetilde{\phi}_{11}^{\vec{q}} = 2 \left(f_1 + f_2 \right) \left\{ \sin^2 \frac{a}{4} \left(q_1 + q_2 \right) + \sin^2 \frac{a}{4} \left(q_1 + q_3 \right) + \sin^2 \frac{a}{4} \left(q_1 - q_2 \right) \right. \\ \left. + \sin^2 \frac{a}{4} \left(q_1 - q_3 \right) \right\} + 4 f_3 \left\{ \sin^2 \frac{a}{4} \left(q_2 + q_3 \right) + \sin^2 \frac{a}{4} \left(q_2 - q_3 \right) \right\}$$
(4.19)
$$\widetilde{\phi}_{12}^{\vec{q}} = 2 \left(f_1 - f_2 \right) \left\{ \sin^2 \frac{a}{4} \left(q_1 + q_2 \right) - \sin^2 \frac{a}{4} \left(q_1 - q_2 \right) \right\}$$

we obtain the results of Table I.

From Table 1 one can see immediately that a nearest-neighbour model in sc and bcc lattices would become unstable for central forces, $f_2 = 0$, because there many eigenvalues vanish, e.g. for one transverse branch each if $\vec{q} \parallel (110)$.

We can use the results of Table I to include further neighbours in correspondingly symmetric positions. As an example let us consider a fcc lattice. The nearest neighbours are in positions equivalent to a/2 (110), neighbours of second order are in a (100) positions. Both neighbours give additive contributions to $\vec{\phi}\vec{q}$ with common eigenvectors for the \vec{q} directions given in Table I. Consequently, the eigenvalues just add up. To obtain the results for a fcc lattice⁸ including second-order neighbours we have to add to the first-neighbour contribution (the fcc column in Table I) the

⁸ If we want to include second-order neighbours in the (110) directions of the sc lattice we can proceed analogously, but have to replace a in the fcc contribution by 2a because the second-order neighbours are in positions a (110) etc. instead of a/2 (110) of the fcc lattice.

second-neighbour contribution (the sc column in Table I, replacing there f_s by f_s' where the dash indicates the c.p.'s corresponding to second neighbours), e.g. the longitudinal eigenvalue for $\vec{q} \mid (100)$ would be given by $8(f_1 + f_2) \sin^2(q_2/4) + 4 f_1^* \sin^2(q_2/2)$. To give an idea of the dispersion curves, Fig. 12 shows the dispersion curves of a fcc lattice with central-spring interaction ($f_1 = f$, $f_2 = f_3 = 0$; $f_1' = f'$, $f_2' = 0$) for an elastically isotropic crystal (4 f' = f).



FIG. 12. Dispersion curves of an isotropic fcc lattice with springs f, f/4 to neighbours of first and second orders

If $qa \ll 1$ the wavelength of the lattice waves is very large compared with the distance between nearest neighbours. The lattice waves must then become identical with the elastic waves of the corresponding elastic continuum. For $qa \ll 1$ only terms quadratic in q remain and $\omega/q = c$ is the velocity of sound belonging to the lattice wave in question. Elastic isotropy means that one has always longitudinal and degenerate transverse eigenvectors with sound velocities c_1 and c_t independent of the direction of q. One can check now the isotropic behaviour of the frequencies given in Fig. 12 and sees that the values of c_1 and c_t are independent of the directions of \vec{q} in Fig. 11. Isotropy can also be checked directly from an expansion of $\tilde{\phi}\vec{q}$:

$$\widetilde{\phi}_{ik}^{\vec{q}} = -\frac{1}{2} \sum_{\vec{h},m,n} \phi(\vec{h}) X_{ik}^{\vec{h}} X_{n}^{\vec{h}} q_{m} q_{n} \qquad (4.20)$$

If this expression assumes the form

$$\widetilde{\phi}_{ik}^{\vec{q}} = M c_t^2 q^2 \delta_{ik} + M (c_1^2 - c_t^2) q_i q_k$$
(4.20a)

the crystal is elastically isotropic because the eigenvectors of (4.20a) are obviously given by: $\vec{e} \parallel \vec{q}$, $M\omega_1^2 = Mc_1^2 q^2$ and $\vec{e}_\perp \vec{q}$, $M\omega_t^2 = Mc_t^2 q^2$. It has to be noted, however, that even though a crystal may be isotropic for small \vec{q} , in general, the polarizations are neither transverse nor longitudinal except for highly symmetrical directions.

The \vec{q} vectors in Eq.(4.8) are not unique. Indeed, there are many equivalent \vec{q} which represent the same eigenoscillation. If q in Eq.(4.8) is replaced by $\vec{q} + \vec{g}$ where

$$\vec{q}R^{h} = 2\pi\mu, \mu = 0, \pm 1, \pm 2, \text{ for all } \vec{h}$$
 (4.21)

neither $\vec{u}^{\vec{n}}$ according to Eq. (4.8) nor $\vec{\phi}^{\vec{q}}$ are changed, i.e. \vec{q} and $\vec{q} + \vec{g}$ are equivalent and represent the same situation. Since $\vec{R}^{\vec{h}} = \sum_{i} h_i \vec{a}^{(i)}$ we

see thaț

$$\vec{g} = 2\pi \sum_{s} n_{s} \vec{b}^{(s)}$$
, where \vec{n} is an integer vector (4.22)

with $\vec{b}^{(s)} \vec{a}^{(i)} = \delta_{is}$ and $\mu = \sum_{s} n_{s}h_{s} = \vec{n}\vec{h}$ solves Eq.(4.21). The vectors

 \vec{q} form a lattice with $2\pi \vec{b}^{(s)}$ as basic vectors, the so-called reciprocal lattice. The quantity $\vec{\phi}\vec{q}$, the eigenvalues, and the eigenvectors $\vec{e}(\vec{q},\sigma)$ are all periodic in \vec{q} with the periods \vec{g} .

The reciprocal lattices of the three cubic lattices are again cubic, as shown in Table II. The \vec{q} values are unique if one confines them to one elementary cell of the reciprocal lattice from which all solutions of Eq.(4.8) can be obtained. It is customary to use a more symmetrical confinement volume in \vec{q} space, the so-called first Brillouin zone which is symmetrical about the origin in q space. Connections are drawn to the neighbouring lattice points from $\vec{q} = 0$, as well as planes which are perpendicular to the connecting straight lines and which pass through the midpoint of every connection. The origin is then enveloped by intersecting planes. The planes which are nearest to the origin form a polyeder defining the first Brillouin zone. This procedure is analogous to that of defining a symmetric atomic volume in a metal by the Wigner-Seitz cell.

Lattice	cubic lattice distance	reciprocal lattice	cubic lattice distance
SC	a	sc	2π/a
bcc	а	fcc	$4\pi/a$
fcc	а	bcc	4π/a

TABLE II. CUBIC LATTICE DISTANCES IN LATTICES AND RECIPROCAL LATTICES

The endpoints of the dispersion curves in Fig.11 $2\pi/a$, $\sqrt{3}\pi/a$, $2\sqrt{2}\pi/a$ are just the points where \vec{q} touches the surface of the Brillouin zone. The equivalence of \vec{q} and $\vec{q} + \vec{g}$ also shows that concepts like longitudinal and transverse do not make sense except for the first Brillouin zone.

In general lattices, the lattice positions are given by Bravais lattice positions \overrightarrow{Ah} which define the corners of the elementary cells and positions within the cell. The equilibrium positions are given by

$$\vec{R}^{\vec{h}} = A\vec{h} + \vec{R}^{\mu}, \quad \mu = 1 \dots s$$
 (4.23)

with s atoms per elementary cell. The atoms labelled with different μ may be like or unlike atoms. Simple examples are:

CsCl structures where Cs occupies the sc lattice positions and Cl the body-centred position, s = 2, and

$$\vec{R}_{Cs}^{\vec{h}} = a\vec{h}, \ \vec{R}_{Cl}^{\vec{h}} = a\vec{h} + \frac{a}{2}(111), \ \vec{R}_{Cs} = 0, \ \vec{R}_{C1} = \frac{a}{2}(111)$$

Diamond structures with like atoms which consist of two fcc lattices shifted by one fourth of the body diagonal, s = 2, $R_1^{\tilde{h}} = A\tilde{h}$, $R_2^{\tilde{h}} = A\tilde{h} + \sqrt{3} a/4$ (111). The procedure applied to obtain lattice waves is analogous to that discussed above. The matrices have the forms $\phi_{\mu\nu}^{(\tilde{h})}$ and $\tilde{\phi}_{\mu\nu}^{\tilde{d}}$. The determinant for the eigenvalues is now 3s-dimensional and therefore more complicated to solve. Three branches with vanishing eigenvalues for $\vec{q} \rightarrow 0$ are obtained. They are called acoustical branches and they agree with the elastic wave. Furthermore, one obtains 3(s-1), so-called optical branches, with nonvanishing eigenvalues for $\vec{q} \rightarrow 0$. Again in cubic lattices and highly symmetrical \vec{q} directions analytic expressions can be obtained by taking the lattice symmetries into account. In some cases, in particular for very different masses contained in one elementary cell, the frequencies of optical and acoustical branches are separated by a gap.

5. ELASTIC THEORY

We have mentioned before that for long waves lattice theory should go over into elastic theory. "Long waves" can be replaced by saying that the displacements vary only little from one lattice point to its

neighbours. This can also be expressed in the following way. We define a continuous displacement field $\vec{u}(\vec{R},t)$ where

$$\vec{u}^{\vec{n}}(t) = \vec{u}(\vec{R}^{n}, t)$$
 (5.1)

In the equation of motion

$$\underset{\vec{u}_{i}(\vec{R}=\vec{R}^{\vec{m}},t)}{\vec{u}_{i}(\vec{R}=\vec{R}^{\vec{m}},t)} \phi_{ik}^{\vec{m}-\vec{n}} \underbrace{u_{k}^{\vec{n}}(t)}_{u_{k}(\vec{R}+\vec{R}^{n}-\vec{R}^{m},t)}$$
(5.2)

we can make use of the fact that u_k varies only slowly within the range of the c.p.'s, expand u_k about $\vec{R} = \vec{R}^m$ in powers of $\vec{R}^{\vec{n}} - \vec{R}^{\vec{m}} = A(\vec{n} - \vec{m})$ and keep only the first non-vanishing terms. In this expansion the zeroorder term vanishes because of $\sum_{\vec{h}} \phi(\vec{h}) = 0$, the first-order term vanishes, too, because of inversion symmetry, $\phi(\vec{h}) = + \phi(\vec{-h})$, and the first nonvanishing term becomes $(\vec{m} - \vec{n} \rightarrow \vec{h})$:

$$M \ddot{u}_{i}(\vec{R}, t) = -\frac{1}{2} \sum_{\vec{h}mn} \phi_{ik}^{(\vec{h})} X_{m}^{\vec{h}} X_{n}^{\vec{h}} u_{k/mn}$$
(5.3)

where $u_{k/mn} = \frac{\partial^2}{\partial X_m \partial X_n} u_k(\vec{R}, t)$.

For better comparison with elastic theory, we divide by the volume per atom V_c and with the equilibrium mass density ρ_0 = M/V_c Eq.(5.3) becomes

$$\rho_0 \ddot{u}_i(\mathbf{R}, t) = \sum_{kmn} \left(-\frac{1}{2V_c} \sum_{\vec{h}} \phi_{ik}^{\vec{h}} X_m^{\vec{h}} X_n^{\vec{h}} \right) u_{k/mn}$$
(5.4)

The fourth-rank tensor \tilde{C} is obviously symmetrical in ik and mn. Equation (5.4) is the elastic equation of motion as derived from lattice theory.

In the elastic theory of a continuum, one starts as above with a continuous displacement field $\vec{u}(\vec{R},t)$ and defines the strain tensor for small displacements by $(u_{k/n} + u_{n/k})/2$ which vanishes for small rotations. The symmetrical stress tensor σ_{im} is a linear function of the strain (Hooke's law):

$$\sigma_{\rm im} = \sum_{\rm kn} C_{\rm im/kn} u_{\rm k/n}$$
(5.5)

where the tensor of elastic moduli C is necessarily symmetrical in im and kn. It can further be shown that C is symmetrical against interchange of the pair im with kn. The stresses represent surface forces and the equation of motion becomes

$$\rho_0 \ddot{u}_i = \sum_m \sigma_{im/m} = \sum_{mkn} C_{im kn} u_{k/mn}$$
(5.6)

The elastic moduli are usually represented by Voigt's moduli $c_{\alpha\beta}(\alpha,\beta=1,2,\ldots6)$ where the symmetries of C are used according to the scheme

ik = 1	1	22	33 .	23	31	12	
α =	1	2	3	4	5	6	(5.7)

e. g. $C_{11/1\bar{1}} c_{11}$, $C_{11/22} = c_{12} = c_{21} = C_{22/11}$, $C_{12/12} = c_{66}$, $C_{23/23} = C_{44}$.

The 6×6 matrix $c_{\alpha\beta}$ is symmetrical in $\alpha\beta$ and therefore contains 21 independent coefficients, in general. If, analogously, coefficients $\tilde{c}_{\alpha\beta}$ are defined from \tilde{C} , the quantity \tilde{c} need not be symmetrical and contains 36 independent coefficients, in general. Consequently, lattice theory seems to have a larger number of elastic moduli and Eq. (5.4) does not seem to agree with Eq.(5.6).

Lattice theory and elastic theory can be made agree if we require \tilde{C} to be symmetric against interchange of ik with mn or $\tilde{c}_{\alpha\beta} = \tilde{c}_{\beta\alpha}$:

$$C_{ik/mn} = C_{mn/ik}$$
(5.8)

which is called the Kun-Huang condition. Now \tilde{C} and C have, at least, the same number of independent coefficients. But still $\tilde{C} \neq C$ because \tilde{C} and C enter in different ways Eqs (5.4) and (5.6). However, only those parts of C which are symmetric enter Eq.(5.6). Consequently, if

$$C_{im/kn} + C_{in/km} = \tilde{C}_{ik/mn}$$
(5.9)

lattice and elastic equations agree. Equation (5.9) which implies that $\tilde{c}_{\alpha\beta} = \tilde{c}_{\beta\alpha}$ allows C to be expressed in terms of C uniquely

$$C_{im/kn} = \widetilde{C}_{ik/mn} + \widetilde{C}_{mk/in} - \widetilde{C}_{mi/nk}$$
(5.10)

Actually, Kun-Huang's condition (5.8) need not be derived by arguing that lattice and elastic theory must agree. It can be proved directly from first principles. It has been discussed in section 4 that for an infinite lattice the first-order coefficients $\phi_{1}^{\vec{n}}$ vanish for reasons of symmetry and cannot be used to define equilibrium. This is an inconvenience occurring when an infinite lattice is used. Actually, we need an additive equilibrium condition, the condition (5.8) to guarantee that the initial state is stress-

free. Relation (5.8) can be proved directly by starting from a finite crystal, by considering the equilibrium conditions on the surface, and then passing to an infinite crystal (see Refs [3,5]). Another possibility is to start with a proper potential in an infinite crystal where the equilibrium is determined by minimizing the energy per atom and to show that Eq. (5.8) is a consequence of the equilibrium conditions. First, one sees that for simple springs, where $\phi_{ik}^{(f)} \sim X_{ik}^{F} X_{ik}^{F}$, the tensor \tilde{C} is symmetrical against interchanges of all indices and Eq. (5.8) is obviously fulfilled. In this case $C = \tilde{C}$ and there are six other relations between the $c_{\alpha\beta}$ such as $c_{11} = c_{44}$. These "Cauchy relations" reduce the number of independent $c_{\alpha\beta}$ to 15. For more general central forces, including central springs under tension, the total antisymmetry of $C = \tilde{C}$ can again be proved. Then one can add three-body forces where the contribution to the potential would be

 $(1/3!) \sum_{mnp} \varphi^{(3)}(\vec{r}^m, \vec{r}^n, \vec{r}^p)$ and one single contribution $\varphi^{(3)}$ contains three

coordinates. Naturally, $\varphi^{(3)}$ must be invariant under translations and rotations. Again, Eq.(5.8) can be proved from the equilibrium conditions. Now, 4-body, etc., potentials can be added and again it can be shown that the equilibrium conditions imply Eq.(5.8).

In cubic crystals the condition (5.8) is valid by symmetry, and does not lead to further restrictions of the c.p. matrices. Cubic symmetry requires

$$\tilde{c}_{11} = \tilde{c}_{22} = \tilde{c}_{33}, \quad \tilde{c}_{12} = \tilde{c}_{21} = \tilde{c}_{23} = \tilde{c}_{31}, \quad \tilde{c}_{44} = \tilde{c}_{55} = \tilde{c}_{66}$$
 (5.11)

All other \tilde{c}_{ij} vanish (axes are parallel to cube edges). The same relations hold for $c_{\alpha\beta}$. Equation (5.10) becomes

$$c_{11} = \tilde{c}_{11}, \quad c_{12} = 2\tilde{c}_{44} - \tilde{c}_{12}, \quad c_{44} = \tilde{c}_{12}$$
 (5.10a)

For the simple cubic lattices with nearest neighbour interaction \tilde{C} is easy to calculate. Values are given in Table III, including the case

Moduli	sc	bcc	fcc	fcc with f and f'
a ĉ ₄₄	0	$\frac{2f_1 - 2f_2}{3}$	f ₁ - f ₂	f
a ĉ ₁₁ = ac ₁₁	f ₁	$\frac{2f_1 + 4f_2}{3}$	$2f_1 + 2f_2$	2f + 4f'
aõ ₁₂ = ac ₄₄	f ₂	$\frac{2f_1 + 4f_2}{3}$	$f_1 + f_2 + 2f_3$	f
ac ₁₂	- f ₂	$\frac{2f_1 - 8f_2}{3}$	$f_1 - 3f_2 - 2f_3$	f
a(c ₁₁ - c ₁₂)/2	$\frac{f_1 + f_2}{2}$	2f2	$\frac{f_1 + 5f_2 + 2f_3}{2}$	$\frac{\mathbf{f}+\mathbf{4f'}}{2}$

TABLE III. CONNECTION BETWEEN COUPLING PARAMETERS AND ELASTIC MODULI of Fig. 11 with two central-spring interactions. They can also be obtained from the elastic expansion of Eqs (4.17-4.19) because expression (4.20) is proportional to \tilde{C}^9 . The most proper combination of elastic moduli is given by the reciprocal compressibility $(c_{11} + 2c_{12})/3$, the two shear moduli, c_{44} for shear along (001) planes in (100) direction $(c_{11} - c_{12})/2$ for shear along (110) planes in (1-10) direction. If all these moduli are positive the crystal is elastically stable. If both shear moduli agree the crystal is isotropic, e.g. sc and bcc: $f_1 = f_2$, fcc: $f_1 - 3f_2 + 2f_3 = 0$ and 4f' = f.

In the fcc lattice there is one obvious possibility of making the nearest-neighbour model compatible with nature, namely by fitting the three f to the three elastic moduli, namely $f_1 = a(c_{11} + c_{12} + c_{44})/4$, $f_2 = a(c_{11} - c_{12} - c_{44})/4$ and $f_3 = a(2c_{44} - c_{11})/4$. This model should be rather good if the forces are really of very short range.

In non-primitive lattices $(\tilde{R}^{\tilde{\mu}}_{\mu})$ elastic theory can be treated along the same lines. The derivation is a little more complicated because the partial lattices μ are shifting against each other under elastic conditions. Therefore, the Cauchy relations are invalid in general even when only central forces¹⁰ are assumed.

6. CLASSICAL EIGENOSCILLATION AND QUANTUM STATES OF A FINITE CRYSTAL

If one is only interested in bulk effects the surface of a finite crystal should play only a minor role, or, in other words, the boundary conditions at the surface should be unimportant. This fact can be made use of by choosing the most convenient boundary conditions. Natural physical boundary conditions would be: given forces on the surface atoms, in particular, no forces, which corresponds to a stress-free crystal, or given displacements on the surface. Because of the inherent difficulties natural boundary conditions of three-dimensional lattices have not yet been treated. As a rule, periodic boundary conditions are used to define a finite volume, i.e., one selects three non-coplanar vectors $\vec{c}^{(s)} = A\hat{N}^{(s)}$ which are compatible with lattice translations if $\vec{N}^{(s)}$ are integer vectors. If the $\vec{N}^{(s)}$ are large they form a periodic volume containing many atoms. Most simply one chooses a volume similar to the elementary cell: \vec{c} (s) = N^(s) \vec{a} (s) which contains N = N⁽¹⁾ N⁽²⁾N⁽³⁾ atoms or elementary cells. In this way, one selects out 3N degrees of freedom or 3N co-ordinates and the problem can be dealt with as in section 2. The main advantage of this periodic condition is that then the eigenoscillations of the finite lattice become a special selection of the oscillation in the infinite lattice.

⁹ One can also compare the $\delta \vec{q}$ tensor in the limit $q \to 0$ with Eq. (5, 6) setting $\vec{u} = \vec{e}(\vec{q}, \sigma) \exp[i(\vec{q} \cdot \vec{R} - \omega t)]$, resulting in $\rho_0 \omega^2 e_i = \sum_{mkn} C_{im/kn} q_m q_n e_k$ which determines the elastic frequencies.

¹⁰ Except for lattices where every atom is a centre of symmetry such as the CsCl structure.

The representation (4.8) remains valid but the periodic boundary condition requires that

$$e^{i\vec{q}\cdot\vec{An}} = i\vec{q}\cdot\left(\vec{An} + \sum_{s}h_{s}N^{(s)}\vec{a}^{(s)}\right) \text{ or } \vec{q}\cdot\sum_{s}h_{s}N^{(s)}\vec{a}^{(s)} = 2\pi\mu \qquad (6.1)$$

$$\mu = 0, \pm 1, \pm 2...$$

This is analogous to the situation in section 4 where the reciprocal lattice was introduced. By expressions (6.1) a discrete set of permitted \vec{q} values is selected

$$\vec{q} = 2\pi \sum_{s} m_{s} \frac{b^{(s)}}{N(s)}$$
, $m_{s} = 0, \pm 1, \pm 2...$ (6.2)

or, if all N^(s) are equal,

$$\vec{q} = \frac{1}{N^{1/3}} 2\pi \sum_{s} m_{s} \vec{b}^{(s)}$$
 (6.2a)

The permitted \vec{q} values then form a lattice which has the structure of the reciprocal lattice but is smaller by a factor N^{1/3}. There are exactly N permitted \vec{q} if \vec{q} is confined to either one elementary cell of the reciprocal lattice or to the first Brillouin zone (Fig. 13). The volume per permitted value in q space is given by $(2\pi)^3/NV_c$ since the volume defined by the b^(s) is the reciprocal of V_c , the volume defined by the a^(s). This is used when passing from lattice sums to integrals.



FIG. 13. Permitted q values in the simple cubic lattice with $N = 10^3$.

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(6.3)

which can be done for large N when the permitted \vec{q} values are closely spaced. Of course, we can also use a simple cubic periodicity condition, e.g. $\vec{c}_1^{(s)} = N^{(s)}$ a δ is for a fcc lattice. Here we have N = 4 N⁽¹⁾ N⁽²⁾ N⁽³⁾ because one elementary cube, a³, contains 4 atoms in the fcc lattice. The permitted values were

$$q_{s} = \frac{2\pi}{a} (m_{s}/N^{(s)}) \rightarrow \frac{2\pi}{(N/4)^{1/3}a} m_{s}$$

and the volume $(2\pi)^2/(Na^3/4)$ is again $(2\pi)^3/NV_c$ since V_c = $a^3/4$.

The eigenoscillations are given by expression (4.8) where \vec{q} must be one of the N values (6.2) in the first Brillouin zone or an equivalent volume in \vec{q} space. The system is now finite, and we can directly employ the methods of section 2. The eigenvectors

$$w_{i\sigma}^{\vec{m}\vec{q}} = e_i(\vec{q},\sigma) e^{i\vec{q}\cdot\vec{R}\vec{m}} / \sqrt{N}, \vec{e}^2 = 1$$
(6.4)

are now complex. But we can still use the method of section 2 by defining the scalar product of two vectors \vec{v} and $\vec{\tilde{v}}$ by

$$\sum_{I} \widetilde{\mathbf{v}}_{I}^{*} \mathbf{v}_{I}$$

The 3N values \dot{q} , σ label the eigenvectors. The relations (2.9) read now $(\vec{e}(\vec{q},\sigma)$ is a unit vector, the factor $1/\sqrt{N}$ guarantees normalization in (6.5a)):

$$\sum_{\substack{\mathbf{n} \\ \mathbf{n} \mathbf{i}}} \mathbf{w} * \mathbf{m} \cdot \mathbf{q} * \mathbf{w} \mathbf{m} \cdot \mathbf{q} * = \delta_{\mathbf{q}, \mathbf{q}} * \delta_{\sigma, \sigma} *$$
(6.5a)

$$\sum_{\vec{q},\sigma} w_{i\sigma}^{\vec{m}} w_{i'\sigma}^{\vec{m}'\vec{q}} = \delta_{\vec{m},\vec{m}'} \delta_{i,i'}$$
(6.5b)

The matrix w of section 2 was orthogonal, the matrix w above is unitary. The complex description is more convenient, in particular, if one wants to describe travelling lattice waves which are needed, e.g., in scattering of neutrons by crystals, and in heat conductivity theory. Of course, a real representation is possible. Because of the $\pm \vec{q}$ degeneracy eigenvectors are obtained also if $\exp(i\vec{q}\cdot\vec{R^m})$ in Eq.(6.4) is replaced by $\cos \vec{q} \cdot \vec{R^m}$ or $\sin \vec{q} \cdot \vec{R^m}$. As in section 2 we can introduce "normal coordinates" $v_{\vec{q}}^a$ by

$$u_{i}^{\vec{m}} = \sum_{\vec{q}\sigma} v_{\sigma}^{\vec{q}} w_{i\sigma}^{\vec{m}\vec{q}}, \quad v_{\sigma}^{\vec{q}} = \sum_{\vec{m}} u_{i}^{\vec{m}} w_{i\sigma}^{\vec{m}\vec{q}} \qquad (6.6)$$

Here the $\vec{v}^{\vec{q}}$ are complex. The reality of $\vec{u}^{\vec{m}}$ reduces the number of complex co-ordinates. This condition depends on the relation between $\vec{e}(\vec{q},\sigma)$ and $\vec{e}(-\vec{q},\sigma)$. The polarizations for \vec{q} and $-\vec{q}$ are the same. The two \vec{e} vectors, can, of course, carry different signs. Putting

$$\vec{e}(-\vec{q},\sigma) = -\vec{e}(\vec{q},\sigma)$$
 (6.7)

is simpler and leads to

$$\mathbf{v}_{\sigma}^{-\vec{q}} = -\mathbf{v}_{\sigma}^{\vec{q}*} \tag{6.8}$$

which guarantees that $\vec{u_i^m}$ is real and removes the redundant co-ordinates. Kinetic and potential energy become

$$E_{kin} = \sum_{\vec{q} \sigma} \frac{M}{2} \dot{v}_{\sigma}^{\vec{q}*} v_{\sigma}^{\vec{q}}, \quad \phi_{h} = \sum_{\vec{q} \sigma} \frac{M}{2} \omega^{2}(\vec{q}, \sigma) v_{\sigma}^{\vec{q}*} v_{\sigma}^{\vec{q}}$$
(6.9)

and the equation of motion is

$$\ddot{\mathbf{v}}_{\sigma}^{\vec{q}} + \omega^2(\vec{q},\sigma) \ \mathbf{v}_{\sigma}^{\vec{q}} = 0$$
 (6.10)

If we go over to real description, using real and imaginary part of v^q , Eq.(6.6) splits into $\cos \vec{q} \cdot \vec{R}^{\vec{m}}$ and $\sin \vec{q} \cdot \vec{R}^{\vec{m}}$ terms. This corresponds to an expansion in standing waves. A very convenient transformation admits a description by travelling waves and a removal of condition (6.8). With $v\vec{q}$ and its canonical conjugate $M\vec{v}\vec{q} = \pi \vec{q}$ which both obey condition (6.8) we introduce^{10a}

$$\mathbf{a}_{\sigma}^{\vec{q}} = C_{\sigma}^{\vec{q}} \left\{ \omega(\vec{q},\sigma) \mathbf{v}_{\sigma}^{\vec{q}} + i \frac{\pi_{\sigma}^{\vec{q}}}{M} \right\} = C_{\sigma}^{\vec{q}} \left\{ \omega(\vec{q},\sigma) \mathbf{v}_{\sigma}^{\vec{q}} + \dot{\mathbf{v}}_{\sigma}^{\vec{q}} \right\}$$

$$C_{\sigma}^{\vec{q}} = \left(\frac{M}{2\hbar\omega(\vec{q},\sigma)}\right)^{1/2}$$
(6.11)

with

where from Eq.(6.10)

$$a\vec{q} + i\omega(\vec{q},\sigma) a\vec{q} = 0$$
 (6.12)

The total harmonic energy becomes

$$E_{kin} + \phi_{h} = \sum_{\sigma} a_{\sigma}^{*\vec{q}} a_{\sigma}^{\vec{q}} h \omega(\vec{q}, \sigma)$$
(6.13)

^{10a}Since $2C_{\sigma}^{\vec{q}}\omega(\vec{q},\sigma) \mathbf{v}_{\sigma}^{\vec{q}} = a_{\sigma}^{\vec{q}} - a_{\sigma}^{*-\vec{q}}$, the condition (6, 8) is automatically fulfilled.
and the Hamiltonian is

$$H = -\sum_{\vec{q},\sigma} i \omega(\vec{q},\sigma) P_{\sigma}^{\vec{q}} a_{\sigma}^{\vec{q}}$$

where $P_{\sigma}^{\vec{q}} = i\hbar a_{\sigma}^{\vec{q}}$ is the momentum conjugate to $a_{\sigma}^{\vec{q}}$. The displacements are given by

$$u_{i}^{\vec{m}} = \sum_{\vec{q},\sigma} \left(\frac{\hbar}{2M\omega(\vec{q},\sigma)}\right)^{1/2} \frac{e^{i\vec{q}\cdot\vec{R}^{\vec{m}}}}{\sqrt{N}} (a_{\sigma}^{\vec{q}} - a_{\sigma}^{*\vec{q}})$$
(6.14)

and analogously for the momenta $p_i^{\vec{m}} = M \dot{u}_i^{\vec{m}}$. Obviously each term in expression (6.14) represents a travelling wave according to Eq.(6.12). The constant C in the canonical transformation (6.11) has been chosen such that the expression for the quantum-theoretical Hamilton operator becomes particularly simple. In quantum theory, P, a and $a^* \Rightarrow a^+$ become operators¹¹ with the commutation relations

$$[P_{\sigma}^{q}, a_{\sigma'}^{q}] = -i\hbar \delta_{q,q'}\delta_{\sigma,\sigma'}$$

$$[a_{\sigma'}^{q}, a_{\sigma}^{+q}] = \delta_{q,q'}\delta_{\sigma,\sigma'}$$
(6.15)

whereas all other operators commute. The Hamilton operator becomes¹²

$$H = \sum_{\vec{q},\sigma} \sum_{n\vec{q}}^{+\vec{q}} a_{\sigma}^{\vec{q}} \hbar \omega (\vec{q},\sigma)$$
(6.16)

where $N_{q}^{\vec{q}}$ can be shown to have the eigenvalues 0,1,2, etc. The state $\psi(\ldots, n_{q}^{\vec{q}}, \ldots)$ of the crystal is given by the eigenvalues $n_{q}^{\vec{q}}$ of the "particle number operator" $N_{q}^{\vec{q}}$ which is the number of phonons \vec{q}, σ .

It should be emphasized that in all the results obtained above the co-ordinate belonging to the centre of mass ($\vec{q} = 0$) has been left out. It ought to be treated separately. The sums all extend over the first Brillouin zone excluding $\vec{q} = 0$. This is irrelevant, however, because in most physical phenomena the centre of mass motion does not enter. We may regard it as fixed. Rotations are excluded anyhow because of the periodicity condition which is incompatible with rotations.

The spectrum according to expression (2.11) is given by (see Fig. 14):

$$z(\omega) = \sum_{\vec{q},\sigma} \delta(\omega - \omega(\vec{q},\sigma)) \qquad (6.17)$$

or

¹¹ a⁺ is the Hermitian conjugate of a.

¹² If we pass to quantum theory before introducing the transformation (6.11) $N_{d}^{\overline{d}}$ in expression (6.16) has to be replaced by $N_{d}^{\overline{d}} + 1/2$ including the "zero-point energy" $\hbar\omega/2$ of the corresponding oscillator. This shifts only the energy scale and is of no physical consequence. It is convenient to keep the 1/2 term in order to remember the zero-point motion within the lattice at zero temperature.

If N is very large the sum $\sum_{\vec{q}}$ can be replaced by the integral $\int_{BZ} d\vec{q}N/V_{BZ}$, $V_{BZ} = (2\pi)^3/V_c$, such that $z(\omega) = 3 N \frac{1}{3} \sum_{\sigma} \frac{1}{V_{BZ}} \int_{BZ} d\vec{q} \delta(\omega - \omega(\vec{q}, \sigma))$ (6.18)

where $z(\omega)$ is normalized to 1, $\int_{0}^{\infty} z(\omega) d\omega = 1$. In contrast to expression

(6.17), $z(\omega)$ is a continuous function of ω except for certain ω values where singularities can occur. The usual way to calculate $z(\omega)$ is to go back to a finite crystal, Eq.(6.17), with a number N not too large, solve the cubic equation for the q values (6.2a), and draw a histogram for the frequencies contained in small intervals. Analytic solutions for three-dimensional crystals have not been given, as yet. Finer analytic details at points where $z(\omega)$ becomes singular have been discussed.



FIG.14. Spectrum of a fcc lattice with nearest neighbour central spring f only (R.B. Leighton, Rev. mod. Phys. 20 (1948) 165. The maximum frequency is about $3\sqrt{f/M}$.

For the linear chain with expression (4.15a) as dispersion curve we obtain $\left(\frac{1}{3}\sum_{\sigma} \operatorname{drops}, V_{BZ} \Rightarrow 2\pi/a, \omega(q) = \omega(-q) = \omega_{\max} |\sin \frac{qa}{2}|\right)$: $z(\omega) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} \delta\left(\omega - \omega_{\max} |\sin \frac{qa}{2}|\right) dq = \frac{2}{\pi} \int_{0}^{1} \delta\left(\omega - \omega_{\max} \sin \eta\right) d\eta$ $= \frac{2/\pi}{\{\omega_{\max}^{2} - \omega^{2}\}^{1/2}} \text{ for } 0 \leq \omega \leq \omega_{\max}$ (6.19)

An example of a three-dimensional spectrum is shown by Fig. 13.

The elastic spectrum for small ω must also be evaluated numerically except for isotropic crystals. In an isotropic crystal, where $\omega(\vec{q},\sigma) \rightarrow c_{\sigma}q$, $c_1 = c_1$ and $c_2 = c_3 = c_t$, Eq.(6.18) becomes

$$z_{el}(\omega) = 3N \frac{1}{3} \sum_{\sigma} \frac{1}{V_{BZ}} \int_{0}^{\infty} \delta(\omega - c_{\sigma}q) 4\pi q^{2} dq$$

$$= \frac{4\pi N}{V_{BZ}} \sum_{\sigma} \frac{\omega^{2}}{c_{\sigma}^{3}} = \frac{4\pi NV_{c}}{(2\pi)^{3}} \left(\frac{1}{c_{1}^{3}} + \frac{2}{c_{t}^{3}}\right) \omega^{2} = \frac{V}{2\pi^{2}} \left(\frac{1}{c_{1}^{3}} + \frac{2}{c_{t}^{3}}\right) \omega^{2}$$
(6.20)

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All elastic spectra of three-dimensional crystals are proportional to ω^2 . After Debye one often uses this spectrum to approximate the lattice spectrum. The elastic spectrum is cut off at the Debye frequency such that

$$\int_{0}^{\omega_{\rm D}} \mathbf{z}_{el}(\omega) \, \mathrm{d}\omega = 3N$$

The average thermal energy can also be expressed in terms of $z(\boldsymbol{\omega}).$

$$\mathbf{E} = \langle \mathscr{H} \rangle = \sum_{\vec{q},\sigma} \hbar \omega_{\sigma}^{\vec{q}} \langle \mathbf{N}_{\sigma}^{\vec{q}} \rangle = \sum_{\vec{q},\sigma} \hbar \omega_{\sigma}^{\vec{q}} \bar{\mathbf{n}}_{\sigma}^{\vec{q}}$$

where the thermal average of the occupation number, $\langle N_{\sigma}^{\vec{q}} \rangle = \bar{n}_{\sigma}^{\vec{q}}$ is given by:

$$\bar{n}_{\vec{\sigma}}^{\vec{q}} = \frac{\sum_{n=0}^{\infty} n \exp\left[-\frac{n\hbar\omega(\vec{q},\sigma)}{kT}\right]}{\sum_{n=0}^{\infty} \exp\left[-\frac{n\hbar\omega(\vec{q},\sigma)}{kT}\right]} = \frac{1}{\exp\left[\frac{\hbar\omega(\vec{q},\sigma)}{kT}\right] - 1}$$

With $\epsilon(\omega,T)$ = $\hbar\omega/(\exp(\hbar\omega/kT)-1)+\hbar\omega/2$ as the average thermal energy per oscillator ω we obtain

$$E = \sum_{\overrightarrow{q},\sigma} \epsilon (\omega(\overrightarrow{q},\sigma),T) \Rightarrow 3N \int_{0}^{\infty} z(\omega) \epsilon(\omega,T) d\omega$$
 (6.21)



FIG. 15. Wave vectors in X-ray scattering.

Another simple example is X-ray scattering (Fig.15). Here an incoming wave $\exp(i\vec{k}\cdot\vec{r})$ is scattered by each atom $(\vec{r}\vec{m})$ of the lattice

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which emits a spherical wave $\operatorname{Sexp}(\operatorname{ik} | \vec{r} - \vec{r}^{\vec{m}} |) / | \vec{r} - \vec{r}^{\vec{m}} |$. The scattered wave of the whole crystal is asymptotically (for $r \gg r^{\vec{m}}$) given by

$$\sum_{\vec{m}} S \exp[i(\vec{k} - \vec{k'}) \cdot \vec{r}^{\vec{m}}] \frac{e^{ikr}}{r}$$
(6.22)

where $\vec{k}^{\dagger} = \vec{k} \cdot \vec{r}/r$ is the \vec{k} vector pointing into the direction of observation, \vec{r}/r . The differential cross-section $d\sigma/d\Omega$ is given by ¹³

$$\frac{d\sigma}{d\omega} = |S|^{2} \left| \sum_{\vec{m}} \exp[i\vec{K} \cdot \vec{r}^{\vec{m}}] \right|^{2}$$

$$= |S|^{2} \sum_{\vec{m},\vec{n}} \exp[i\vec{K} \cdot (\vec{r}^{\vec{m}} - \vec{r}^{\vec{n}})] \qquad (6.23)$$

$$= |S|^{2} \sum_{\vec{m},\vec{n}} \exp[i\vec{K} \cdot (\vec{R}^{\vec{m}} - \vec{R}^{\vec{n}})] \exp[i\vec{K} \cdot (\vec{u}^{\vec{m}} - \vec{u}^{\vec{n}})]$$

where $\vec{K} = \vec{k} - \vec{k'}$.

This result has to be averaged over the thermal distribution, denoted by $\langle \ \rangle$, where for any quantity F:

$$\langle \mathbf{F} \rangle = \frac{\sum_{m,n_{\sigma}^{q},\dots} (\psi(\dots,n_{\sigma}^{q},\dots), \mathbf{F} \psi(\dots,n_{\sigma}^{q},\dots)) \exp\left(-\frac{\mathbf{E}\dots,n_{\sigma}^{q}\dots}{\mathbf{kT}}\right)}{\sum_{m,n_{\sigma}^{q}\dots} \exp\left(-\frac{\mathbf{E}\dots,n_{\sigma}^{q}\dots}{\mathbf{kT}}\right)}$$

In the expression

$$d\sigma/d\Omega = |S|^{2} \sum_{\vec{m} \cdot \vec{n}} \exp[i\vec{K} \cdot (\vec{R}^{\vec{m}} - \vec{R}^{\vec{n}}) \langle \exp[i\vec{K} \cdot (\vec{u}^{\vec{m}} - \vec{u}^{\vec{n}})] \rangle \qquad (6.24)$$

the average can be readily determined because it can be shown that the thermal distribution of the displacement is Gaussian. Therefore, also the distribution of $\vec{K} \cdot (\vec{u} \cdot \vec{m} - \vec{u} \cdot \vec{n})$ is Gaussian, with zero average and if the distribution of a quantity η is Gaussian, $D(\eta) = \exp(-H^2/2\langle \eta^2 \rangle)/(2\pi\langle \eta^2 \rangle)^{1/2}$ we obtain $\langle \exp(\zeta \eta) \rangle = \exp(\zeta^2 \langle \eta \rangle^2/2)$ such that we obtain:

$$\langle \exp[i\vec{K} \cdot (\vec{u}^{\vec{m}} - \vec{u}^{\vec{n}})] \rangle = \exp[-\frac{1}{2} \langle \{\vec{K} \cdot (\vec{u}^{\vec{m}} - \vec{u}^{\vec{n}})\}^{2}]$$

$$= \underbrace{\exp[-\frac{1}{2} \{\langle \vec{K} \cdot \vec{u}^{\vec{m}} \rangle^{2} \rangle + \langle (\vec{K} \cdot \vec{u}^{\vec{n}})^{2} \rangle \}]}_{e^{-qW}} \exp[\langle \vec{K} \cdot \vec{u}^{\vec{m}} \rangle (\vec{K} \cdot \vec{u}^{\vec{n}}) \rangle]$$

$$(6.25)$$

 $^{^{\}rm 13}{\rm The}$ atomic scattering amplitude S also depends on K.

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The first factor is the Debye-Waller factor which is independent of $\vec{m}, \vec{n}, W = \frac{1}{2} \langle (K u^m)^2 \rangle$. The second factor is usually expanded, the first term being called zero-phonon, and the second term one-phonon cross-section, etc. The first two terms become

$$\frac{d\sigma}{d\Omega} = |S|^2 e^{-2W} \sum_{\vec{m},\vec{n}} \exp[i\vec{K} \cdot (\vec{R}^{\vec{m}} - \vec{R}^{\vec{n}})] (1 + \langle (\vec{K} \cdot \vec{u}^{\vec{m}}) (\vec{K} \cdot \vec{u}^{\vec{n}}) \rangle)$$
(6.26)

Here $\sum_{\vec{m},\vec{n}} \exp[i\vec{K} \cdot (\vec{R}^{\vec{m}} - \vec{R}^{\vec{n}})] = L(\vec{K})$ represents the scattering by a static

lattice; it is periodic in the reciprocal lattice and sharply peaked near the points g of the reciprocal lattice (Laue spots). For many purposes it can be replaced by a δ -function which is periodic in the reciprocal lattice

$$L(\vec{K}) \cong NV_{BZ} \ \delta_{P}(\vec{K}) = NV_{BZ} \sum_{all \ q} \delta(\vec{K} - \vec{q})$$
(6.27)

The first term in Eq.(6.26) permits the reciprocal lattice and from there the lattice structure to be determined by Laue techniques.

For $\vec{u}^{\vec{m}}$ and $\vec{u}^{\vec{n}}$ we may insert the representation by the operators $a\vec{q}$ and $a\vec{q}$:

$$\vec{K} \cdot \vec{u}^{\vec{m}} = \sum_{\vec{q},\sigma} \left(\frac{\hbar}{2M\omega(\vec{q},\sigma)N} \right)^{1/2} (\vec{K} \cdot \vec{e}(\vec{q},\sigma) e^{i\vec{q} \cdot \vec{R}^{\vec{m}}} (a_{\sigma}^{\vec{q}} - a_{\sigma}^{+\vec{q}})$$
(6.28)

$$\langle (\vec{K} \cdot \vec{u}^{\vec{m}}) (\vec{K} \ \vec{u}^{\vec{n}}) \rangle = \sum_{\vec{q} \sigma} \frac{\hbar (\vec{K} \cdot \vec{e}(\vec{q}, \sigma)) (\vec{K} \cdot \vec{e} (\vec{q'}, \sigma'))}{2MN \{\omega(\vec{q}, \sigma) \ \omega (\vec{q'}, \sigma')\}^{1/2}} \exp[i(\vec{q} \cdot \vec{R}^{\vec{m}} + \vec{q'} \cdot \vec{R}^{\vec{n}}) \\ \vec{q'} \sigma' \\ \times \langle (a_{\sigma}^{\vec{q}} - a_{\sigma}^{+-\vec{q}}) (a_{\sigma'}^{\vec{q'}} - a_{\sigma'}^{+-\vec{q'}}) \rangle$$

$$(6.29)$$

This average can now be easily calculated from the average of pairs of the creation and annihilation operators a and a^+ . These averages are

$$\langle \mathbf{a}_{\sigma}^{\dagger \mathbf{q}}, \mathbf{a}_{\sigma}^{\mathbf{q}'} \rangle = \mathbf{n}_{\sigma}^{\mathbf{q}} \delta_{\mathbf{q}\mathbf{q}'} \delta_{\sigma\sigma},$$

$$\langle \mathbf{a}_{\sigma}^{\mathbf{q}'}, \mathbf{a}_{\sigma}^{\mathbf{q}'} \rangle = (\mathbf{n}_{\sigma}^{\mathbf{q}} + 1) \quad \delta_{\mathbf{q}}_{\mathbf{q}}^{\dagger}, \delta_{\sigma\sigma},$$

$$(6.30)$$

All other averages containing two a or a⁺ vanish. The fact that only averages with equal \vec{q} and σ remain is due to the independency of the oscillators \vec{q} , σ and to the vanishing of the averages over a or a⁺.

With

$$\langle (a_{\sigma}^{\vec{q}} - a_{\sigma}^{+ - \vec{q}})(a_{\sigma}^{\vec{q}'} - a_{\sigma'}^{+ - \vec{q}'}) \rangle = -\delta_{\vec{q}' - \vec{q}} \delta_{\sigma\sigma'} \cdot (\bar{n}(-\vec{q}, \sigma) + \bar{n}(\vec{q}, \sigma) + 1)$$

and

$$\overline{\mathbf{n}}(-\vec{\mathbf{q}},\sigma) = \overline{\mathbf{n}}(\vec{\mathbf{q}},\sigma), \ \mathbf{e}(-\vec{\mathbf{q}},\sigma) = -\mathbf{e}(\vec{\mathbf{q}},\sigma), \ \omega(-\vec{\mathbf{q}},\sigma) = \omega(\vec{\mathbf{q}},\sigma)$$

we obtain finally

$$\langle (\vec{K} \cdot \vec{u}^{\vec{m}}) (\vec{K} \cdot \vec{u}^{\vec{n}}) \rangle = \sum_{\vec{q},\sigma} \frac{\hbar (\vec{K} \cdot \vec{e}(\vec{q},\sigma))^2}{MN \, \omega(\vec{q},\sigma)} \, (\bar{n}_{\sigma}^{\vec{q}} + \frac{1}{2}) \, \exp[i\vec{q} \cdot (\vec{R}^{\vec{m}} - \vec{R}^{\vec{n}})] \qquad (6.29a)$$

and the one-phonon cross-section is given by

$$\frac{d\sigma}{d\Omega} = |S|^2 e^{-2W} \sum_{\vec{q},\sigma} \delta_P(\vec{K} + \vec{q}) V_{BZ} \frac{\epsilon(\omega(\vec{q},\sigma),T)}{M\omega^2(\vec{q},\sigma)} (\vec{K} \cdot \vec{e}(\vec{q},\sigma))^2$$
(6.31)

where $\epsilon(\omega, T) = \hbar\omega(\bar{n}(\omega, T) + \frac{1}{2})$.

While $(d\sigma/d\Omega)_0$ vanishes outside the Laue spots $\vec{K} = \vec{q}$, the one-phonon cross-section has a non-vanishing intensity everywhere in the reciprocal lattice. The intensity is given at $\vec{K} = \vec{q}$ by the factor in the summand. Therefore, from the intensity between the Laue spots frequencies $\omega(\vec{q},\sigma)$ can be concluded, and experimental dispersion curves can be obtained. The Debye-Waller factor is contained in Eq.(6.29a)

$$\frac{1}{2} \langle (\vec{K} \cdot \vec{u}^{\vec{m}})^2 \rangle = \frac{1}{2N} \sum_{\vec{q},\sigma} \frac{\epsilon \left(\omega(\vec{q},\sigma) T \right)}{M\omega^2(\vec{q},\sigma)} (\vec{K} \cdot \vec{e}(\vec{q},\sigma))$$
(6.32)

This also gives an expression for $\langle (\vec{u}^{\vec{m}})^2 \rangle$ by putting $K_s = \delta_{is}$ in Eq.(6.32) and summing over s

$$\langle (\vec{u}^{\vec{m}})^2 \rangle = \frac{1}{N} \sum_{\vec{q},\sigma} \frac{\epsilon(\omega(\vec{q},\sigma),T)}{M\omega^2(\vec{q},\sigma)} \rightarrow 3 \int \frac{\epsilon(\omega,T)}{M\omega^2} z(\omega) d\omega$$
 (6.33)

if the summation is replaced by integration over the spectral distribution. Moreover, in cubic crystals, the average of any component gives the same

 $\text{result} \left< (u_x^{\vec{m}})^2 \right> = \int \varepsilon \ z \ d\omega / \omega^2.$

In one- and two-dimensional lattices a corresponding derivation has to be done a little more carefully. The initial equation (6.24) contains only differences between \vec{m} and \vec{n} , but in the Debye-Waller factor and in the one-phonon expansion \vec{m} and \vec{n} appear separately. This procedure breaks down in one- and two-dimensional crystals. This can be

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see best in Eq.(6.33). The integral exists in three dimensions because $z(\omega) \sim \omega^2$ for small ω . It does not exist, however, in one and two dimensions where $z \sim const$ and $z \sim \omega$.

Again, the theory is essentially the same for non-primitive lattices.

7. LATTICE GREEN'S FUNCTIONS

Green's functions are needed to solve the equation of motions with forces $% \left({{{\left[{{{\left[{{{\left[{{{c}} \right]}} \right]}_{i}}} \right]}_{i}}}} \right)$

$$M \ u_{i}^{\vec{m}} + \sum_{n \ k} \phi_{i \ k}^{\vec{m}} u_{k}^{\vec{n}} = f_{i}^{\vec{m}}(t)$$
(7.1)

where $f^{m}(t)$ is the force acting on atom \vec{m} at time t. It is convenient to study first a harmonic time dependence

$$\widetilde{f}_{i}^{\vec{m}}(\omega) e^{-i\omega t}$$
 where $f_{i}^{m}(t) = \int_{-\infty}^{\infty} d\omega \widetilde{f}_{i}^{\vec{m}}(\omega) e^{-i\omega t}$ (7.2)

and analogously by introducing $\tilde{u}_{i}^{\vec{m}}$.

If we further introduce a small damping constant $\gamma > 0$ i.e. a term $\gamma u_{\vec{m}}^{\vec{m}}$ in Eq.(7.1) we obtain

$$(-M\omega^{2} - i\gamma\omega)\widetilde{u}_{i}^{\vec{m}} + \sum_{\vec{n}k} \phi_{ik}^{\vec{m}}\widetilde{u}_{k}^{\vec{m}} = \widetilde{f}_{i}^{\vec{m}}$$
(7.3)

This equation can be solved by

$$\widetilde{u}_{i}^{\vec{m}} = \sum_{\vec{n},k} \widetilde{G}_{ik}^{\vec{m}\vec{n}} \widetilde{f}_{k}^{\vec{n}}$$
(7.4)

where $\tilde{G}_{ik}^{\vec{m}\,\vec{n}}(\omega)$ is the Green's function or Green's function matrix (rather its Fourier transform). The Green's function can be easily represented by the eigenvectors and eigenvalues of ϕ . We expand the displacements and the forces according to

$$\widetilde{u}_{i}^{\vec{m}} = \sum_{\vec{q} \sigma} \widetilde{u}(\vec{q}, \sigma) e_{i}(\vec{q}, \sigma) \frac{e^{i\vec{q}\cdot\vec{R}^{\vec{m}}}}{\sqrt{N}}$$

$$\widetilde{u}(\vec{q}, \sigma) = \sum_{\vec{m} i} \widetilde{u}_{i}^{\vec{m}} e_{i}(\vec{q}, \sigma) \frac{e^{-i\vec{q}\cdot\vec{R}^{\vec{m}}}}{\sqrt{N}}$$
(7.5)

and analogously for $\vec{f}_i^{\vec{m}}$, compare the coefficients of the eigenvectors, and transform back. The result is

$$\widetilde{\mathbf{u}}_{i}^{\vec{m}} = \sum_{\vec{n},k} \left\{ \sum_{\vec{q},\sigma} \frac{\mathbf{e}_{i}(\vec{q},\sigma) + \mathbf{e}_{k}(\vec{q},\sigma)}{\lambda(\vec{q},\sigma) - M\omega^{2} - i\gamma\omega} \exp\left[i\vec{q}\cdot(\vec{R}^{\vec{m}} - \vec{R}^{\vec{n}})\right] \right\} \widetilde{\mathbf{f}}_{k}^{\vec{n}} \quad (7.6)$$
$$\widetilde{\mathbf{G}}_{ik}^{\vec{m}} = \widetilde{\mathbf{G}}_{ik}^{(\vec{m}} - \vec{n})}$$

Up to now we have treated a finite lattice. If we pass to an infinite lattice

$$\left(\sum_{\vec{q}} \rightarrow \int_{BZ} d\vec{q} / V_{BZ}\right)$$
 we have

$$\widetilde{G}_{ik}^{(\vec{h})} = \frac{1}{V_{BZ}} \sum_{\sigma} \int d\vec{q} \frac{e_i(\vec{q},\sigma) e_k(\vec{q},\sigma)}{\lambda(\vec{q},\sigma) - M\omega^2 - i\gamma\omega} e^{i\vec{q}\cdot\vec{R}\vec{h}}$$
(7.7)

where $\lambda(\vec{q},\sigma) = M\omega^2(\vec{q},\sigma)$ are the eigenvalues of ϕ . We verify easily that $\widetilde{G}_{1k}^{(m)}$ has the same symmetry properties as $\phi_{1k}^{(m)}$. If the frequency ω is within the spectrum we have a singularity in the integrand and the term $i\gamma\omega$ tells how to integrate around that singularity, $\gamma \rightarrow +0$. So far damping has only been an artificial device to define the proper integration. If ω is outside the spectrum the γ term can be dropped. This choice of $\gamma \rightarrow +0$ means that a periodic force acting on one atom produces "outgoing" waves which emerge from that atom. If we transform back to time $\gamma \rightarrow 0$ means that a force produces displacements only after it has been applied. Further it can be shown that for values of ω lying outside the spectrum $\widetilde{G}(\vec{n})$ decreases essentially exponentially with the distance $\vec{R}^{\vec{h}}$. There are not yet analytic results available for three-dimensional Green's functions. But the properties listed above are easily demonstrated by the results for the linear chain with nearest-neighbour interaction f, $M\omega_{max}^2 = 4f = \lambda_{max}$:

$$\widetilde{G}^{(h)} = \frac{i \exp(i \operatorname{sgn} \omega |\operatorname{qah}|)}{\operatorname{sgn} \omega 2f \sin|\operatorname{qa}|}, \quad 1 \ge \frac{\omega^2}{\omega_{\max}^2} = \sin^2 \frac{\operatorname{qa}}{2}$$

$$= \frac{\exp(-i\pi |h| - |\kappa h|)}{2f \sinh|\kappa h|}, \quad 1 \le \frac{\omega^2}{\omega_{\max}^2} = \cosh^2 \frac{\kappa a}{2}$$
(7.8)

Of particular interest is $\tilde{G}_{ik}^{(\vec{h}=0)} = \tilde{G}_{u}^{(0)} \delta_{ik}$ because it has the same symmetries as $\phi_{ik}^{(\vec{h})}$:

$$\widetilde{G}_{\parallel}^{(0)} = \frac{1}{3} \sum_{i} \widetilde{G}_{ii}^{(0)} = \frac{1}{3V_{BZ}} \sum_{\sigma} \int_{BZ} d\vec{q} \frac{1}{\lambda (\vec{q}, \sigma) - M \omega^2 - i\gamma \omega}$$
$$= \int_{\overline{\lambda} - M \omega^2 - i\gamma \omega} (7.9)$$

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where $\hat{z}(\lambda) d\lambda$ is the fraction of eigenvalues $\lambda(\vec{q},\sigma)$ in the interval $(\lambda, \lambda + d\lambda), \hat{z}(\lambda) d\lambda = z(\omega) d\omega, \int z(\lambda) d\lambda = 1$. Since

$$\frac{1}{\lambda - M\omega^2 - i\gamma\omega} \quad \overrightarrow{\gamma \to + 0} \quad i\pi \, \operatorname{sgn} \omega \, \delta(\lambda - M\omega^2)$$

$$+ P \, \frac{1}{\lambda - M\omega^2}$$
(7.10)

where P denotes Cauchy's principal value we see that the imaginary part of $\tilde{G}^{(0)}$ is related to the spectrum ($\delta(\lambda - M\omega^2) = (1/M) \ \delta(\lambda/M - \omega^2) = (1/2M\omega) \ \delta(\lambda/M - \omega) = (1/2M\omega) \ \delta(\omega(\vec{q},\sigma) - \omega) \text{ for } \omega > 0)$:

$$\operatorname{Im} \widetilde{G}_{\mathfrak{h}}^{(0)}(\omega) = \frac{\pi}{2M\omega} z(\omega) = \pi \hat{z}(\lambda) \qquad (7.11)$$

The method of Green's functions permits a rather transparent treatment of the effects caused by lattice defects. If the lattice contains one single "point defect" the lattice waves are no longer eigensolutions. The lattice waves are scattered by the defect. There is further the possibility of "localized modes", usually at frequencies¹⁴ $\omega_{loc} > \omega_{max}$ where the amplitudes decrease exponentially with distance from the defect. Also resonant modes with particularly strong resonance-like scattering for certain frequencies $\omega_{res} < \omega_{max}$ are possible. All these phenomena are analogous to the behaviour of a free electron: a defect corresponds to introducing a potential at which the electron is scattered (resonance scattering is also possible); localized modes correspond to bound states.

The theory of lattice defects is rather simple, in principle. Let us rewrite Eq.(7.3) in the following form:

$$(-M\omega^2 - i\gamma\omega + \phi) \tilde{\vec{u}} = \vec{f}, \quad \gamma \to +0$$
(7.12)

where \vec{u} and \vec{f} are vectors with $(\frac{\vec{m}}{i})$ components and ϕ is a matrix in this space which operates on \vec{u} as indicated in Eq.(7.3), M and γ are diagonal matrices. In a defect lattice masses and c.p. are changed $(M \rightarrow M^{\dagger} = M + \delta M, \phi \rightarrow \phi^{\dagger} = \phi + \delta \phi$, e.g. if the mass at the origin is changed by μ and no other changes, then $\delta \phi = 0$, $\delta M \overline{\lim_{k=1}^{m} \mu} = \mu \delta_{\vec{m}0} \delta_{\vec{n}0} \delta_{ik}$), and the equation of motion for harmonic time dependence is

$$(-M^{\dagger}\omega^{2} - i\gamma\omega + \phi^{\dagger})\vec{\widetilde{u}} = \vec{\widetilde{f}}, \ \gamma \to +0 \text{ or } (-M\omega^{2} - i\gamma\omega + \phi)\vec{\widetilde{u}} = \underbrace{(\delta M\omega^{2} - \delta\phi)\vec{\widetilde{u}} + \vec{\widetilde{f}}}_{\mathscr{T}}$$

$$(7.13)$$

where $\mathcal T$ represents the deviation from the ideal lattice.

¹⁴ Rayleigh waves at the surface of crystals are a counterexample where $\omega_{\rm loc} < \omega_{\rm max}$.

In a scattering problem ($\tilde{f} = 0$) we have an incoming lattice wave

$$\stackrel{(1)}{\vec{\mathfrak{u}}} = (\mathbf{e}_{i}(\vec{\mathfrak{q}},\sigma) \; \mathbf{e}^{i\vec{\mathfrak{q}}\cdot\,\vec{\mathfrak{R}}\vec{\mathfrak{m}}}), \; \omega(\vec{\mathfrak{q}},\sigma) = \omega$$

and look for a solution \vec{u} , which consists of the incoming wave and a (sc) scattered wave \vec{u} , which contains only outgoing waves (completely analogous to quantum-mechanical potential scattering where \mathscr{F} represents the potential):

Equation (7.13) can be solved by

because $\tilde{\tilde{u}}$ is a solution of the homogeneous equation (J = 0) and because of the properties of \tilde{G} the scattering wave contains only outgoing waves. Consequently,

$$\vec{\tilde{u}} = \frac{1}{1 - \tilde{G}J} (\vec{\tilde{u}} = \vec{\tilde{u}} + \frac{1}{1 - \tilde{G}J} \vec{G}J \vec{\tilde{u}}$$
(7.16)
$$(\vec{\tilde{u}} = \tilde{G}J \frac{1}{1 - \tilde{G}J} (\vec{\tilde{u}})$$

The scattered wave behaves as though forces $J(1 - \tilde{G}J)^{-1}\tilde{u}^{(i)}$ were acting in the ideal lattice or forces $J\tilde{u}$ in the defect lattice because we see immediately that $(1 - \tilde{G}J)^{-1}\tilde{G}$ is Green's function of the defect lattice. The procedure is again as in potential scattering, Eq. (7.15) corresponds to Born's integral equation, and Born's approximation would be $\tilde{u} = \tilde{G}J\tilde{u}$. Cross-sections can be defined in the familar way, and it can be shown that the results are independent of whether we use classical or quantum theory to calculate them (in the harmonic approximation). A localized mode is a state where \tilde{u} according to Eq. (7.15) exists without an incoming wave. Consequently,

$$\vec{\tilde{u}} = GJ\vec{\tilde{u}} \rightarrow Det |1 - \tilde{G}J| = 0$$
 (7.17)

determines the localized frequencies $\omega_{loc}\,.\,$ The matrix elements of J are concentrated near the defect, symbolically

$$J = \left(\overline{J}\right) \tag{7.18}$$

 $\tilde{G}J = \left(\begin{bmatrix} \tilde{g} \end{bmatrix} \right)$

so that we have

and

$$Det | 1 - GJ | = Det | 1 - gJ | = 0$$

i.e., for calculating the localized frequencies we need only the finite submatrix \tilde{g} of \tilde{G} which has the same range as the defect. If one introduces a defect matrix D

$$D = (1)$$

which cuts out the defect range, we have $D^2 = D$, JD = DJ = J, $\tilde{g} = D\tilde{G}D$, i.e. D cuts down \tilde{G} to defect size, \tilde{g} . Equation (7.19) determines only those displacements belonging to the defect, $D\tilde{u}$, where changes in M and ϕ are present. We then obtain from relation (7.17) the amplitudes outside the defect

$$\tilde{d} = \tilde{G}J\tilde{d} = \tilde{G}JD\tilde{d}$$
 (7.20)

The simplest example is the isotopic defect where (7.17) becomes

$$(J_{ik}^{\vec{m}\,\vec{n}} = \mu \omega^{2} \delta_{\vec{m}\,0} \delta_{\vec{n}\,0} \delta_{ik})$$

$$u_{i}^{\vec{m}} = \sum_{\vec{n}} \mu \omega^{2} \tilde{G}_{ik}^{\vec{m}\,0} \delta_{\vec{n},0} u_{k}^{\vec{n}} = \mu \omega^{2} G_{ik}^{(\vec{m})} u_{k}^{0}$$

$$(7.21)$$

The term $\vec{m} = 0$ leads to

$$u_{i}^{0} = \mu \omega^{2} \tilde{G}_{\mu}^{(0)} u_{i}^{0} \text{ or } 1 = \mu \omega^{2} G_{\mu}^{(0)} (\omega)$$
 (7.22)

as a condition for ω_{loc} , and Eq.(7.20) gives then the amplitudes $m \neq 0$ once ω_{loc} is determined. The displacement \vec{u}^0 is obtained from normalization. Because $\omega_{loc} > \omega_{max}$ the term containing γ in (7.9) can be dropped:

$$1 - \mu \omega^2 G_{\mu}^{(0)}(\omega) = 1 - \mu \omega^2 \int \frac{\hat{z}(\lambda) d\lambda}{\lambda - M\omega^2} = 1 + \frac{\mu}{M} \underbrace{\int \frac{\hat{z}(\lambda) d\lambda}{1 - \lambda/M\omega^2}}_{B(\omega)} = 0 \quad (7.22a)$$

The function $B(\omega)$ is positive for $\omega > \omega_{max}$ and decreases monotonously with increasing ω (Fig. 16). Its value at $\omega = \omega_{max}$ depends on the behaviour of $z(\lambda)$ near $\lambda = \lambda_{max} = M\omega_{max}^2$. As a rule it will be finite. The condition

(7.19)



FIG. 16. Determination of the localized frequency for an isotopic defect.

for ω_{loc} is now $B(\omega) = -M/\mu = -M/(M^0 - M) = M/(M - M^0)$. Obviously, M_0 must be smaller than M. A localized state occurs if $B_{max} \ge M/(M - M_0) \ge 1$. If $B_{max} = \infty$ which holds for the linear chain all isotopes with $M^0 < M$ produce a localized state. The localization becomes more and more pronounced if M_0 becomes smaller and ω_{loc} increases accordingly. For very strongly localized defects $M\omega_{loc}^2 \gg \lambda_{max} = M\omega_{max}^2$ we can expand in (7.22a):

$$1 + \frac{\mu}{M} \int \hat{\mathbf{z}}(\lambda) \, d\lambda \, \left\{ 1 + \frac{\lambda}{m\omega^2} \right\} \cong 0 = 1 + \frac{\mu}{M} \, \left\{ 1 + \frac{1}{M\omega^2} \int \hat{\mathbf{z}}(\lambda) \, \lambda \, d\lambda \right\}$$

where $\int \hat{z}(\lambda) \lambda \, d\lambda = \int M \omega^2 \, z(\omega) \, d\omega = M \overline{\omega^2}$ and $\overline{\omega^2}$ is the average of ω^2 over

the spectral distribution. In cubic crystals $\sqrt{\omega^2}$ is the frequency with which an atom would vibrate if its surroundings were fixed. For strong localization the environment of M^0 can be assumed to be fixed. Therefore,

$$M_0 \omega_{loc}^2 \cong M \overline{\omega^2} \text{ or } \overline{\omega^2} / \omega_{loc}^2 = M_0 / M$$

which agrees with the statement made above. Furthermore,

$$\omega^2/\omega_{\text{loc}}^2 \cong -\frac{1+\mu/M}{\mu/M}\cong 1+\mu/M = M^0/M$$

because $\mu/M^0 = -1$.

The reduced Green's function \tilde{g} has still another meaning. Consider the motion of a defect lattice with forces acting only on the defect atoms, $D\tilde{f} = \tilde{f}D = \tilde{f}$.

From

$$(-M\omega^2 - i\gamma\omega + \phi)\tilde{\vec{u}} = J\tilde{\vec{u}} + \vec{f}$$

it follows that

$$\vec{\widetilde{u}} = \vec{\widetilde{G}} J \vec{\widetilde{u}} + \vec{\widetilde{G}} \vec{\widetilde{f}} \rightarrow \vec{\widetilde{u}} = \frac{1}{1 - \vec{\widetilde{G}} J} \vec{\widetilde{Gf}}$$

The motion of a defect atom, $D\vec{u}$, is given by

$$D\tilde{t} = D \frac{1}{1 - \tilde{G}J} \tilde{G}\tilde{f} = D \frac{1}{1 - \tilde{G}J} \tilde{G}D\tilde{f}$$
$$= D \frac{1}{1 - \tilde{g}J} \tilde{g}D\tilde{f} \qquad (7.23)$$
$$= \frac{1}{1 - \tilde{g}J} \tilde{g}\tilde{f}$$

Here \widetilde{G} can be replaced by \widetilde{g} because G always stands between two D. Consequently,

$$\tilde{g}^{-1}(1 - \tilde{g}J) D\vec{u} = (\tilde{g}^{-1} - J) D\vec{u} = \tilde{f}$$
 (7.24)

represents the motion of defect atoms under the action of forces. The influence of the surrounding lattice is included.

For an isotopic defect, we have

$$\left\{\frac{1}{G_{\parallel}^{(0)}(\omega)} - \mu\omega^{2}\right\} \widetilde{\vec{u}}^{0} = \vec{f}^{0} = \left\{-M^{0}\omega^{2} + M\omega^{2} + \frac{1}{G_{\parallel}^{(0)}(\omega)}\right\} \widetilde{\vec{u}}^{0}$$
(7.25)

and $-(M\omega^2 + 1/G^{(0)})\tilde{u}^0$ is the force on the isotope by the surrounding lattice consisting of restoring forces by the surrounding springs and damping due to eradiation of lattice waves. The friction by eradiation will be lowest for small frequencies. Resonance motions are such that the motion is almost stationary. Therefore we shall expect resonance-like motions for very heavy isotopes at low frequencies. For small ω we can expand $1/G_{ij}^{(0)}$ in powers of ω :

$$\frac{1}{G_{\parallel}^{(0)}(\omega)} = 2\hat{f} + i\hat{\gamma}\omega$$

and Eq.(7.24) becomes $(M^0 \gg M)$:

$$(-M^{0}\omega^{2} - i\hat{\gamma}\omega + 2\hat{f})\tilde{t}^{0} = \hat{f}^{0}$$
(7.26)

This corresponds to an equation of motion

$$M^{0}\ddot{\vec{u}}^{0} + \hat{\gamma}\dot{\vec{u}}^{0} + 2\hat{f}\vec{u}^{0} = \vec{f}^{0}$$
 (7.26a)

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The restoring forces by the lattice are given by the effective spring constants \hat{f} , the damping by sound waves is given by $\hat{\gamma}$. The (static!) restoring force and the damping by emitting sound waves can be obtained directly without using Green's functions. Sharp resonances occur for

$$M^{0}\omega_{res}^{2} = 2\hat{f} \quad if \quad \hat{\gamma}\omega_{res} \ll M^{0}\omega_{res}^{2} = 2\hat{f} \qquad (7.27)$$

These resonances imply strong scattering of lattice waves with frequencies of about ω_{res} . This can be experimentally demonstrated in heat conductivity where at $kT_{res} = \hbar\omega_{res}$ the heat conductivity should show a dip due to the strong scattering of ω_{res} phonons which contribute most to heat conductivity in this temperature range. The resonance also shows up in the spectral distribution. For many defects in the lattice $z(\omega)$ exhibits a peak at ω_{res} which is in first order proportional to the defect concentration and which can be seen in scattering experiments.

8. MODELS FOR POTENTIALS AND COUPLING PARAMETERS

The simplest model for c.p.'s is the near-neighbour model which has been discussed extensively in section 4. It can be used if the forces are short-range ones which is not too bad an assumption in metals. The c.p.'s can be determined from macroscopic data such as the elastic moduli or electrical polarizabilities in ionic crystals. More refined c.p.'s can be obtained by fitting them to experimental dispersion curves which are usually given only for symmetrical directions. Once the c.p.'s are determined we can then obtain frequencies and polarizations off symmetry directions by numerical calculation.

In ionic crystals the Coulomb forces are long-range ones. Here we often use a model potential consisting of the Coulomb potentials between the ionic charges e, and repulsive potentials between the ions of Born-Mayer type, $A_{\mu\nu} exp - r_{\mu\nu}/a_{\mu}$, which come from the overlap of the ionic cores. Here the $A_{\mu\nu}$ and $\dot{a}_{\mu\nu}$ are parameters to be fitted to experimental data. More sophisticated spring models can also be employed, such as the so-called shell model. In its simplest form it replaces an ion μ by a core with charge e_{μ}^{+} and an "electronic" shell of charge e_{μ}^{-} . Core and shell are connected by a spring and cores and shells of different nearestneighbour ions are also connected by a spring. Figure 17 shows an example where only one spring $f_{\mu\nu}$ between the shells of two ions is present. The spring $f_{\mu\nu}$ should be repulsive and correspond to the repulsive Born-Mayer potentials ($f_{\mu\nu} < 0$). The springs f_{μ} and f_{ν} are related to the polarizability of the ions. This model then contains near-neighbour spring constants and long-range Coulomb forces. The spring constants and the charges have to be fitted. The shell model contains many-body forces because it includes polarization. In symmetric ionic lattices, it does not produce deviations from the Cauchy relation because in elastic deformation every atom remains a centre of symmetry. This means that the polarization of every ion vanishes and that, therefore, this particular kind of manybody forces does not give deviation from Cauchy's relation. If an overlap between the shells is taken into account Cauchy's relations are destroyed. Several attempts have been made to discuss three- and four-body interactions either phenomenologically or by applying quantum-mechanical

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perturbation theory (compare Ref.[5]). In simple metals such as Al and the alkali halides, great progress has been made during the last few years. The contribution due to the conduction electrons can be calculated in a self-consistent way in quite good agreement with experimental dispersion curves.

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FIG,17. Simple Shell Model.







FIG.18. Planar force constants of the alkali metals: a) (100) shear wave; b) uniform displacement of the plane x = a; c) distances used to calculate the potential of a periodic dipole chain.

c

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A particularly simple example is the calculation of the transverse dispersion curves in symmetrical direction of the bcc alkali metals (see Ref. [5]). The ionic cores of the alkalis are so small that their interaction may be neglected in a first approximation. The lattice energy consists mainly of Coulomb energy ($\epsilon_{At} \sim -e^2/a$) where the conduction electrons can be thought of as distributed uniformly, and the kinetic energy (Fermi energy) of the conduction electrons ($\epsilon_{At} \sim 1/a^2$) which approximately depends only on the volume per atom. If only transverse waves in the symmetrical directions are considered the volume per atom remains constant (Fig. 18a). Consequently, only electrostatic forces between the ions submerged in a sea of electrons need to be taken into account. For the shear wave (Fig. 18a), $\vec{q} = q(100)$, $\vec{e} = (001)$, all the planes x = (a/2)n with integer n remain rigid in themselves and move against each other such that the atomic volume remains unchanged. From Eq.(4. 7a) we obtain for the frequency of this wave

$$M\omega^{2} = \tilde{\phi}_{33}^{\vec{q}} = -2 \sum_{\vec{h}} \phi_{33}^{(\vec{h})} \sin^{2} \frac{\vec{q} \cdot \vec{R}^{\vec{h}}}{2} = -2 \sum_{\vec{h}} \phi_{33}^{(\vec{h})} \sin^{2} \frac{q X^{(\vec{h})}}{2}$$
(8.1)

The equilibrium positions of the lattice $(\vec{R}^{\vec{h}} = \vec{A}\vec{h}$ with integer \vec{h}) can be written more conveniently:

$$\vec{R}^{\{h_1h_2h_3\}} = \left(h_1 \frac{a}{2}, h_2 a + \frac{a}{4} (1 - (-)^{h_1}), h_3 a + \frac{a}{4} (1 - (-)^{h_1})\right)$$

$$0 \text{ for } h_1 \text{ even}$$

$$a/2 \text{ for } h_1 \text{ odd}$$

Here again \vec{h} is an integer vector, h_1 labels the planes, and h_2 , h_3 label the position in the planes. Equation (8.1) remains unchanged:

$$M\omega^{2} = -2 \sum_{\vec{h}} \phi_{33}^{\{\vec{h}\}} \sin^{2} \frac{qX^{\{\vec{h}\}}}{2}$$

= $-2 \sum_{\vec{h}} \phi_{33}^{\{\vec{h}\}} \sin^{2} \frac{qX^{\{h_{1}\}}}{2} = -2 \sum_{h_{1}} \phi_{33}^{\{h_{1}\}} \sin^{2} \frac{qX^{\{h_{1}\}}}{2}$ (8.2)

with

$$\phi \{ \mathbf{h}_{1} \} = \sum_{\mathbf{h}_{2}\mathbf{h}_{3}} \phi \{ \mathbf{h}_{1}\mathbf{h}_{2}\mathbf{h}_{3} \}$$

and

$$X^{\{h_1\}} = h_1 a/2$$

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As before $-\phi^{\{\vec{h}\}} u^{\vec{h}}$ is the z component of the force on the atom in the origin if only atom $\{\vec{h}\}$ is displaced by $u^{\vec{h}}_3$ in z direction and analogously $-\phi^{\{h_i\}} u^{\{h_i\}}$ gives the force if the plane h_1 is displaced as a whole. The calculation of the planar force constants $\phi^{\{h_i\}}_{33}$ is simple. The situation for the plane $h_1 = 2$ is shown in Fig.18b. The force $eE_z(u_3)$ on the charge . e in the origin is given by the electrical field at $\vec{r} = 0$, $\vec{E}(u_3)$, produced by the displacement u_3 . The contribution by the plane is $e\{E_z(u_3) - E_z(0)\}$ because the forces must vanish for $u_3 = 0$. The field corresponds to charges e in the displaced position and charges -e in the original positions (Fig.18b) which form dipoles of moment eu_3 . The quantity $\phi^{\{h_1\}}_{33}$ is then given by

$$\frac{\partial}{\partial u_3} e \left\{ E_z(u_3) - E_z(0) \right\}_{u_3 = 0} = -e \frac{\partial}{\partial u_3} E_z(u_3) \Big|_{u_3 = 0}$$

The plane can obviously be resolved into periodic dipole chains. The potential ψ of a single chain for the situation in Fig. 18c is given by (see Ref.[1]):

$$\psi(\xi,\rho) = -\frac{2e}{d} \sum_{\substack{n=-\infty\\(n\neq 0)}}^{\infty} K_0\left(\frac{2}{d} \mid n \mid \rho\right) \exp\left(i 2\pi n \frac{\xi}{d}\right) \left[1 - \exp\left(-12\pi n \frac{u}{d}\right)\right]$$
(8.3)

Here $K_0(\eta)$ is the modified Hankel function of zero order which decreases exponentially for $\eta\gtrsim 1$

$$K_0(\eta) \sim \left\{\frac{\pi}{2\eta}\right\}^{1/2} e^{-\eta}$$
 (8.4)

The contribution to $\phi_{33}^{\{h_i\}}$ by one row is

$$-\frac{\partial}{\partial u} e - \frac{\partial}{\partial \xi} \psi(\xi, \rho) \Big|_{u=0} = e \frac{\partial^2}{\partial u \partial \xi} \psi(\xi, \rho) \Big|_{u=0} = \sum_{n \neq 0} \frac{2\mathscr{L}(2\pi n)^2}{d^3} \times K_0 \left(\frac{2\pi}{d} |n|\rho\right) \exp\left(2\pi n \frac{\xi}{d}\right)$$
(8.5)

and $\phi_{13}^{\{h_1\}}$ is the sum over all chains in the h_1 plane e.g. in the plane $h_1 = 1$, we have $\xi = a/2$, d = a and $\rho = [(a/2)^2 + (ma + a/2)^2]^{1/2}$, $m = 0, \pm 1, \pm 2, \pm 3$, etc. Because of the exponential decrease of K_0 , only few terms have to be calculated, in one plane only the chains with small ρ and only terms with small n are significant. For planes with larger distances $h_1 a/2$ the contributions also can be neglected. This is a case where only the nearest planes are important (compare Table IV). In this way we can easily calculate the planar force constants to a high degree of accuracy. The results are given in Table IV. The last column gives the relation between sound velocity c and elastic moduli which is valid for all cubic lattices. The comparison with experimental dispersion curves is gratifying (Fig. 19). From Table IV we see that for the (100) and (110) directions we obtain an almost pure sin-function because the

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चे	e	1st neighbour plane	2nd neighbour plane	3rd neighbour plane	distance between planes	$\rho_0 c^2 = \rho_0 \omega^2 / q^2$
q(100)	т₫	- 2, 088	0.164	-0.006	a/2	C ₄₄
	n q					с ₁₁
$\frac{q}{\sqrt{3}}(111)$	⊥ q	2, 795	- 1.055	0.719	a/√3	$\frac{c_{11} - c_{12} + c_{44}}{3}$
	q					$\frac{c_{11} + 2c_{12} + 4c_{44}}{3}$
$\frac{q}{\sqrt{2}}(110)$	$\frac{1}{2}(1-10)$	- 0, 109	0.0024	0		$\frac{c_{11} - c_{12}}{2}$
	(001)	- 0, 756	0.0038	-0.0003	a/√2	C ₄₄
	॥ व्					$\frac{c_{11} + 2c_{44}}{2}$

TABLE IV. PLANAR FORCE CONSTANTS FOR bcc LATTICE (IN UNITS OF e^2/a^3) AND RELATION BETWEEN SOUND VELOCITIES c AND ELASTIC MODULI $c_{\alpha\beta}$ FOR WAVES IN SYMMETRICAL DIRECTIONS

contributions of the nearest-neighbour planes are so large. In the (111) direction more planes have to be taken into account. From the last column we can calculate the two shear moduli c_{44} and $(c_{11} - c_{12})/2$. For the sake of simplicity, we consider only the nearest planes, where for small q according to Eq.(8.1):

$$M\omega^{2} = -4 \phi^{\{np\}} \left(\frac{qX_{p}}{2}\right)^{2} = -\phi^{\{np\}} X_{p}^{2} q^{2}$$

or $c^2 = -\phi^{\{np\}} \frac{X_p^2}{M}$

Here $\phi^{\{np\}}$ is the force constant of the nearest plane according to Table IV and X_p is the distance between the planes. Consequently, for

$$\vec{q} = q(100) \ (\rho_0 = M/V_z = M2/a^3)$$

we have $c^2 \approx 2.088 \frac{e^2}{a^3} \frac{a^2}{4M} \approx c_{44}/\rho_0$, $c_{44} \approx 2.088 \frac{e^2}{2a^4}$ and for $\vec{q} = \frac{q}{\sqrt{3}}$ (110), $e = \frac{1}{\sqrt{2}}$ (1 -10)

are get $c^2 \approx 0.109 \frac{e^2}{a^3} \frac{a^2}{2M} \approx (c_{11} - c_{12})/2\rho_0$, $\frac{c_{11} - c_{12}}{2} \approx 0.109 \frac{e^2}{a^4}$



FIG. 19. Transverse dispersion curves for

Na, $\omega_{\rm p} = \left\{ \frac{8\pi e^2}{{\rm Ma}^3} \right\}^{\frac{1}{2}} = 4.5 \times 10^{-13} {\rm s}^{-1}$ for Na.

calculated from Table IV.

 \circ \circ experimental points (A.D.B. Woods in Inelastic Scattering of Neutrons in Solids and Liquids (Proc. Symp. Chalk River, 1962) 2, IAEA, Vienna (1963) 3.

It is seen that the alkalis must be highly anisotropic because the two shear moduli differ by about a factor of 10 which is also observed experimentally. The absolute magnitude agrees with experimental moduli rather well, too.

One world should be said about fitting to macroscopic data, dispersion curves, etc. These data depend on temperature. For high temperatures (T > Debye temperature) the experimental data depend linearly on T. The harmonic data can be obtained by extrapolating the experimental data down to T = 0. Otherwise, the data at elevated temperatures can show, for example, deviations from the Cauchy relations even for simple crystals with central forces. This extrapolation to T = 0 from high temperatures allows us to avoid anharmonic effects which are also present at T = 0.

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ELECTRON DYNAMICS AND TRANSPORT IN METALS AND SEMICONDUCTORS

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Abstract

1. DYNAMICS OF BLOCH ELECTRONS. 1.1. The velocity of a Bloch state. 1.2. The effect of an external field. 1.2.1. Wannier functions. 1.2.2. Equivalent Hamiltonian. 1.3. Bloch electrons in magnetic fields.

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APPENDIX.

1. DYNAMICS OF BLOCH ELECTRONS

The main object of our attention in this course is the fact that "free" conduction electrons, inside a solid crystal, are constantly under the influence of a periodic field. We assume that the many-body problem has already been dealt with, the simple particle picture derived, etc. Still our particle cannot behave as an entirely free electron, always being subject to the field inside the crystal. But it is this object, the electron constrained by its interaction with the periodic field, which is always responding to the forces we apply from the outside in our experiments so that we need a description in terms of Bloch electrons dynamics.

1.1. The velocity of a Bloch state

The first question to ask is: How does a Bloch electron move by itself? Follow Weinreich (1965, Chapter 6).

Take an electron in a stationary Bloch state

$$\psi_{\vec{n}\vec{k}}(\vec{r}) = u_{\vec{n}\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$
(1)

obeying stationary state Schrödinger equation

$$\mathcal{H}\psi_{\vec{n}\vec{k}} = \mathscr{B}_{\vec{n}}(\vec{k})\psi_{\vec{n}\vec{k}} = \left\{-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right\}\psi_{\vec{n}\vec{k}}$$
(2)

Using (1) in (2), we rewrite

$$\mathscr{H}_{\vec{k}} u_{\vec{n}\vec{k}}(\vec{r}) \equiv \left\{ -\frac{\hbar^2}{2m} \left(\nabla + i\vec{k} \right)^2 + U(\vec{r}) \right\} u_{\vec{n}\vec{k}}(\vec{r}) = \mathscr{E}_{\vec{n}}(\vec{k}) u_{\vec{n}\vec{k}}(\vec{r})$$
(3)

Taking the expectation value of the electron momentum

$$\langle \vec{p} \rangle_{\vec{n}\vec{k}} = \int u_{\vec{n}\vec{k}}^{*} \vec{r} \cdot e^{-\vec{i}\vec{k}\cdot\vec{r}} \frac{\hbar}{i} \nabla u_{\vec{n}\vec{k}}(r) e^{\vec{i}\vec{k}\cdot\vec{r}} d^{3}r$$
(4)

we can redefine, due to crystal periodicity, our wave functions so that they are normalized in one unit cell and, transforming (4), write

$$\langle \vec{\mathbf{p}} \rangle_{\vec{\mathbf{n}}\vec{\mathbf{k}}} = \int u_{\vec{\mathbf{n}}\vec{\mathbf{k}}}(\vec{\mathbf{r}}) \left(\frac{\hbar}{i} \nabla + \hbar \vec{\mathbf{k}} \right) u_{\vec{\mathbf{n}}\vec{\mathbf{k}}}(\vec{\mathbf{r}}) d^{3}\mathbf{r}$$
(5)

where the integration is carried out over one unit cell.

With

$$\nabla_{\vec{k}} \mathcal{H}_{\vec{k}} = \frac{\hbar}{m} \left(\frac{\hbar}{i} \nabla + \hbar \vec{k} \right)$$
(6)

we obtain

$$\langle \mathbf{p} \rangle_{\mathbf{n}\vec{k}} = \frac{\mathbf{m}}{\hbar} \int \mathbf{u}_{\mathbf{n}\vec{k}}^{*}(\vec{\mathbf{r}}) \left\{ \nabla_{\vec{k}} \mathcal{H}_{\vec{k}} \right\} \mathbf{u}_{\mathbf{n}\vec{k}}(\vec{\mathbf{r}}) d^{3}\mathbf{r}$$
 (7)

Now, there is a nice theorem due to Hellmann and to Feynman (1939) which comes in very handy. This theorem has been recovered by Morgan and Landsberg (1965) from a study of sum rules and the hypervirial theorem in Quantum Mechanics, which is rather interesting in itself. We can state it as follows: Let $\mathscr{H}(\alpha)$ be a Hermitian operator which depends on a parameter (or set of parameters) α , and let $\varphi_{\alpha}(\mathbf{r})$ be a normalized eigenfunction of $\mathscr{H}(\alpha)$, with eigenvalue $\lambda(\alpha)$. Then

 $\langle \varphi_{\alpha} | \frac{\partial \mathscr{H}}{\partial \alpha} | \varphi_{\alpha} \rangle = \frac{\partial}{\partial \alpha} \langle \varphi_{\alpha} | \mathscr{H} | \varphi_{\alpha} \rangle = \frac{\partial \lambda(\alpha)}{\partial \alpha}$ (8)

Thus, from (7) and (3), the velocity of a Bloch state is

 $\langle \vec{\mathbf{v}} \rangle_{\overrightarrow{\mathbf{n}}\overrightarrow{\mathbf{k}}} = \langle \frac{1}{m} \vec{\mathbf{p}} \rangle_{\overrightarrow{\mathbf{n}}\overrightarrow{\mathbf{k}}} = \frac{1}{n} \nabla_{\overrightarrow{\mathbf{k}}} \mathscr{B}_{n}(\vec{\mathbf{k}})$ (9)

which we shall often write as $\vec{v}_{n\,\vec{k}}$ or $\vec{v}_{\vec{k}}$, when the band index can be omitted without confusion.

This is a rather interesting result, and one which constitutes a typical result of quantum theory. It turns out that the particle moves quite easily through an array of obstacles. Now, a particle in a stationary state would correspond to a monochromatic wave of frequency (in this case) $\hbar^{-1} \mathscr{E}_{n}(\vec{k})$. Moreover, unless we invoke some perturbation to destroy this state of affairs the stationary state is never destroyed, which corresponds to a wave propagating through a non-dissipative medium. The only difference to the vacuum is the fact that frequency ω and propagation vector \vec{k} are related by a non-linear dispersion relation $\omega(\vec{k})$, determined by the structure of the band. Thus, each frequency has a different propagation velocity and, being a monochromatic wave in a non-dissipative medium, this is given by the group velocity

$$\vec{\mathbf{v}}_{\vec{k}} = \nabla_{\vec{k}} \omega \tag{10}$$

which is the same formula as (9) and constitutes its interpretation in terms of waves instead of particles.

1.2. The effect of an external field

How, then, does a Bloch electron respond to external forces? It is clear that we cannot describe this simply by a straight-forward application of Newton's law, since the acceleration of the momentum is given by the <u>total</u> force, of which that due to the external field is only a part. Once we have "dressed" the particle, to account for its constant interaction with the field inside, we have to use a more involved language to describe its response to the external forces. Since the state of motion is determined by its wave vector \vec{k} , we seek the way in which \vec{k} changes with time, as a result of an external potential $U(\vec{r})$. Then, in the new states, we know how to calculate the velocity again, and so on.

A fully rigorous answer to this question constitutes a rather difficult problem. Detailed discussions have been given by Weinreich (1965), Wannier (1959) and Blount (1962) and, in less rigorous but more readable terms, by Callaway (1964), Ziman (1964) and Slater (1967) among others. We shall mostly follow Ziman's treatment.

1.2.1. Wannier functions

Now suppose we want to describe the electron as being <u>here</u> or <u>there</u> in the crystal. Taking all Bloch functions of a band and adding them up, we obtain the sum

$$\frac{1}{\sqrt{N}}\sum_{\vec{k}}\psi_{\vec{n}\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}}e^{i\vec{k}\cdot\vec{r}}u_{\vec{n}\vec{k}}(\vec{r})$$
(11)

(N = number of unit cells)

At the origin (r = 0), this simply adds up all amplitudes $u_{nk}(0)$; the sum has its greatest value. But, for non-zero values of r, the effect of including

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all possible phase factors is to produce a kind of destructive interference, as in the theory of wave diffraction by a central slit. It turns out, after due calculation, that when r is of the order of the radius of the unit cell the interference has become sufficiently destructive that the resulting wave function essentially describes an electron localized within a unit cell, although the actual amplitude still has small wiggles outside the cell. This can (and to achieve full rigour, must) be said in a more technical language, but the result is quite plausible. If we remember that $h\vec{k}$ is something like the momentum (we shall come back to this), and that the size of the Brillouin zone is of the order of π/a (a = lattice constant), we expect that on going from a definite "momentum" $h\vec{k}$ to a state like Eq.(11) in which the uncertainty in the momentum is spread over a size of the order of h/a, the uncertainty in position is approximately reduced to within a unit cell.

There is an easy trick in localizing the electron at any other unit cell labelled by position vestor \vec{R} . Just form

$$a_{n}(\vec{r} - \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-\vec{i}\vec{k} \cdot \vec{R}} \psi_{n\vec{k}}(\vec{r})$$
(12)

and everything is now shifted to the cell \vec{R} instead of the cell at the origin. In fact Eq.(12) defines a unitary transformation from the basis $\psi_{\vec{nk}}(\vec{r})$ to the basis $a_n(\vec{r} \cdot \vec{R})$, which we may sometimes denote by $a_{\vec{nR}}$. It is formally proved that these functions (the <u>Wannier functions</u>) form a proper basis and it is easily seen that

$$\langle \mathbf{a}_{\vec{n}\vec{R}} | \mathbf{a}_{\vec{n}\vec{R}}, \rangle = \frac{1}{N} \sum_{\vec{k},\vec{k}'} \mathbf{e}^{i(\vec{k}\cdot\vec{R}-\vec{k}\cdot\vec{R}')} \langle \psi_{\vec{n}\vec{k}} | \psi_{\vec{n}\vec{k}'} \rangle$$

$$= \frac{1}{N} \sum_{\vec{k}} \mathbf{e}^{i\vec{k}\cdot\vec{(R}-\vec{R}')} = \delta_{\vec{R},\vec{R}'}$$

$$(13)$$

Thus, Wannier functions centered on adjacent lattice sites are orthogonal.

Notice also that there is one set of Wannier functions for each different band. It is also proved that functions with different band indices are orthogonal.

Thus, we have changed to a new orthonormal basis. Now, what do we do with it? In a conductor, where charge carriers run freely from cell to cell, this description in terms of localized states is not the most appropriate for a direct physical picture. In fact, Wannier functions are not typically used for actual calculations, but they are useful for proving theorems.

1.2.2. Equivalent Hamiltonian

Clearly, the $a_{n\vec{R}}$ are not eigenfunctions of the Bloch Hamiltonian. Instead,

$$\mathcal{H}a_{n}(\vec{r} - \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-\vec{i}\vec{k} \cdot \vec{R}} \psi_{n\vec{k}}(\vec{r})$$

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$$= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-\vec{i}\vec{k}\cdot\vec{R}} \mathscr{G}_{n}(\vec{k}) \psi_{n\vec{k}}(\vec{r})$$
$$= \frac{1}{N} \sum_{\vec{k},\vec{R'}} e^{-\vec{k}\cdot\vec{R}} \mathscr{G}_{n}(\vec{k}) e^{i\vec{k}\cdot\vec{R'}} a_{n}(\vec{r}-\vec{R'})$$
(14)

The last equality follows from inverting Eq.(12). Defining the Fourier transform

$$\mathscr{B}_{n}(\vec{R}) = \frac{1}{N} \sum_{\vec{k}} e^{-\vec{i}\vec{k} \cdot \vec{R}} \mathscr{B}_{n}(\vec{k})$$
(15)

(since $\mathscr{O}_n(\vec{k})$ is periodic with the periodicity of the reciprocal lattice) we have from Eq.(14):

$$\mathcal{H}a_{\vec{n}\vec{R}} = \sum_{\vec{R}'} \mathscr{E}_{\vec{n}}(\vec{R} - \vec{R}') a_{\vec{n}\vec{R}}, \qquad (16)$$

Let us now suppose that an external potential $U(\vec{r})$ is applied. This will change the stationary states of motion, so we look into the time-dependent Schrödinger equation for a time dependent wavefunction:

$$(\mathscr{U} + \mathbf{U})\psi(\vec{\mathbf{r}}, t) = i\hbar \frac{\partial\psi(\vec{\mathbf{r}}, t)}{\partial t}$$
 (17)

and use a Wannier representation

$$\psi(\vec{\mathbf{r}},t) = \sum_{n\vec{R}} f_n(\vec{R},t) a_{n\vec{R}}$$
(18)

Our task is to find the $f_{n\vec{R}}$. Substituting into Eq.(17), taking the scalar product with $a_{n'\vec{R}'}$ and writing

$$U_{nn'}(\vec{R},\vec{R}') = \langle a_{n\vec{R}} | U | a_{n'\vec{R}} \rangle$$
(19)

we have with the help of Eq.(16):

$$\sum_{n\vec{R}} \left\{ \delta_{nn'} \mathscr{E}_{n}(\vec{R} - \vec{R}') + U_{nn'}(\vec{R}, \vec{R}') \right\} f_{n}(\vec{R}, t) = i\hbar \frac{\partial f_{n'}(\vec{R}, t)}{\partial t}$$
(20)

So far, this is a mere (and exact) rewriting of Eq.(17). The idea behind the equivalent Hamiltonian formulation is to consider the inversion of Eq.(15), i.e. $\nabla \vec{x} \neq \vec{x}$

$$\mathscr{B}_{n}(\vec{k}) = \sum_{\vec{k}''} e^{i\vec{k}\cdot\vec{R}''} \mathscr{B}_{n}(\vec{R}'')$$
(21)

to rewrite this in terms of a crystal momentum $\hbar \vec{k}$, to replace it by the operator $-i\hbar \nabla$, which means replacing \vec{k} by $-i\nabla$, and to see how this is inserted in Eq.(20).

It is easy enough to do the calculation, but let us pause for a brief digression. We know from general quantum theory (Dirac, 1947, section 25) that the momentum, being canonically conjugate to the position, is the displacement operator which generates infinitesimal translations. For a system with translational invariance, an infinitesimal translation is a symmetry operation of the system and a symmetry invariance is always related to a constant of the motion. The momentum, indeed, is a constant of the motion for such a system. But now we are dealing with a <u>lattice</u>, with discrete positions \vec{R} , and the symmetry operations are the discrete translations \vec{R} . Indeed, if we investigate the effect of the momentum operator on a Bloch wave function we find

$$-i\hbar\nabla\psi_{\vec{n}\vec{k}}(\vec{r}) = -i\hbar\nabla\left\{u_{\vec{n}\vec{k}}(\vec{r})e^{\vec{n}\vec{k}\cdot\vec{r}}\right\} = \hbar\vec{k}\psi_{\vec{n}\vec{k}}(\vec{r}) - i\hbar e^{\vec{n}\vec{k}\cdot\vec{r}}\nabla u_{\vec{n}\vec{k}}(\vec{r})$$
(22)

and, what do we do with the extra term on the right-hand side?

Let us <u>define</u> a crystal momentum operator $ec{P}$ through the eigenvalue equation

$$\hat{\vec{P}}\psi_{\vec{n}\vec{k}}(\vec{r}) = \hbar \vec{k}\psi_{\vec{n}\vec{k}}(\vec{r})$$
(23)

and let us investigate its effect on an arbitrary function $F(\vec{r})$, which we shall naturally expand in the basis of \vec{P} :

$$\mathbf{F}(\vec{\mathbf{r}}) = \sum_{n\vec{\mathbf{k}}} \mathbf{A}_{n}(\vec{\mathbf{k}}) \psi_{n\vec{\mathbf{k}}}(\vec{\mathbf{r}})$$
(24)

What we actually want is the effect of the exponential operator $\exp(i \vec{\vec{P}} \cdot \vec{\vec{R}} / \hbar)$. From Eqs (23) and (24), we have:

$$e^{i\vec{\vec{p}}\cdot\vec{\vec{k}}/\hbar} F(\vec{r}) = \sum_{n\vec{k}} A_{n'}(\vec{k}) e^{i\vec{\vec{p}}\cdot\vec{\vec{k}}/\hbar} \psi_{n\vec{k}}(\vec{r})$$

$$= \sum_{n\vec{k}} A_{n}(k) e^{i\vec{k}\cdot\vec{\vec{k}}} \psi_{n\vec{k}}(r)$$

$$= \sum_{n\vec{k}} A_{n}(\vec{k}) u_{n\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{(r+\vec{k})}}$$
(25)

Now, if and only if \vec{R} is a lattice translation, the periodicity of $u_{n\vec{k}}(\vec{r})$ allows us to replace its argument by $\vec{r} + \vec{R}$, whereby Eq.(25) becomes

$$e^{i\vec{\vec{p}}\cdot\vec{\vec{k}}/\hbar} F(\vec{r}) = F(\vec{r}+\vec{R})$$
(26)

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Thus, the operator whose eigenfunctions are the Bloch functions and whose eigenvalues are the allowed values of $\hbar \vec{k}$, generates the lattice translations, which are the symmetry operations of our problem. This is why \vec{k} is a good quantum number, a constant of the motion, and serves to label the Bloch states. Therefore, this operator is <u>not</u> canonically conjugate to the position operator with continuous eigenvalues \vec{r} and the replacement of \vec{k} by $-i\nabla$ "must be taken with a tablespoon of salt" as remarked by Weinreich, who follows this up with detail. However, after due regard for formal considerations it turns out that the procedure we shall presently continue is justified provided one is dealing with slowly varying perturbations, etc. Thus, we shall simply notice that there is here a non-trivial formal question, and shall carry on with what is done in practice.

We now come back to Eqs (21) and (20), and regard the expansion coefficients $f_n(\vec{R}, t)$ as the numerical values taken at position \vec{R} by a smooth, continuous, differentiable function $f_n(\vec{r}, t)$, replace \vec{k} by $-i\nabla$ and obtain

$$\mathscr{E}_{n}(-i\nabla)f_{n}(\vec{\mathbf{r}},t) = \sum_{\vec{\mathbf{R}}^{n}} \mathscr{E}_{n}(\vec{\mathbf{R}}^{n})e^{\vec{\mathbf{R}}^{n}\nabla}f_{n}(\vec{\mathbf{r}},t)$$
$$= \sum_{\vec{\mathbf{R}}^{n}} \mathscr{E}_{n}(\vec{\mathbf{R}}^{n})f_{n}(\vec{\mathbf{r}}+\vec{\mathbf{R}}^{n},t) \qquad (27)$$

Thus, Eq.(20) reads

$$\begin{bmatrix} \mathscr{G}_{n'}(-i\nabla)f_{n'}(\vec{r},t) - i\hbar\frac{\partial f_{n}(\vec{r},t)}{\partial t} \end{bmatrix}_{\vec{r}=\vec{R}'} + \sum_{n,\vec{R}} U_{nn'}(\vec{R},\vec{R}')f_{n}(\vec{R},t) = 0$$
(28)

We are back to a kind of Schrödinger equation in which the perturbation is written in the Wannier representation, and the effective unperturbed Hamiltonian is obtained by replacing \vec{k} by $-i\nabla$ in the unperturbed eigenvalues \mathscr{G}_{n} . (\vec{k}) .

This is still a rather clumsy differential equation but, if we are not explicitly interested in perturbations capable of inducing interband transitions, then $U_{n\,n'}$ is diagonal in the band index and we only have to use Wannier functions of one band. If, furthermore, the external potential is sufficiently slowly warying, as is usually the case with electric fields in conductors, then we can take $U_{n'}(\vec{R}, \vec{R}')$ as diagonal in the lattice position indices, and we are reduced to the diagonal matrix element

$$U_{n'n'}(\vec{R}, \vec{R}) = [U(\vec{r})]_{\vec{r}=\vec{R}}$$
(29)

At last we happily forget about discrete lattice positions and we write the effective equation of motion (dropping the prime from the band index)

$$\left\{\mathscr{B}_{n}(-i\nabla) - i\hbar\frac{\partial}{\partial t}\right\}f_{n}(\vec{r},t) + U(\vec{r})f_{n}(\vec{r},t) = 0$$
(30)

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Thus, we are describing the problem in terms of an equivalent classical Hamiltonian

$$\mathscr{H}(\vec{\mathbf{r}},\vec{\mathbf{h}}\,\vec{\mathbf{k}}) = \mathscr{G}(\vec{\mathbf{k}}) + U(\vec{\mathbf{r}})$$
(31)

in which we take $h\vec{k}$ as canonically conjugate to \vec{r} and replace \vec{k} by $-i\nabla$. Taking all this for granted, we need only write down at once Hamilton's equations

$$\dot{\vec{r}} = \nabla_{\vec{h}\vec{k}} \mathcal{H}; \quad \dot{\vec{h}} = -\nabla \mathcal{H}$$
 (32)

The first one reproduces Eq.(9) for the unperturbed velocity, while the second one gives the equation we were seeking as a substitute for Newton's law. With U = $-q \vec{E} \cdot \vec{r}$, we obtain

$$\vec{h} \vec{k} = q \vec{E}$$
(33)

Thus, the quantity whose rate of change is the <u>external force</u> is the <u>crystal</u> <u>momentum</u>, not the electron momentum. As emphasized by Kittel (1954), this has a simple physical interpretation in terms of the momentum transferred between the electron and the lattice.

Expanding the periodic function of Eq.(22) as

$$u_{\vec{n}\vec{k}}(\vec{r}) = \sum_{\vec{k}} \alpha_{\vec{n}\vec{K}}(\vec{k}) e^{i\vec{K}\cdot\vec{r}}$$
(34)

the expectation value of the electronic momentum (dropping the band index) is

$$\langle \vec{p} \rangle = \langle \psi_{\vec{n}\vec{k}} | -i \nabla | \psi_{\vec{n}\vec{k}} \rangle = \vec{n}\vec{k} + \vec{n}\sum_{\vec{k}}\vec{K} | \alpha_{\vec{k}}(\vec{k}) |^2$$
(35)

Suppose under the influence of an external field the state of motion of the electron is changed so that its crystal momentum changes from $h\vec{k}$ to $h(\vec{k}+\delta\vec{k})$. The true momentum of the electron then changes by

$$\delta \langle \vec{p} \rangle = \hbar \,\delta \,\vec{k} + \sum_{\vec{k}} \hbar \,\vec{K} \left\{ \nabla_{\vec{k}} \left| a_{\vec{k}} (\vec{k}) \right|^2 \,\delta \,\vec{k} \right\}$$
(36)

Since the electron interacts with the lattice, a change in electronic momentum entails a momentum transfer to the lattice and, since $\hbar \delta \vec{k}$ is the total momentum change seen from the outside, the above equation is equivalent to

$$\hbar \,\delta \,\vec{k} = \delta \langle \vec{p} \rangle + \delta \,\vec{p}_{lat} \tag{37}$$

whence

$$\delta \vec{\vec{p}}_{lat} = -\sum_{\vec{k}} \hbar \vec{\vec{K}} \left\{ \nabla_{\vec{k}} | \alpha_{\vec{k}}(\vec{k}) |^2 \delta \vec{k} \right\}$$
(38)

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that is to say, the lattice sees the process as a superposition of Bragg scattering events, with momentum transfer $-\hbar \vec{K}$, with a weight factor arising from the corresponding admixture of \vec{K} vector in Eq.(34), i.e. in the Bloch state of wave function $\psi_{\vec{nk}}$. It is always instructive to interpret the interaction of the electron with the lattice from the viewpoint of diffraction theory, as one may realize from band theory.

Furthermore, from Eqs (35) and (32), we have

$$\nabla_{\mathbf{k}} \mathscr{E}(\vec{\mathbf{k}}) = \frac{\hbar^2}{m} \left\{ \vec{\mathbf{k}} + \sum_{\vec{\mathbf{k}}} \vec{\mathbf{K}} \left| \alpha_{\vec{\mathbf{k}}}(\vec{\mathbf{k}}) \right|^2 \right\}$$
(39)

whence the standard formula for the inverse effective mass tensor yields

$$\left[\vec{\mathscr{M}}\right]_{ij}^{1} = \frac{1}{\hbar^{2}} \frac{\partial^{2} \mathscr{E}(\vec{k})}{\partial k_{i} \partial k_{j}} = \frac{1}{m} \left\{ \delta_{ij} + \sum_{\vec{k}} K_{i} \frac{\partial}{\partial k_{j}} \left| \alpha_{\vec{k}}(\vec{k}) \right|^{2} \right\}$$
(40)

Comparing with Eq. (36) we find another interpretation of the crystal momentum:

$$\frac{\delta \langle \vec{\mathbf{p}} \rangle}{m} = \vec{\mathcal{M}}^{-1} \hbar \, \delta \, \vec{\mathbf{k}}$$
(41)

Thus, the usual definition of the effective mass gives the apparent coefficient of inertia with which Bloch electrons respond to the external field when we describe the dynamics in terms of the apparent Newton's law of Eq.(33).

1.2.3. Bloch electrons in magnetic fields

The case of a magnetic field is very different, and always more subtle. We could for example quickly obtain a result like Eq. (33) in the following (more intuitive than rigorous) way: let an electron be in a state \vec{k} with energy $\mathscr{E}(\vec{k})$. After a time interval dt, equating the energy change to the work done by the field; we get:

$$d\mathscr{B} = \frac{d\mathscr{B}}{dt} dt = \nabla_{\vec{k}} \mathscr{B} \cdot \vec{k} dt = q \vec{E} \cdot \vec{v} dt = \hbar \vec{v} \cdot \vec{k} dt$$
(42)

thus $\hbar \vec{k} = q\vec{E}$. Now we try to play the same tric for the Lorentz force

$$\vec{F}_{I} = \frac{q}{c} \vec{v} \times \vec{H}$$
(43)

and we get nothing at all because, F_L being at a right angle with $\vec{v},$ it does not perform any work.

Let us consider the difficulties of the quantum mechanical treatment. We might start with a Hamiltonian in the presence of a magnetic field, which is then perturbed by the periodic potential. We can do this because the magnetic field (unlike the electric field) has stationary states (the quantized cyclotron orbits, or Landau states), which are the eigenstates of the Hamiltonian

$$\frac{1}{2m} \left(\tilde{\vec{p}} - \frac{q}{c} \tilde{\vec{A}} \right)^2$$
(44)

where \vec{A} is the vector potential ($\vec{H} = \operatorname{curl} \vec{A}$) and \vec{p} is the canonical momentum, conjugate to the position, i.e. the vector in brackets is the kinetic momentum (Appendix). An explicit solution of the problem of adding the perturbation of the crystal potential to this Hamiltonian would be, in the first place, very cumbersome and, in the second place, it would be rather more like attempting a band structure calculation in the presence of a magnetic field. Such a standpoint may be suitable for other purposes, but what we really want is an acceleration equation for Bloch electrons, i.e. we want to start from the stationary states of the crystal and to see how these states change in time due to the effect of the magnetic field. Thus we write down the Hamiltonian

$$\frac{1}{2m}\left(\vec{\tilde{p}} - \frac{q}{c}\vec{A}\right)^2 + V(\vec{r})$$
(45)

and look at it as the Bloch Hamiltonian perturbed by the addition of \vec{A} . We are, however, dealing with a theoretically infinite crystal, and for a homogeneous magnetic field, a vector potential increasing linearly with \vec{r} and, therefore, capable of assuming arbitrarity large values cannot be treated as a perturbation.

One possible way (Wilson, 1954, Chapter 2; Slater, 1967, Appendix A) is to form a wave packet and to choose a gauge in which the mean value of \vec{A} is zero. This consists essentially of making \vec{A} assume instantaneous values such that it becomes vanishingly small on getting close to the centre of the packet. The term in A^2 can then be neglected and the linear term, which involves the spatial derivatives of \vec{A} , gives in fact a perturbation linear in the magnetic field strength. One can then proceed to study the acceleration of the wave packet by time-dependent perturbation theory. This procedure is not entirely desirable; it is not too elegant since it depends on a particular choice of gauge, and it finally establishes the desired result provided the magnetic field strength is less than a certain upper value which, in view of later developments, seems too restrictive.

There is a more attractive promise in the effective Hamiltonian approach. The perturbation due to the electric field is also linear in \vec{r} (it is equal to $\vec{q} \cdot \vec{E}$, for a uniform electric field). But the effective Hamiltonian theory is designed to cope with extended perturbations, provided they are slowly varying. The kind of argument we would like to put forward runs as follows:

For $\vec{A} = 0$ we start from the actual Hamiltonian

$$\frac{1}{2m}$$
 p² + V

and arrive at the effective Hamiltonian

$$\mathscr{F}_{n}(\vec{k}) ; \vec{k} = -i\nabla$$
(46)

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for states in the n-th band. Thus, for $\vec{A} \neq 0$ we start from the actual Hamiltonian (45) and arrive at the effective Hamiltonian

$$\mathscr{B}_{n}(\hat{\vec{k}}) \ \vec{k} = -i \ \nabla - \frac{q}{\hbar c} \ \vec{A}$$
(47)

It is this last step which creates difficulties which are specifically due to the nature of the vector potential. The crux of the matter lies in the diagonalization with respect to the band index. If this cannot be achieved, there is no point in the effective Hamiltonian theory (we do not want to have to use wave functions from different bands together). Luttinger and Kohn (1955) derived the effective Hamiltonian theory using a representation in which one can see very directly (Kohn, 1959) that the Hamiltonian (45) has non diagonal matrix elements between bands of different indices. Thus the derivation of (47) as an effective Hamiltonian for states in <u>one</u> band, requires an explicit justification, and this is done in the specialized articles (see also Weinreich, 1965, Chapter 9).

One would now think that in the presence of crossed electric and magnetic fields, with

$$\vec{E} = -\nabla \varphi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t}, \quad \vec{H} = \nabla \times \vec{A}$$
(48)

having justified (31) and (47) separately, the total equivalent Hamiltonian is obviously

$$\mathscr{E}_{n}(\vec{k}) + q \varphi; \quad \vec{k} = -i \nabla - \frac{q}{\hbar c} \vec{A}$$
 (49)

However (Zak and Zawadzki, 1966), this also involves some subtleties. To put it briefly, when two perturbations are acting simultaneously and if a diagonalization procedure has to be carried out, the non-diagonal elements of <u>one</u> perturbation must be small also compared with the diagonal elements of the <u>other</u> perturbation. This ultimately imposes a restriction on the ratio E/H (in the case where qEa $\ll \hbar \omega_c$, where a is the lattice constant and ω_c is the cyclotron frequency).

The above digression is only meant to give an informative glimpse into the rigorous quantum dynamics of Bloch electrons, which is a very difficult problem and is still far from being completely solved. However, for the kind of problems we shall cover in this course a semiclassical picture is sufficient (Lifshitz and Kaganov, 1960). Thus, for the practical purpose of deriving acceleration equations we proceed as in the case of an electric field alone. We go back to the semiclassical Hamiltonian (49) and use Hamilton's equations.

$$\frac{d\vec{p}}{dt} = -\nabla \mathscr{B}_{n} - q \nabla \varphi = \frac{q}{c} \nabla_{\vec{p}} \mathscr{B}_{n} \cdot \nabla \vec{A} - q \nabla \varphi$$
(50)

$$\frac{d\vec{r}}{dt} = \nabla_{\vec{p}} \, \mathscr{E}_n = \nabla_{\vec{p}} \, \mathscr{E}_n \tag{51}$$

and

Furthermore

$$\mathbf{h}\,\vec{\mathbf{k}} = \frac{d\vec{p}}{dt} - \frac{\mathbf{q}}{\mathbf{c}}\frac{\partial\vec{A}}{\partial t} - \frac{\mathbf{q}}{\mathbf{c}}\nabla\vec{A}\cdot\frac{d\vec{\mathbf{r}}}{dt}$$
(52)

Putting together these equations, and using the identity

$$-\vec{v}\cdot\nabla\vec{A} + \nabla\vec{A}\cdot\vec{v} \equiv \vec{v}\times(\nabla\times\vec{A})$$
(53)

we finally obtain putting back the indices for the sate, etc.

$$\hbar \vec{k} = q \left(\vec{E} + \frac{1}{c} \vec{v} \times \vec{H} \right)$$
(54)

which is the expected equation for the "crystal kinetic momentum" under the influence of the complete Lorentz force. Notice that, since $\vec{v}_{\vec{k}}$ is proportional to $\nabla_{\vec{k}} \mathscr{E}(k)$ and is therefore normal to the constant energy surface, the state of the particle is, under the influence of the magnetic field alone, precisely the curve (in \vec{k} space) determined by the intersection of the surface of energy \mathscr{E} and the plane perpendicular to the direction of the magnetic field.

2. TRANSPORT THEORY IN SOLIDS WITH NO MAGNETIC FIELD

While the electronic theory of the solid state, and the scope of the band picture, have recently undergone significant changes and are at present in a state of effervescence, there has been nothing really spectacular, which would be likely to have a similar impact at the level of the everyday practitioner, in the field of transport theory in solids. There are, of course, profound questions concerning the rigorous quantum theoretical foundation of the Boltzmann equation, byzantine questions concerning ergodicity, etc. But, by and large, this topic is rather a "classic" in solid state theory. The Boltzmann equation has been rederived in countless different ways, sometimes gaining further understanding of the limitations of its validity, the implications of manybody interactions have been carefully scrutinized, but in the end almost always one comes around to the Boltzmann equation and the practical question is how to solve it. In these lectures we shall approach the subject in this "classic" mood, and we shall work in a semiclassical frame. Lack of time prevents us from going into specifically quantum effects in high magnetic fields. As a matter of fact, such effects are of paramount importance in the study of the magnetic susceptibility of the conduction electrons, and you will see it in the lectures on Fermiology (de Haas-van Alphen effect). But in transport phenomena the quantization due to a magnetic field only introduces (when the field is very high) small variations on top of a classical pattern of behaviour. The typical situation consists in, say, a curve plotting the resistivity of a metal as a function of magnetic field, which exhibits, in the high field limit, small ripples on top of a curve continuing the previous trend. And this curve can be predicted by the semiclassical theory, and is the part of the story which conveys the greater information.

This will then be the frame of these lectures. We shall take the semiclassical Boltzmann equation picture for granted. It is not the most rigorous procedure one can follow, but it works very well in practice. Lewis (1958) gave a very good discussion, with simple physico-mathematical apparatus, largely explaining why this is the case. Finally, although this is outside our scope, there is the question of why some solids are conductors while others are insolators. It might be in order to remark that, although we shall constantly use the band picture, it has its limitations. The idea of <u>screening</u> is more important and powerful than the usual story about exclusion principle and filled and empty bands. These ideas, stressed by Mott (1958), are reviewed in qualitative tutorial terms by Cottrell. See also Ziman (1964).

More related to what we have just seen is the curious fact that, granted that a solid has "free" conduction electrons, and is allowed by all respectable theories to be a conductor, it would be radically prevented from carrying any current at all by the very same facts which determine the ability of Bloch electrons to sort out the array of obstacles. We have just seen in Eq. (33) how they are accelerated by an electric field. Let us look at the trajectory in <u>real</u> space. Suppose, for simplicity, that the electric field is in a symmetry direction, so we are dealing with a one-dimensional problem. We simply have to integrate:

$$\mathbf{r} - \mathbf{r}_{0} = \int_{0}^{t} \mathbf{v} \, dt = \int_{0}^{t} \frac{1}{\hbar} \frac{\partial \mathscr{B}_{n}}{\partial \mathbf{k}} \, dt = \int_{0}^{t} \frac{1}{\hbar} \frac{\partial \mathscr{B}_{n}}{\partial \mathbf{k}} \frac{dt}{d\mathbf{k}} \, d\mathbf{k}$$
(55)

$$= \frac{1}{qE} \int_{0}^{L} \frac{\partial \mathscr{B}_{n}}{\partial k} dk = \frac{1}{qE} \left[\mathscr{B}_{n} \left\{ k(t) \right\} - \mathscr{B}_{n} \left\{ k(0) \right\} \right]$$

Thus, unless the field is sufficiently strong to provoke tunnelling into the next band, as the energy reaches the top value it meets the gap and does not increase any further. At this instant, \vec{k} reaches the frontier of the Brillouin zone and the electronic wave undergoes a Bragg reflexion: The velocity is reversed, the state of motion, having climbed up to the top of the \mathscr{E}_n versus k curve (view it in the repeated zone scheme), starts going down this curve, \mathscr{E}_n decreases again and the actual position in real space recedes. And so on, back and forth, within a span of length equal to the width of the band divided by qE. It turns out, after all, that if a conducting crystal carries any net current at all, it is precisely because of the collisions, which disrupt the otherwise oscillating motion of the conduction electrons. The actual displacements, even after striving to achieve conditions as near to ideal as possible, are always, in real samples, much smaller than the length calculated from Eq. (55). This means that the change in crystal momentum is very small compared with the dimensions of the Brillouin zone, and such a situation permits a displaced distribution which carries a net current. But, after the very existence of scattering has made conduction possible, it is precisely this mechanism which gives rise to the resistance to charge flow.

The topics we shall see in the following lectures are well covered in a number of books and reviews: Beer (1963), Blatt (1959), Brooks (1955), Fan

(1955), Jan (1957), Jones (1956), Lifshitz and Kaganov (1966), Smith (1959), Tsidil'kovskii (1962), Wilson (1954) and Ziman (1960), 1964). Kittel's book (1963) contains also one chapter on the semiclassical theory of magnetoresistance in metals.

2.1. The Boltzmann equation

We shall use a distribution function

 $f(\vec{k}, \vec{r})$

such that

$$f(\vec{k},\vec{r}) d^3k d^3r$$
(56)

gives the probability of finding an electron in the volume element $d^3k d^3r$ of the 6-dimensional phase space (\vec{k}, \vec{r}) . The \vec{r} dependence will be omitted when the sample is homogeneous (which for us, who will not mention real inhomogeneity, means isothermal conduction). In this case we may write the distribution function as $f_{\vec{k}}$. In any case, remembering that on quantizing the momentum space we assign a "volume" h^3 to each quantum state, which means a "volume" $(2\pi)^3$ in \vec{k} space, the number of electrons per unit volume (of real space) with the \vec{k} vector in the element d^3k will be, after (56)

dn = $2 f_{\vec{k}} \frac{d^3 k}{(2\pi)^3}$ (57)

The factor 2 is due to the twofold spin degeneracy. We shall indicate

$$\frac{\mathrm{d}^{3}\mathbf{k}}{(2\pi)^{3}} \equiv \mathbf{d}\vec{\mathbf{k}}$$
(58)

and thus the real concentration of the electron gas will be

$$n = 2 \int f_{\vec{k}} d\vec{k}$$
 (59)

n itself, may be a function of r. In the presence of a thermal gradient, e.g. the distribution function depends on temperature T, which is assumed to be a function of \vec{r} and on the chemical potential, which is also a function of \vec{r} . The very use of these concepts involves an important approximation. In thermal equilibrium (no electric field, no thermal gradient), the distribution is known. We shall indicate it by $f_{\vec{k}}^0$. It is the Maxwell-Boltzmann distribution, for the gas of conduction electrons (or holes) in non-degenerate semiconductors, or the Fermi-Dirac distribution for metals or degenerate semiconductors. The concepts of temperature and chemical potential are then well defined. When the thermal equilibrium is upset, the straightforward use of these concepts is unwarranted. What we do is to assume that the disturbed distribution

$$f_{\vec{k}} = f_{\vec{k}}^{0} + \delta f_{\vec{k}}$$
(60)

is still sufficiently close to equilibrium such that

$$\delta f_{\vec{k}} \ll f_{\vec{k}}^0 \tag{61}$$

and so we linearize in $\delta f_{\vec{k}}$, which is due to the external disturbances. Thus, from the computational point of view, we are performing a linear approximation in the strengths of E and ∇T . From the thermodynamical point of view we assume that the departure from thermal equilibrium is sufficiently small that we can assume, at every local volume element, a <u>local</u> thermal equilibrium, with its own local value for $T(\vec{r})$ and $\zeta(\vec{r})$ (ζ = chemical potential). That is to say, we assume that it is a good approximation to calculate n at every point by inserting $f_{\vec{k}}^0$ in Eq.(59) instead of the actual perturbed distribution.

But we cannot do this to calculate the net flow of anything (mass, charge, energy). We know that the equilibrium distribution does not carry any net flow. The zero-order evaluation yields nothing, and we must evaluate the flows to first order. This requires the knowledge of the true distribution, at least to first order in the driving forces. It is easy enough to describe the changes due to these forces. Liouville's theorem, in statistical mechanics, states that the representative points in phase space move about as if they formed in incompressible fluid. Thus, the total time derivative

$$\frac{\partial \mathbf{f}_{\vec{k}}}{\partial t} + \dot{\vec{k}} \cdot \nabla_{\vec{k}} \mathbf{f}_{\vec{k}} + \dot{\vec{r}} \cdot \nabla_{\vec{k}} \mathbf{f}_{\vec{k}}$$
(62)

ought to be zero. We shall not be interested, in these lectures, in the partial derivative, which is needed when $f_{\overrightarrow{k}}$ is explicitly time-dependent, (the case of variable fields). But we must include another fact in our description: No conduction electron ever does travel through an ideal crystal lattice. All crystals contain imperfections of some sort, and these random obstacles are really felt by the electrons in the form of collisions by which they are scattered. Even if a lattice does not contain any constitutional imperfections all lattices vibrate as a consequence of thermal agitation, and an electron reaching a lattice point would find the local ion randomly displaced and bump off. And even if this were not the case, we would still have to enquire about mutual collisions between the electrons. Thus, from whatever source, we must include the effect of collisions through a term which we shall indicate by

$$(f_{\overrightarrow{k}})_{k \text{ col}}$$

The derivative written in (62) is not zero but, instead,

$$\vec{k} \cdot \nabla_{\vec{k}} \vec{f}_{\vec{k}} + \vec{r} \cdot \nabla_{\vec{k}} = (\vec{f}_{\vec{k}})_{\text{coll}}$$
(63)

It is instructive to interpret this equation. Representative points in the 6-dimensional element $d^3k d^3r$, centred at (\vec{k}, \vec{r}) at time t were all, at
time t-dt, in the volume element of the same extension centred at the point $(\vec{k} - d\vec{k}, \vec{r} - d\vec{r})$. During this time interval the electric field has been accelerating \vec{k} at a rate $q\vec{E}/\hbar$, pushing the representative point along the 3-dimensional trajectory such that

$$d\vec{k} = \vec{k}dt = q\vec{E}dt$$
 (64)

Meanwhile, a varying chemical potential induces a physical diffusion from $\vec{r} \cdot d\vec{r}$ to \vec{r} so that

 $d\vec{r} = \dot{\vec{r}}dt$

Thus, if we sit at (\vec{k}, \vec{r}) , the density of representative points at time t is given by:

 $f(\vec{k}, \vec{r})$

At time t + dt, all these points have drifted out and all the points from $(\vec{k} \cdot d\vec{k}, \vec{r} \cdot d\vec{r})$ have drifted in, so that we have now exactly for the density:

$$f(\vec{k} - d\vec{k}, \vec{r} - d\vec{r})$$

Thus we see a rate of change

$$(\dot{f}_{\vec{k}})_{drift} = \lim_{dt\to 0} \frac{f(\vec{k}-d\vec{k},\vec{r}-d\vec{r}) - f(\vec{k},\vec{r})}{dt} = -\dot{\vec{k}} \cdot \nabla_{\vec{k}} f_{\vec{k}} - \dot{\vec{r}} \cdot \nabla f_{\vec{k}}$$
(65)

But also, collisions are all the time bringing representative points in and out of the element at (\vec{k}, \vec{r}) , resulting in an extra rate of change of $f_{\vec{k}}$. Liouville's theorem, all counted, says that we must have the same total density of representative points, thus

$$(\mathbf{f}_{\vec{k}})_{\text{drift}} + (\mathbf{f}_{\vec{k}})_{\text{coll}} = 0$$
(66)

which is Eq.(63). Writing now, more carefully, $\vec{v}_{\vec{k}}$ instead of simply \vec{r} , we take the following as our starting form of the Boltzmann equaltion (henceforth denoted as B.E.):

$$\vec{\hat{v}}_{\vec{k}} \cdot \nabla f_{\vec{k}} + \frac{1}{\hbar} q \vec{E} \cdot \nabla_{\vec{k}} f_{\vec{k}} = (\dot{f}_{\vec{k}})_{\text{coll}}$$
(67)

We shall presently see that the collision term is a complicated integral of the unknown distribution. But the problem is formulated in this integrodifferential equation. If we can solve it we can calculate the density of charge and energy flow:

$$\vec{J} = 2 \int q \vec{v}_{\vec{k}} f_{\vec{k}} d\vec{k}; \quad W = 2 \int \mathscr{B}_{\vec{k}} \vec{v}_{\vec{k}} f_{\vec{k}} d\vec{k}$$
(68)

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A first simplification is achieved by using the assumption of small departures from equilibrium. Thus, we start by evaluating the left-hand side of (67) to lowest order, i.e., we write

$$\vec{\mathbf{v}}_{\vec{k}} \cdot \nabla \mathbf{f}_{\vec{k}}^{0} + \frac{1}{\hbar} \mathbf{q} \, \vec{\mathbf{E}} \cdot \nabla_{\vec{k}} \mathbf{f}_{\vec{k}}^{0} \tag{69}$$

and then we look into what determines the dependence of $f_{\vec{k}}$ on \vec{r} and \vec{k} . The latter is trivial,

$$\nabla_{\overrightarrow{k}} \mathbf{f}_{\overrightarrow{k}}^{0} = \frac{\partial \mathbf{f}_{\overrightarrow{k}}^{0}}{\partial \mathscr{E}_{\overrightarrow{k}}} \nabla_{\overrightarrow{k}} \mathscr{E}_{\overrightarrow{k}} = \mathbf{h} \frac{\partial \mathbf{f}_{\overrightarrow{k}}^{0}}{\partial \mathscr{E}_{\overrightarrow{k}}} \nabla_{\overrightarrow{k}}$$
(70)

For \vec{r} we consider the explicit form

$$f_{\vec{k}}^{0} = \frac{i}{e^{(\mathscr{O}_{\vec{k}} - \zeta)/k_{B}^{T}} + 1}$$
(71)

and assume that, at each point \vec{r} , there is a meaningful T and ζ . Thus

$$\nabla f_{\vec{k}}^{0} = \frac{\partial f_{\vec{k}}^{0}}{\partial T} \nabla T + \frac{\partial f_{\vec{k}}^{0}}{\partial \zeta} \nabla \zeta$$
(72)

It is more convenient to lean on the explicit form of $f_{\vec{r}}^0$ and rewrite (72) as

$$\nabla \mathbf{f}_{\vec{k}}^{0} = \frac{\partial \mathbf{f}_{\vec{k}}^{0}}{\partial \mathscr{B}_{\vec{k}}} \left\{ \left(\mathscr{B}_{\vec{k}} - \varsigma \right) \mathbf{T} \nabla \left(\frac{\mathbf{i}}{\mathbf{T}} \right) - \nabla \varsigma \right\}$$
(73)

Hence

$$\left(\frac{\partial \mathbf{f}_{\vec{k}}^{0}}{\partial \mathscr{B}_{\vec{k}}}\right) \vec{\mathbf{v}}_{\vec{k}} \cdot \left\{ \left(\mathscr{B}_{\vec{k}} - \boldsymbol{\zeta}\right) \mathbf{T} \nabla \left(\frac{\mathbf{i}}{\mathbf{T}}\right) + q\left(\vec{\mathbf{E}} - \frac{\mathbf{i}}{q} \nabla \boldsymbol{\zeta}\right) \right\} = \left(\mathbf{f}_{\vec{k}}\right)_{\text{coll}}$$
(74)

(A Boltzmann equation describing size effects would have an extra term which we are not considering here. See Ziman (1960, Section 11.2). The reason for the term $qE - \nabla \zeta$ is obvious: in moving a charged particle into another position we must perform electrostatic work and <u>chemical</u> work as well (this is the <u>definition</u> of the chemical potential). Thus, the total force acting on the charge carrier is given by the gradient of the <u>electrochemical</u> potential, and is precisely equal to

$$q \tilde{E}' = - \nabla(q \phi + \zeta)$$

As to the other term, we shall presently come back to it.

We still have to deal with the collision term. Let $Q(\vec{k}, \vec{k}')$ be the elementary probability per unit time that an electron known to be occupying

the state \vec{k} , be scattered_into the state \vec{k}' known to be <u>unoccupied</u>. Then, obviously, for Fermi statistics

$$\left(\dot{f}_{\vec{k}}\right)_{\text{coll}} = \int \left\{- Q_{\vec{k}}(\vec{k},\vec{k}') f_{\vec{k}}\left(1 - f_{\vec{k}}\right) + Q(\vec{k}',\vec{k}) f_{\vec{k}'}\left(1 - f_{\vec{k}}\right)\right\} d\vec{k}'$$
(75)

In thermal equilibrium the collisions alone do not change the total density of representative points at any one particular point, and (75) vanishes. Thus we define a symmetric function

$$P(\vec{k}, \vec{k'}) = Q(\vec{k}, \vec{k'}) f_{\vec{k}}^{0} \left(1 - f_{\vec{k'}}^{0}\right) = P(\vec{k}, \vec{k})$$
(76)

This symmetry states concisely the <u>principle of detailed balancing</u> for a system in thermal equilibrium.

It is customary to write the perturbed distribution as

$$f_{\vec{k}}^{0} + \delta f_{\vec{k}} = f_{\vec{k}} \equiv f_{\vec{k}}^{0} - \frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{B}_{\vec{k}}} \Phi_{\vec{k}} = f_{\vec{k}}^{0} + \frac{1}{k_{B}T} f_{\vec{k}}^{0} (1 - f_{\vec{k}}^{0}) \Phi_{\vec{k}}$$
(77)

This suggests the idea of a first-order expansion about the equilibrium value. We redefine our unknown as $\Phi_{\vec{k}}$, which will be linear in the forces. Thus, we use (77) and (76) in (75), linearize, substitute in (74) and finally obtain

$$\left(\frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{B}_{\vec{k}}}\right)\vec{v}_{\vec{k}} \cdot \left\{ \left(\mathscr{B}_{\vec{k}} - \zeta\right)T\nabla\left(\frac{i}{T}\right) + q\left(\vec{E} - \frac{i}{q}\nabla\zeta\right) \right\} = \frac{1}{k_{B}T}\int\left(\Phi_{\vec{k}} - \Phi_{\vec{k}}\right)P\left(\vec{k}, \vec{k}'\right)d\vec{k}' \quad (78)$$

It is from this equation that we shall start the calculation of the phenomenological transport coefficients.

2.2. The phenomenological transport coefficients: Relation to the thermodynamics of irreversible processes

We now have two tasks. On the one hand, we must write down the precise formulae for the quantities measured experimentally. On the other hand we must calculate them from our Boltzmann equation.

The electric current is quite clear. It is given by \vec{J} in (68). The <u>heat</u> flow (or thermal current) is <u>not</u> the energy flow W written in (68). Allowing ourselves to use the first law of thermodynamics for a small volume element, i.e.

$$\delta \mathscr{E} = T\delta S + \zeta \delta n = \delta Q + \zeta \delta n$$

(\mathscr{E} = internal energy, S = entropy, Q = heat) we see that an energy flow $\delta \mathscr{E}/\delta t$ involves a heat flow

$$\frac{\delta Q}{\delta t} = \frac{\delta \mathscr{B}}{dt} - \zeta \frac{\delta n}{\delta t}$$

Thus, we must subtract from W the particle current times ζ , i.e.

$$\vec{U} = W - 2\zeta \int \vec{v}_{\vec{k}} \cdot f_{\vec{k}} d\vec{k} = 2 \int \left(\mathscr{B}_{\vec{k}} - \zeta \right) \vec{v}_{\vec{k}} f_{\vec{k}} d\vec{k}$$
(79)

This is the meaning of $(\mathscr{B}_{\vec{k}} - \zeta)$ in Eq.(78). As for $\nabla(i/T)$, we simply observe that a heat flow \vec{U} is an entropy flow \vec{U}/T whose divergence

$$\nabla \cdot \left(\frac{1}{T} \ \vec{U}\right) = \vec{U} \cdot \nabla \left(\frac{1}{T}\right) = \vec{S}_{ther}$$
 (80)

gives the thermal $\underline{entropy \ production}$ associated with the irreversible heat flow in the steady state.

Let us write the r.h.s. of (78) as

$$\frac{1}{\mathbf{k}_{B}T} \int \left(\Phi_{\vec{k}} - \Phi_{\vec{k}} \right) \mathbf{P} \left(\vec{k}, \vec{k}' \right) d\vec{k}' \equiv \mathbf{L} \Phi_{\vec{k}}$$
(81)

We have <u>defined</u> the linear integral collision operator L. Let us use the notation

$$\left(\mathbf{F}_{\vec{k}},\mathbf{G}_{\vec{k}}\right) \equiv \int \mathbf{F}_{\vec{k}} \mathbf{G}_{\vec{k}} \mathbf{d}\vec{k}$$
(82)

Then from (78), remembering (77) and the fact that $f_{\vec{k}}^0$ carries no flow whatever

$$T \vec{U} \cdot \nabla \left(\frac{1}{T}\right) + \vec{J} \cdot \vec{E}' = 2 \left(\Phi_{\vec{k}}, L \Phi_{\vec{k}}\right)$$
(83)

The second term on the left-hand side is also familiar, it is the Joule heat, or T times the "electrical entropy production". It is easy to show, using the definitions (81) and (82), interchanging dummy integration variables and manipulating a little, that

$$\left(\mathbf{F}_{\vec{k}}, \mathbf{L} \mathbf{G}_{\vec{k}}\right) = \left(\mathbf{G}_{\vec{k}}, \mathbf{L} \mathbf{F}_{\vec{k}}\right); \quad \left(\mathbf{F}_{\vec{k}}, \mathbf{L} \mathbf{F}_{\vec{k}}\right) \ge 0$$
(84)

That is to say, the operator L is self-adjoint (it is real, symmetric and positive definite). This mathematical fact has an immediate physical consequence, namely, from (83)

$$\mathring{S} = \mathring{S}_{ther} + \mathring{S}_{el} = \frac{1}{T} \left(\Phi_{\overrightarrow{k}}, L \Phi_{\overrightarrow{k}} \right) \ge 0$$

The entropy production is <u>positive definite</u>. As written in (83), the lefthand side expresses S in terms of the macroscopic quantities of the

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experiment, i.e. the <u>thermodynamic forces and flows</u> (Prigogine, 1961); the right-hand side gives the formula for calculating S from the statistical theory. The inequality of (84) expresses Boltzmann's H-theorem: Collisions, creating disorder, always increase entropy. Our formulae for \vec{J} and \vec{U} may be complicated integrals depending on the details of the band structure and scattering mechanisms, but we know that, irrespective of the model, any transport calculation we perform based on Eq.(78) will give results in agreement with the thermodynamics of irreversible processes.

We can see this more explicitly by actually evaluating the phenomenological transport coefficients. The explicit formulae are given in all textbooks. It suffices here to notice that, since the operator L is selfadjoint, it can be inverted (no fear of singularities, as L is positive definite) and its reciprocal is also symmetric. Let us put

 $K = L^{-1}$

Then, formally solving (78), we see that $\Phi_{\underline{t}}$ will be of the form

$$\Phi_{\vec{k}} = T K \vec{F}_{\vec{k}} \cdot \nabla \left(\frac{1}{T}\right) + K \vec{G}_{\vec{k}} \cdot \vec{E}'$$
(85)

where

$$\vec{F}_{\vec{k}} = -\frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{E}_{\vec{k}}} \cdot \left(\mathscr{E}_{\vec{k}} - \zeta \right) \vec{v}_{\vec{k}} \qquad G_{\vec{k}} = -\frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{E}_{\vec{k}}} \cdot q \vec{v}_{\vec{k}} \qquad (86)$$

Thus, the flows will be

$$\vec{U} = T\left(\vec{F}_{\vec{k}}, \vec{K} \cdot \vec{F}_{\vec{k}}\right) \cdot \nabla\left(\frac{1}{T}\right) + \left(\vec{F}_{\vec{k}}, \vec{K} \cdot \vec{G}_{\vec{k}}\right) \cdot \vec{E}'$$
(87)

 and

$$\vec{J} = T\left(\vec{G}_{\vec{k}}, \vec{K} \cdot \vec{F}_{\vec{k}}\right) \cdot \nabla\left(\frac{1}{T}\right) + \left(\vec{G}_{\vec{k}}, \vec{K} \cdot \vec{G}_{\vec{k}}\right) \cdot \vec{E}'$$
(88)

which we can concisely rewrite as

$$\vec{U} = T \vec{K}_{TT} \cdot \nabla \left(\frac{1}{T}\right) + \vec{K}_{TE} \cdot \vec{E}'$$

$$\vec{J} = T \vec{K}_{ET} \cdot \nabla \left(\frac{1}{T}\right) + \vec{K}_{EE} \cdot \vec{E}'$$
(89)

We have written the solution of our transport problem in the canonical form of linear relationships between flows and associated <u>thermodynamic forces</u>. Notice:

i) An electrochemical/thermal gradient contributes to a thermal/ electric flow. Thus, our result describes thermoelectric effects ii) Because K is positive definite and symmetric we have

$$\vec{K}_{TT} \ge 0, \ \vec{K}_{EE} \ge 0, \ \vec{K}_{TE} - \vec{K}_{ET}$$
 (90)

The inequalities are somewhat symbolic, since K_{TT} and K_{EE} , in general, may be second-rank tensors (although crystal symmetry may reduce them to scalars). In any case what we mean is that, in turn, they are symmetric tensors, with positive definite principal values. The equality is a new and important statement. It is an example of the reciprocity relations or Onsager relations in the general thermodynamical theory of irreversible processes (The complete Onsager relations include also the positive definiteness of the diagonal kinetic coefficients. However, in the context of our discussion this adds nothing new to the statement of the H-theorem already made. It is the symmetry between kinetic coefficients which reveals something new).

As obtained from the canonical form (89), these relations are not yet expressed in terms of the actually measured coefficients, but the change is very easy.

a) Electrical measurement. Although \vec{E} is derived from the electrostatic potential, we would actually include the effect of $\nabla \zeta$ in the observed E.M.F. in the circuit, so we shall simply write \vec{E} for the "observed" electric field instead of \vec{E}' .

b) Thermal measurement. We just use the trivial identity

$$T \nabla \left(\frac{1}{T}\right) = T^{-1}(-\nabla T)$$

Our phenomenological equations then read

$$\vec{U} = T^{-1} \vec{K}_{TT} \cdot (-\nabla T) + \vec{K}_{TE} \cdot \vec{E}$$

$$\vec{J} = T^{-1} \vec{K}_{ET} \cdot (-\nabla T) + \vec{K}_{FF} \cdot \vec{E}$$
(91)

And the <u>experimental</u> definitions are:

Thermal conductivity $\vec{\kappa}$. Open circuit.

$$\vec{U} = \vec{\kappa} \cdot (-\nabla T)$$
, under the condition $J = 0$ (92)

Isothermal electrical conductivity

$$\vec{J} = \vec{\sigma} \cdot \vec{E}$$
, under the conditions $\nabla T = 0$ (93)

Seebeck coefficient (thermopower) \vec{Q} .

$$\vec{E} = \hat{Q} \cdot \nabla T$$
, under the condition $\vec{J} = 0$ (94)

Peltier coefficient $\vec{\pi}$

$\vec{U} = \vec{\pi} \cdot \vec{J}$, under the condition $\nabla T = 0$ (95)

These coefficients are easily extracted from Eq. (91).

The point is that the Onsager relations we have just verified in our solutions, when re-expressed in terms of the experimental coefficients, yield immediately the Kelvin relations in thermoelectricity. Thus, the solution of the Boltzmann equation describes thermoelectric phenomena correctly.

Incidentally, we are referring here to the electronic thermal current. There is, of course, a phonon heat current. Although these two contributions can be disentangled, and the predictions of the electronic theory checked independently, it is also possible to extend the theory here sketched to describe electron and phonon transport simultaneously, by studying two coupled Boltzmann equations. This provides a correct frame to account for some details of the electron-phonon scattering processes which are important in real life. For example, on considering the electronic Boltzmann equation, we ought to account for the fact that the electrons meet phonons which, for $\nabla T \neq 0$, are not in thermal equilibrium. This is correctly described if the phonon distribution is obtained from the simultaneous Boltzmann equation for phonons.

We shall no longer deal with this field although it is very interesting and attractive. The connection with the thermodynamics of irreversible processes is itself a very fundamental aspect, and the formal transport theory is aesthetically very appealing. Think, for example, how much we have obtained from the simple statement that L is self-adjoint (and still more can be obtained). The phenomenology of thermoelectricity is rich and rewarding in terms of solid state physics. Excellent accounts can be found in the books of Ziman (1960, 1964), and MacDonald (1962). But we shall now give up treating this particular aspect now and concentrate on the isothermal electrical conductivity, paying more attention to the actual models from solid state theory.

As we see from Eqs (86) through (93), the actual evaluation of σ involves first inverting the collision operator, and then evaluating an integral in k space. Thus, the basic ingredients of the model (scattering mechanisms, band structure and statistical rules) are reflected in the ultimate result. Leaving Fermi-Dirac and Maxwell-Boltzmann statistics as they are, we can hope to learn something about scattering and/or band structure from the interpretation of the observed conductivity.

2.3. Scattering and the relaxation time approximation

The collision term involves a complicated integral over the unknown function and "inverting L", as we have been happily writing, is often easier said than done. A very powerful help can be obtained again from the statement that L is self-adjoint. As is known from the general theory of integral equations, one can then associate a variational principle to be satisfied by the solution, and this can be turned into a practical method for constructing a convergent sequence of approximations to the exact solution. Some ingenuity is needed to guess appropriate trial functions, so that a combination of just a very few (or, if possible, only one) will do in practice. In any case, the variational principle gives the ultimate criterion for doing the best out of the chosen trial functions. It can be proved that, if we proceed in this way, the approximations to the same order satisfy the correct Onsager relations. Here is another formal advantage: the successive approximations are thermodynamically consistent. The power of the variational principle comes in very handy when we have to deal with tricky scattering mechanisms, and it proves very useful in clarifying some finer aspects of transport phenomena, like the validity or otherwise of the <u>Wiedeman-Franz</u> law at low temperatures, which is a relationship between electric and thermal conductivities, or <u>Matthiessen's rule</u>, which concerns the total resistivity when two sources of resistance are acting simultaneously. But in many ordinary cases we can make certain assumptions which greatly simplify the problem. The standard simplification consists in the <u>relaxation time</u> approximation. Let us see how this comes about.

The collisions suffered by the electrons may involve a change of momentum and a change of energy. The main thing for the theory of electrical conductivity is the change in \vec{k} , as this change determines the loss of forward drift, which measures the transport of charge. The change in energy is rather a nuisance. But there are many cases in which we may practically neglect this change as small compared with the energy of the average conduction electron. Obvious examples of elastic scattering are the collisions of electrons with structural defects. (It is, however, no idle speculation to think that an incoming electron may hit an impurity and set it in vibrating motion, thus losing energy. But this would be just one of the many particular effects one can always dream up, and sometimes actually observe).

Electron-phonon collisions appear to be very different; we clearly must express an energy balance in which the energy of the electron changes by an amount equal to the energy of the phonon absorbed or emitted. However, in many cases this energy turns out to be very small compared with the initial energy of the electron. Let us, for example, consider the case of acoustic phonon scattering in a typical semiconductor. One would tend to think that this case is harder to justify than that of a metal, because the average energy of the conduction electron in a metal is of the order of the Fermi energy (a few eV), while in a semiconductor it is of the order of almost the opposite. It is true that at room temperature the relaxation-time approximation (for which, as we shall see immediately, we must have elastic scattering) is sufficiently justified in a metal. But a much more elaborate calculation is needed to describe correctly at all temperatures the full complexity of the electron-phonon interaction.

On the other hand, it is easy to see that the case of semiconductors is, on this account, simpler. The point is that, with thermal energies, the average wavelength of the electronic waves is of the order of

$$\lambda = \frac{h}{mv} \simeq \frac{h}{\sqrt{3 m k_B T}} \simeq 5 \times 10^{-7} cm$$

for a free electron value of m and at room temperature. This is larger than the interatomic distance, so that the electrons can interfere with long

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lattice waves, i.e., with phonons with a small wavevector q. Thus the typical energy of phonons able to scatter electrons will be small, of the order of

$$\hbar \omega_{q} \simeq \hbar \, sq \simeq \hbar sk \simeq smv \equiv \left(2 \frac{s}{v}\right) \left(\frac{1}{2} m \, v^{2}\right)$$

In the first equality we use the fact that we are dealing with the longwave side of the phonon spectrum; in the second equality we express the matching between lattice and electron waves. Here s means the speed of sound. Now, we have:

At room temperature $v \simeq 10^7$ cm/s Even at liquid-helium temperature $v \simeq 10^6$ cm/s whereas the typical values of the speed of sound $s \simeq 10^5$ cm/s

Thus we expect electron-phonon scattering to be, to a good approximation, elastic in a typical semiconductor. Of course, this is only a very crude estimate (although it can be made more precise) and it can fail at very low temperatures but, by then, defect scattering of some sort predominates anyway.

A curious case is that of conduction electrons at low temperatures in a polar crystal. The electron is strongly coupled to the polarization waves carried by the optical modes. These optical phonons have much higher energies than the electrons (their frequencies are in the infrared, of the order of 10^{13} rad/s, corresponding to about 10^{-1} eV, compared with, say 4×10^{-3} eV, which is $k_{B}T$ at $T\simeq 50^{\circ}K$. It is a paradoxical case in which the scattering, because it is very inelastic, becomes elastic again. This is one of those predictions which could only come out of quantum theory, and it is not only amusing but also instructive to consider it. Briefly. what happens is that an electron with a small energy absorbs an optical phonon and jumps up into a state of very high energy. According to the incertainty principle, this state lives for a very short time and it comes back down again very quickly, emitting another phonon. It all happens so quickly that it is as if the two elementary first order processes merged together into one second-order process, in which the energy of the electron remains unchanged (Fig. 1). The detailed treatment can be considerably more involved, but in the end boils down to establishing that we could calculate the current on the basis of elastic scattering, in which only \vec{k} changes.

We have seen with a few examples that it is often justifiable in practice to assume elastic scattering, but we still should consider another question: Is the resistivity only caused by the collisions of the conduction electrons with phonons and/or imperfections? The answer is really no. If the size of the sample is sufficiently small compared with the average distance traversed by the electrons between collisions, then we must account for the <u>reflection from the surface</u> (not necessarily specular reflection!). We shall not consider size and shape effects which may take place in this case. It is also possible for a transport problem to involve a large sample, but



FIG. 1. a) Two separate inelastic electron-phonon collisions. b) The first collision is very inelastic, resulting in a very short-lived state. Phonon reemission follows very quickly. The net result is a composite second order process. Finally $E(\vec{k})=(and \hbar \omega_{\vec{q}}^{2} = \hbar \omega_{\vec{q}}^{2})$, but $\vec{k} \neq \vec{k}'$. Process (b) is elastic but tends to destroy the forward drift acquired by the electron.

to concern only charge carriers in a layer very near the surface, e.g., due to skin effect in metals, or to very narrow boundary layers in semiconductors. We shall also not be concerned with these cases. This still leaves a wide realm of phenomena to consider, but we still have another question to answer: what about electron-electron collisions?

It is obvious that collisions between free electrons would not result in yielding resistivity. Consider a momentum-conservation balance like

$$\vec{k}_1 + \vec{k}_2 - \vec{k}_3 - \vec{k}_4 = 0$$
 (96)

Two incoming electrons have exchanged momentum with one another, but this does not affect the transport of charge. It does not matter which one carries more than the other, provided both add up to the same total forward momentum. But the conduction electrons are in a lattice. Even if we can reasonably make a kind of free electron model, with some numerical effective mass and a practically spherical Fermi surface, our electrons still can interchange <u>crystal momentum</u> with the lattice. The selection rules for the collisions now allow for a more general process than that of (96). These are the <u>umklapp</u> processes, which you will see in the course on electron-phonon interactions. A more general condition than (96) is allowed, namely

$$\vec{k}_1 + \vec{k}_2 - \vec{k}_3 - \vec{k}_4 = \vec{K}$$
(97)

 \overline{K} is any reciprocal lattice vector. Now the total momentum of the two carriers can change, and we may suspect this to be a source of resistance in a metal. Rather, we should ask whether it is likely to be an <u>appreciable</u> source of resistance. On the one hand, the mutual screening of the interaction between any two electrons by the presence of the other ones weakens this interaction changing it from a long-range Coulomb potential into a GARCIA-MOLINER

short-range potential. On the other hand, the requirements of the exclusion principle on all four states represented in Eq. (97) impose very severe restrictions on the entire process. Altogether, this scattering seems to be reduced to rather weak proportions. As a matter of fact, a theoretical calculation of the resistivity of this mechanism (Ziman 1960, Sections 4.6, and 9.14) predicts a law for the temperature dependence of the resistivity which is not observed experimentally. There is one important exception to this argument, namely, the case of transition metals. But we cannot then easily talk about collisions between Bloch electrons in the same way as with non-transition metals. It is more appropriate to think of nearly free electrons scattering off nearly bound electrons (namely, those in the d-orbitals, or whatever these free atom states have become in the metallic crystal). We shall also exclude this case.

Thus, our final model (and this is a statement of the limitations set to our scope in this course) is the following: Conduction electrons, in single isolated events, collide with other objects and the collisions are elastic. Let us then see what happens to the collisions integral in our final Boltzmann equation

$$q\left(-\frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{B}_{\vec{k}}}\right)\vec{v}_{\vec{k}}\cdot\vec{E} = \frac{1}{k_{B}T}\int\left(\Phi_{\vec{k}}-\Phi_{\vec{k}}\right)P(\vec{k},\vec{k'})d\vec{k'}$$
(98)

for isothermal electrical conduction.

At this stage, let us be more intuitive and heuristic than rigorous. We expect that the effect of the external field will be to pull somewhat the distribution so that a net flow results. Let us imagine that each electron is acted on by the force $q\vec{E}$ so that, in between two collisions, it gains an energy $q\vec{E} \cdot \vec{l}$, where \vec{l} is a measure of the <u>mean free path</u>. Let us write

$$\vec{\ell} = \tau \vec{v}_{\vec{k}}$$
(99)

for the electron \vec{k} . Thus, τ measures the mean time between collisions. We may expect, to first order, that the distribution will be something like a slighly displaced equilibrium distribution. That is, we shift the origin of energies by

$$\Delta \mathscr{E}_{\vec{k}} \simeq q \, \vec{E} \cdot \tau \, \vec{v}_{\vec{k}} \tag{100}$$

and try for $f_{\vec{r}}$ an expression of the form

$$f^{0}\left(\mathscr{B}_{\vec{k}} - \Delta \mathscr{B}_{\vec{k}}\right) \simeq f_{\vec{k}} - q \vec{E} \cdot \tau \vec{\nabla}_{\vec{k}} \frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{B}_{\vec{k}}}$$
(101)

What we are doing is to view the effect of the electric field as imparting an extra "ordered" kinetic energy, but only for an average time interval τ . Thus, we try for Φ_{τ} a solution of the form

$$\Phi_{\vec{k}} = q \vec{E} \cdot \tau \vec{v}_{\vec{k}}$$
(102)

This is only a provisional postulate. We now must see whether this solution is permitted by the integral equation (98). If the test is positive,

then we have <u>calculated</u> τ . In the frame of our working assumptions we shall allow τ to be a function of $\mathscr{E}_{\vec{k}}$, but not of the vector k.

Now, with elastic scattering,

$$f_{\vec{k}}^{0}\left(1-f_{\vec{k}}^{0}\right) = f_{\vec{k}}^{0}\left(1-f_{\vec{k}}^{0}\right) = -k_{B}T \frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{O}_{\vec{k}}}$$
(103)

Thus, from (98) and (76):

$$q \vec{v}_{\vec{k}} \cdot \vec{E} = q \tau \vec{E} \cdot \int \left(\vec{v}_{\vec{k}} - \vec{v}_{\vec{k'}} \right) Q(\vec{k}, \vec{k'}) d\vec{k'}$$
(104)

This will make sense if τ , literally evaluated from here, i.e.

$$\frac{1}{\tau} = \frac{\vec{E}}{\vec{v}_{\vec{k}} \cdot \vec{E}} \cdot \int \left(\vec{v}_{\vec{k}} - \vec{v}_{\vec{k'}} \right) Q(\vec{k}, \vec{k'}) d\vec{k'}$$
(105)

turns out to be independent of \vec{E} .

We have already made so many assumptions that we might as well assume spherical energy surfaces. With these hypotheses we write, for the scattering probability, the following expression:

$$Q(\vec{k}, \vec{k}') = \mathcal{P}(\mathcal{B}_{\vec{k}}, \theta) \,\delta(\mathcal{B}_{\vec{k}} - \mathcal{B}_{\vec{k}'})$$
(106)

Here $\mathscr{P}(\mathscr{C}_{\vec{k}}, \theta)$ depends only on the energy of the incoming electron and on the <u>scattering angle</u> θ between \vec{k} and $\vec{k'}$. Using spherical trigonometry we can now manipulate (105) so that $\vec{E} \cdot \vec{v}_{\vec{k}}$ is pulled out of the integral, leaving a factor $(1 - \cos \theta)$, i.e.

$$\frac{1}{\tau} = \int (1 - \cos \theta) \, \mathscr{P}\left(\mathscr{B}_{\vec{k}}, \theta\right) \, \delta\left(\mathscr{B}_{\vec{k}} - \mathscr{B}_{\vec{k}'}\right) \, d\vec{k'} \tag{107}$$

This formula reveals very much. Let us remember the definition of the density of states in energy (for <u>one</u> spin only):

$$\int \mathcal{N}(\mathscr{B}) \, \mathrm{d}\mathscr{B} = \int \frac{\mathrm{d}k}{(2\pi)^3} \int k^2 \, \mathrm{d}\,\Omega \tag{108}$$

where $d\Omega$ is an element of solid angle in \vec{k} space. (Let us simply write $\mathscr{E}, \mathscr{E}'$ instead of $\mathscr{E}_{\vec{k}}, \mathscr{E}_{\vec{k}'}$, etc., just for brevity). Thus, we can rewrite (107) as follows:

$$\frac{1}{\tau} = \int \frac{\mathrm{d}\mathbf{k}^{\mathbf{1}}}{(2\pi)^3} \int \mathbf{k}^{\mathbf{1}^2} (1 - \cos\theta) \, \mathscr{P}(\mathscr{E}, \theta) \, \delta \, (\mathscr{E} - \mathscr{E}^{\mathbf{1}}) \, \mathrm{d}\Omega$$

$$= \int d \mathscr{B}' \delta (\mathscr{E} - \mathscr{E}') \int \mathscr{N} (\mathscr{E}') (1 - \cos \theta) \mathscr{P} (\mathscr{E}, \theta) d\Omega'$$
(109)

$$= \int \mathcal{N}(\mathcal{E}) (1 - \cos \theta) \mathcal{P}(\mathcal{E}, \theta) \, \mathrm{d}\Omega'$$

and now we see the meaning of all the factors affecting the collision time:

 $\mathcal{N}(\mathscr{E})$ is just the density of final states available. $\mathcal{N}(\mathscr{E})\mathcal{P}(\mathscr{E},\theta)$ is the net differential scattering cross-section. $(1 - \cos \theta)$ is the fractional loss of forward drift velocity.

We would not have guessed this from a naive picture, thinking that τ^{-1} is the collision frequency and therefore it should be given by the integral over the differential cross-section. We have now verified that what determines the resistence is the weighted cross-section: it is the collisions through large angles which contribute most effectively. To put it differently, τ is the mean free time between momentum-destroying collisions, which was not at all apparent from the naive argument leading to (102).

What we have derived is the standard elementary solution of the Boltzmann equation, together with a formula for the calculation of τ , leaving only the application of perturbation theory to evaluate the scattering probability as an explicit calculation to be performed in each case.

The collision-time approximation could be phrased a bit more generally. Consider the scattering term in the form

$$\left(\frac{\mathrm{d}\mathbf{f}_{\vec{k}}}{\mathrm{d}\mathbf{t}}\right)_{\mathrm{coll}} = \left[\frac{\mathrm{d}(\delta \mathbf{f}_{\vec{k}})}{\mathrm{d}\mathbf{t}}\right]_{\mathrm{coll}} = -\int \left(\delta \mathbf{f}_{\vec{k}} - \delta \mathbf{f}_{\vec{k}'}\right) Q(\vec{k}, \vec{k}') \, \mathrm{d}\vec{k}' \tag{110}$$

which holds for elastic scattering. If it is possible to pull $\delta f_{\vec{k}}$ out of the integral, so that the remainder is independent of \vec{E} , then after integration over \vec{k} , we are left on the right-hand side of (110) with - $\delta f_{\vec{k}}^{-1}$ multiplied by a function of \vec{k} only. We can define this function as $\tau_{\vec{k}}^{-1}$ and then we have

$$\left[\frac{d\left(\theta f_{\vec{k}}\right)}{dt}\right]_{coll} = -\frac{\delta f_{\vec{k}}}{\tau_{\vec{k}}}$$
(111)

That is to say, τ may be in general a function of the vector \vec{k} . However, there is no easy general procedure for evaluating $\tau_{\vec{k}}$ in this case. In fact the elementary solution we have just worked out is the only really obvious example of this kind.

Now, Eq.(111) says that if we have a disturbance $\delta f_{\vec{k}}$ and, at time 0, we switch off the field, then the disturbances decays exponentially

$$\left(\delta f_{\vec{k}}\right)_{t} = \left(\delta f_{\vec{k}}\right)_{0} e^{-t/\tau_{\vec{k}}}$$
(112)

The distribution relaxes back to equilibrium with a relaxation time. If we maintain a constant field, we have a steady state in which

$$\delta f_{\vec{k}} = -q \vec{E} \cdot \tau_{\vec{k}} \vec{\nabla}_{\vec{k}} \frac{\partial f_{\vec{k}}^{0}}{\partial \theta_{\vec{k}}}$$
(113)

resulting in a current density

$$\vec{J} = 2 \int q^2 \tau_{\vec{k}} \vec{v}_{\vec{k}} \vec{v}_{\vec{k}} \left(-\frac{\partial f_{\vec{k}}}{\partial \theta_{\vec{k}}} \right) d\vec{k} \cdot \vec{E}$$
(114)

whence a conductivity tensor

$$\sigma = 2 \int q^2 \tau_{\vec{k}} \vec{v}_{\vec{k}} \vec{v}_{\vec{k}} \left(-\frac{\partial f_{\vec{k}}^0}{\partial \mathscr{G}_{\vec{k}}} \right) d\vec{k}$$
(115)

2.4. The electrical conductivity of solids

At last, after many simplifications, we have derived an explicit formula, ready for immediate evaluation. Most of the standard theory of the conductivity of solids is based on this formula (perhaps with some \vec{k} -vector dependence fudged into τ , which for the time being we shall disregard). It turns out to work rather well in many cases of everyday practice, and it exhibits all three factors determining the conductivity: Band structure, statistics and scattering. The detailed application of this formula to the analysis of the experimental observations is well covered in the books of Ziman (1960) and Smith (1959), and we shall here make only some broad remarks.

To begin with, the general effect of symmetry. Take a symmetry axis in the crystal and decompose all vectors in two components labelled 1 and 2, the first one being the projection along the axis and the second one normal to it. The experimental definition of the resistivity is

$$\rho = \frac{\vec{E} \cdot \vec{J}}{J^2}$$
(116)

i.e., we maintain a steady current, measure the voltage, drop along the current, and divide by J. Thus,

$$\rho(\varphi) = \frac{E_1 J_1 + E_2 J_2}{J^2} - \frac{E_1}{J_1} \left(\frac{J_1}{J}\right)^2 + \frac{E_2}{J_2} \left(\frac{J_2}{J}\right)^2 = \rho_1 \cos^2 \varphi + \rho_2 \sin^2 \varphi \quad (117)$$

where φ is the angle between \vec{J} and the symmetry axis. Thus, two independent measurements suffice to determine the two principal values of the resistivity tensor. Its reciprocal, the conductivity tensor, has also two principal values. However, if the plane perpendicular to the symmetry axis contains another axis equivalent to it, then clearly $\rho_1 = \rho_2$, and the tensor becomes a scalar. This is the most frequent case; e.g. cubic symmetry. We shall restrict ourselves to isotropic conduction. The conductivity is then simply the reciprocal of the resistivity. This distinction between a scalar and a tensor will become very important when we consider conduction in the presence of a magnetic field.

The formula for σ is now written in different forms, to suit convenience, depending on the system one is studying.

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2.4.1. Metals

We can write, for instance.

$$\sigma = \frac{q^2}{3} \int \int \tau \, \mathbf{v}_{\vec{k}}^2 \left(-\frac{\partial f_{\vec{k}}^0}{\partial \mathscr{B}_{\vec{k}}} \right) \, \frac{\mathrm{d}S_{\mathscr{I}}}{\left| \nabla_{\vec{k}} \, \mathscr{B}_{\vec{k}} \right|} \, \frac{\mathrm{d}\mathscr{B}}{4\pi^3} \tag{118}$$

where $dS_{\mathscr{G}}$ is the element of area of the surface $\mathscr{E}_{\overrightarrow{k}} = \mathscr{E}$. For a degenerate electron gas

$$\sigma = \frac{q^2}{12\pi^3\hbar} \int \tau \, v \, dS_F = \frac{q^2}{12\pi^3\hbar} \int \ell dS_F$$
(119)

 $(S_F = Fermi \text{ surface})$. This explains why metals with large Fermi surfaces are good conductors. Denoting by a bar the average over the Fermi surface:

$$\sigma = \frac{q^2 S_F \ell}{12\pi^3 \hbar}$$
(120)

which is the familiar form in practice.

Only the Fermi electrons (in fact, those within the thermal layer on the Fermi surface) can take part in the charge transport. The others are prevented by the exclusion principle. However, take a spherical Fermi surface. Then

$$4\pi k_{\rm F}^2 = S_{\rm F} - \frac{1}{4\pi^3} \frac{4\pi}{3} k_{\rm F}^3 = n - u_{\rm F} = \frac{h}{m} k_{\rm F}$$
(121)

and (120) becomes

$$\sigma = \frac{nq^2\tau}{m}$$
(122)

This is what we would have guessed from a very crude estimate: A force q/m per unit electric field, during an average time τ , imparts an average drift velocity $q\tau/m$. With a carrier concentration n, each one with charge q, we expect a current per unit field which is just what we have in (122). But it is the value of τ at the Fermi surface, i.e. the mean free Fermi electrons, which must be used in the formula for σ .

We see that simple-minded pictures are often a good guess, but everyonce in a while there are some subtle catches.

2.4.2. Semiconductors

Our simple-minded picture would have been more appropriate for a non-degenerate semiconductor, because all conduction electrons can take part in the process of charge transport. Let us follow our deductive

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method again. We return to (115) and write

$$\sigma = \frac{2}{3} \frac{q^2}{k_B T} \int \tau v_{\vec{k}}^2 f_{\vec{k}}^0 \left(1 - f_{\vec{k}}^0\right) d\vec{k} \qquad (123)$$

In a non-degenerate gas

$$f_{\vec{k}}^0 \ll 1$$

hence

$$\sigma = \frac{2q^2}{3k_BT} \int \tau v_{\vec{k}}^2 f_{\vec{k}}^0 d\vec{k}$$
(124)

But

$$\frac{3}{2}nk_{B}T = 2\int \mathscr{B}_{\vec{k}}f_{\vec{k}}^{0}d\vec{k}$$
(125)

hence

$$\sigma = nq^{2} \frac{\int \tau \frac{1}{2} v_{\vec{k}}^{2} f_{\vec{k}}^{0} d\vec{k}}{\int \mathscr{B}_{\vec{k}} f_{\vec{k}}^{0} d\vec{k}} \equiv \frac{nq^{2}}{m} \langle \tau \rangle$$
(126)

where

$$\langle \tau \rangle = \frac{\int_{0}^{\infty} \mathscr{E}^{3/2} \tau(\mathscr{E}) e^{-\mathscr{E}/k_{B}T} d\mathscr{E}}{\int_{0}^{\infty} \mathscr{E}^{3/2} e^{-\mathscr{E}/k_{B}T} d\mathscr{E}}$$
(127)

is the average of the relaxation time over the energy distribution. This is sometimes written as

 $\sigma = n q \mu, \qquad \mu = \frac{q}{m} \langle \tau \rangle \qquad (128)$

where μ is the <u>mobility</u> (acquired drift velocity per unit field) as measured macroscopically.

We have assumed spherical energy surfaces; perhaps we should have written m* everywhere. The emphasis now is on the energy dependence of τ . For many scattering mechanisms it turns out to be, to a good approximation, of the form

$$\tau(\mathscr{E}) = c\mathscr{E}^{\circ} \tag{129}$$

and s is called the scattering index. Then

$$\mu = \frac{q \tau_0}{m} (k_B T)^s \frac{\Gamma\left(\frac{5}{2} + s\right)}{\Gamma\left(\frac{5}{2}\right)}$$
(130)

in terms of gamma functions. In this case it is very easy to see the temperature dependence of the mobility. Then n itself has an easy temperature dependence (in a metal, on the contrary, n is constant, but the temperature dependence of the phonon resistivity is considerably more involved). This practical formula is frequently used, although there are many instances in which τ is more complex.

Of course, if we have electrons and holes, we simply add up the conductivities (notice that they are proportional to q^2). Altogether

$$\sigma = n_e q \mu_e + n_h q \mu_h \tag{131}$$

Imagine that both types of carriers had the same $\langle \tau \rangle$ (a very artificial assumption). We could then write

$$\sigma = (n_e + n_h) q \mu \qquad \mu = \frac{q \langle \tau \rangle}{m^*}$$

where

$$\frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_h}$$
(132)

This hypothetical argument tells us how to write a formula for the "conductivity effective mass", when carriers of different mass participate simultaneously.

Sometimes one sees the complete formula for μ in the case of, say, acoustic phonon scattering. It goes like m^{-5/2}. It is important to remember that only the factor m⁻¹ comes from the form of (128). The rest, m^{-3/2}, comes from the evaluation of τ : the collision rate is proportional to an integral over the density of states, as we saw in (109), and this goes like m^{-3/2}. This, incidentally, warns us that an effective mass obtained from a different experiment which reflects, more or less, a measure of the density of states would correspond to a different average, e.g. the "thermal effective mass", obtained from the electron specific heat.

A case in point is the rather important ellipsoidal model, which describes so well the structure of the conduction band of Ge and Si near the energy minima. An ellipsoidal energy surface would exhibit in principle 3 (in practice 2) principal values of the effective mass, say, m_1 , m_2 , m_3 . Hence we have three principal values of the mobility, going like m_1^{-1} . But these ellipsoids are arranged in a symmetric disposition, and we have seen that the effect of macroscopic symmetry is to reduce the conductivity tensor to a scalar. So we can write at once the conductivity (or mobility) effective mass

$$\frac{1}{m_{e}} = \frac{1}{3} \left(\frac{1}{m_{1}} + \frac{1}{m_{2}} + \frac{1}{m_{3}} \right)$$
(133)

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to insert in the formula for the macroscopic mobility, since the macroscopic current will be, say, transverse for some ellipsoids and longitudinal for others, and we just add up all the contributions to the total current. But now, assuming acoustic phonon scattering again, we would have a density of states effective mass given by

$$m_d^{3/2} = (m_1 m_2 m_3)^{1/2}$$
 (134)

and, altogether,

$$\mu \propto \left(\frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3}\right) \frac{1}{(m_1 m_2 m_3)^{1/2}}$$

or, with two equal transverse effective masses

$$\mu \propto \left(\frac{1}{m_{\ell}} + \frac{2}{m_{t}}\right) \frac{1}{m_{\ell}^{1/2} m_{t}}$$

It is easy to verify these results from detailed calculations. The point to notice is how a certain "experimental" effective mass is related to the parameters of the band structure. (The cyclotron effective mass, for instance, is a very different function of m_{ℓ} and m_{τ} . It is obvious from what we saw in section 1.3 that we could, in fact, measure m_{ℓ} and m_{τ} independently, for suitable orientations of \vec{H} .)

As usual, the complete story is more complex. We have taken no account, e.g., of <u>intervalley</u> scattering, which takes a carrier from one ellipsoid to another one. Brooks (1955) has discussed Ge and Si in detail.

2.4.3. Insulators

It may seem nonsensical to talk about the electrical conductivity of insulators. Indeed, no one has ever measured it. But there are interesting experimental and theoretical studies of electronic charge transport in insulators like, e.g. alkali halides or silver halides only that the conditions are somewhat peculiar. There is obviously no hope of maintaining a measurable steady current, but it is possible to excite (e.g. by light absorption) just a few carriers into the conduction or valence band and to measure directly their drift velocity. This is where the semiconductor nomenclature becomes essential. We no longer talk about σ , we never know n for sure (except that we are certain that it is very small, and perhaps have an idea of its order of magnitude), the only object of study in this field is the mobility, which is the direct experimental result. The experiment is very difficult indeed, but the theoretical analysis is much more exciting than it is with any ordinary semiconductor, and it is a very neat example of the application of field theory.

3. TRANSPORT THEORY IN SOLIDS IN A MAGNETIC FIELD

The presence of a magnetic field both complicates the theory and makes it more rewarding. The features of band structure and scattering mechanisms are reflected in the <u>galvanomagnetic</u> effects to a larger

degree of sensitiveness, and make it possible to catch finer details. We shall separate in our discussion the general phenomenological aspects from the statistical and microscopic theory as such.

3.1. Phenomenological aspects of transport in a magnetic field

The phenomenological analysis is very important in the case of a magnetic field because there is a great variety of possible experimental arrangements. In fact the realm of <u>galvano-thermomagnetic</u> effects is bewildering, but we shall restrict ourselves to isothermal galvanomagnetic phenomena. We shall be dealing with a set of linear relations of the form

$$\mathbf{J}_{i} = \sum_{j} \sigma_{ij} (\vec{\mathbf{H}}) \mathbf{E}_{j}$$
(135)

The general thermodynamical theory of irreversible processes says that the reciprocity relations must now read

$$\sigma_{ii}(\vec{H}) = \sigma_{ii}(-\vec{H})$$
(136)

Therefore, the conductivity tensor can be split into a symmetric part, which is an even function of \vec{H} , and an antisymmetric part, which is an odd function of \vec{H} . This general principle constitutes a useful guide in practice.

3.1.1. Galvanomagnetic effects and crystal symmetry

Suppose we start with an isotropic model, one in which the crystal anisotropy is not anywhere reflected (i.e. isotropic τ , spherical energy surfaces). Then we add a magnetic field. This introduces anisotropy into the system. We now have one axis of cylindrical symmetry. We know then that we need two independent measurements to determine the longitudinal and the transverse conductivities. Thus we seek two conductivity coefficients, which may themselves be isotropic functions of H², and two magnetoconductivity tensors. Since the medium, in the absence of all fields (É and H), is isotropic, we take any reference frame X and impose the condition that a relationship of the form

$$\vec{J} = s(\vec{H}) \times \vec{E}$$

must be invariant when we transform to another frame X'. We are then asserting that the physical properties are the same no matter which frame we use. We seek two tensors having this property. It is well known that the definition of the dyadic product has this property, i.e.

 $\vec{H} \vec{H} \longrightarrow \vec{H}' \vec{H}'$

This is then all we need. The other invariant is obviously the unit tensor \vec{I} .

But we know from (136) that there is another term which is antisymmetric and odd in \vec{H} . It does not require too much imagination, knowing the form of the Lorentz force, to guess that this is just $\vec{E} \times \vec{E}$.

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The complete magnetoconductivity tensor is then expressed by

$$\vec{J} = \lambda \vec{E} + \nu \vec{H} \vec{H} \cdot \vec{E} + \xi \vec{E} \times \vec{H}$$
(137)

where λ , ν and ξ may be functions of H². If we set out to solve the Boltzmann equation, for example, we can be guided by the fact that the solution must have this form.

The situation is a bit more involved in the case where the crystal is anisotropic, but the doctrine is really beautifully clear. This is what we can use group theory for. We start with a second-rank tensor $\sigma(\vec{H})$, split it into symmetric and antisymmetric parts and expand in powers of the components of a pseudovector \vec{H} . With the convention of summation over repeated indices we have

$$s_{ij}(\vec{H}) = s_{0, ij} + s_{2, ijk\ell} H_k H_\ell + s_{u, ijk\ell mn} H_k H_\ell H_m H_n + - - (138)$$
$$a_{ij}(\vec{H}) = a_{1, ijk} H_k + a_{3, ijk\ell m} H_k H_\ell H_m + - - -$$

We know the transformation properties of the galvanomagnetic coefficients appearing to various orders: the s coefficients are symmetric in (i, j), the <u>a</u> coefficients are antisymmetric. Then, they are all obviously symmetric in the dummy summation indices, but we must remember that \vec{H} is a pseudovector. Thus, the transformation properties are those of: symmetric second-rank tensor X, totally symmetrized n-th rank tensor, for n-th order <u>s</u> coefficients; pseudovector X totally symmetrized n-th rank axial tensor, for n-th order <u>a</u> coefficients.

Let R be an orthogonal transformation

$$x \rightarrow cx + sy y \rightarrow - sx + cy z \rightarrow \pm z$$

(c = $\cos \varphi$, φ = rotation angle about z axis). It is well known that the characters of such a group element are given by (Baghavantam and Venkatarayudu, 1951)

(i) $X(R) = 2c \pm 1$

(ii)
$$\left[\chi^{2}\right](R) \equiv \frac{1}{2} \left\{ \left[\chi(R)\right]^{2} + \chi(R^{2}) \right\} = 4 c^{2} \pm 2 c$$
 (139)

(iii)
$$\left\{\chi^{2}\right\}(R) \equiv \frac{1}{2}\left\{\left[\chi(R)\right]^{2} - \chi(R^{2})\right\} = \pm 2c + 1$$

in the representations having, as a basis, functions which transform like the components of a

- (i) vector
- (ii) 2nd rank symmetric tensor
- (iii) pseudovector

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Then, if we can find the characters in the representation whose basis functions transform like the components of a totally symmetrized n-th rank tensor, and we call them χ_{sm} , we can write down at once the characters in the representations whose basis functions transform like our <u>s</u> and a coefficients. For the n-th order, they will be

$$\frac{s}{a}: (4c^2 \pm 2c) \chi_{sn}^{(140)}$$

$$\frac{a}{a}: (\pm 2c + 1) (\pm 1)^n \chi_{sn}^{(140)}$$

Now, what we have in (138) is a completely general statement. For each crystal, the symmetry of its point group will restrict the number of independent galvanomagnetic coefficients to exactly the number of linearly independent combinations thereof which are invariant under all the transformations of the group, i.e., which are bases of the <u>unit representation</u>. Therefore, we must calculate the number of times that the unit representation of a crystal point group is contained in the representation whose basis functions are the galvanomagnetic coefficients and whose characters we have written down in (140). There is a standard formula for this: If χ (R) are the characters in a given representation and χ^i (R) are the characters in the i-th irreducible representation, then the number of times the i-th irreducible representation is contained in the given representation is

$$\nu^{i} = \frac{1}{N} \sum_{j} h_{j} X_{j} (\mathbf{R}) X_{j}^{i} (\mathbf{R})$$
(141)

where N is the order of the group and h_j is the number of elements in the class of R. We now have all the elements for calculating this number; all we have to do is to evaluate (139) for the rotations of the group of interest, which is trivial, and to calculate χ_{sn} , which is also rather easy. We only need to take a Cartesian frame appropriate to each rotation and to watch the effect of the transformation on a monomial of the form $x^a y^b z^c$ (in our case a+b+c = n). Only those monomials which transform into themselves contribute to the character.

Consider, for example, the operations of the cubic symmetries. -E(i).- Take any frame.

$$\begin{array}{c} x \rightarrow x \\ E : y \rightarrow y \\ z \rightarrow z \end{array}$$

All monomials are invariant. All contribute + 1. The number of monomials we can form is

$$\binom{n+2}{2}$$

Then

$$\chi_{sn}(E) = {n+2 \choose 2}$$
$$\chi_{sn}(i) = (-1)^n \chi_{sn}(E)$$

- $C_3(S_6)$. Take the diagonal of the first octant as the rotation axis.

$$\begin{array}{c} x \rightarrow y \\ C_3 : y \rightarrow z \\ z \rightarrow x \end{array}$$

The contribution to the character is 1 if a = b = c, and 0 otherwise:

$$1 \text{ if } n = 3$$

 $\chi_{sn}(C_3) = 0 \text{ if } n \neq 3$

- $\sigma_h(C_2)$. Take the z axis perpendicular to the reflection plane.

$$\begin{array}{c}
x \to x \\
\sigma_h : y \to y \\
z \to z
\end{array}$$

Contribution: $(-1)^c$. We calculate the number of decompositions of n in three summands, so that c is even or odd, and we subtract.

$$\chi_{sn}(\sigma_h) = \frac{n}{2} + 1$$
 if $n = even$
= $\frac{n-1}{2} + 1$ if $n = odd$

- C_4 . Take the rotation axis as z.

$$\begin{array}{c} x \to y \\ C_4 : y \to -x \\ z \to z \end{array}$$

Contribution: 0 if a \neq b; $(-1)^a$ if a = b. The first five characters are easily found. They are 1, 1, 0, 0, 1. Then

$$X_{s,n+4}(C_4) = X_{sn}(C_4) X_{s4}(C_4) = X_{sn}(C_4)$$

 $C_6(S_3)$. Take the rotation axis as z

$$x \rightarrow \frac{1}{2} x + \frac{\sqrt{3}}{2} y$$

$$C_6: y \rightarrow -\frac{\sqrt{3}}{2} x + \frac{1}{2} y$$

$$Z \rightarrow Z$$

Explicit evaluation of the first seven characters yields

Then

$$X_{s, n+6}(C_6) = X_{sn}(C_6) X_{s6}(C_6) = X_{sn}(C_6)$$

With this we can immediately form our table of characters, use them in (141) and evaluate the ν_n for the O_h group (and also for the groups O and T_d , which are in the same Laue symmetry. We find

$$n : 0 1 2 3 4 \dots$$

$$\nu_{n} : 1 1 3 2 6 \dots$$
(142)

Now, if we set out to solve a Boltzmann equation by a power series expansion in H (for the experimentally interesting case of moderate magnetic fields), we know the <u>maximum</u> number of different galvanomagnetic coefficients, i.e., also that of different galvanomagnetic tensors which must appear to each order. This number, of course, is an upper limit, as permitted by symmetry. Some of the coefficients may be zero for specific physical reasons, e.g., due to idiosyncrasies of the model.

This is a great help to the phenomenological analysis of the experiments, but we also would like to know not only how many independent experimental arrangements to plan on, but <u>how</u> must we set them up. That is to say, knowing that there are v_n permitted galvanomagnetic tensors of n-th order we want to write them down, so that the relationship between \vec{J} and \vec{E} , to order n, takes an explicit form. This, again, concerns invariance arguments. For the O_h symmetry the result, to second order, referred to the cubic axes, is

$$\vec{J} = \sigma_{\vec{n}} \vec{E} + \alpha \vec{E} \times \vec{H} + \beta \vec{H}^2 \vec{E} + \gamma \vec{H} \vec{H} \cdot \vec{E} + \delta \vec{D} \cdot \vec{E}$$
(143)

where \vec{D} is the diagonal tensor of elements

$$D_{ij} = H_i^2 \delta_{ij}$$
(144)

This formula, first derived by Seitz, has been endlessly used in the analysis of low field galvanomagnetic phenomena. The standard practical procedure in semiconductors is to measure the <u>Seitz coefficients</u>.

Incidentally, we could rewrite (143) in matrix form a

$$\sigma = \sigma_0 \mathbf{I} + \alpha \mathbf{A} + \beta \mathbf{E} + \gamma \mathbf{S} + \delta \mathbf{D}$$
(145)

where

A is the antisymmetric matrix of $\vec{E} \times \vec{H}$, E is $H^2 \vec{I}$, S is the symmetric matrix of \vec{H} and D is the diagonal matrix of \vec{D} . These matrices are invariant, and so are their products, so we can easily carry on the expansion beyond (143) by simple matrix multiplication. In fact we must remember the Onsager symmetry, so that we must form symmetrized products, i.e.

$$[AB] \equiv AB + BA$$
 if $AB - BA \neq 0$

AB if AB-BA = 0

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Thus, to third order we have

$$[AE] = H^{2}A$$

[AS] = 0 (146)
[AD] = AD + DA

Indicating by $((\vec{H}))$ the skew-symmetric pseudotensor, such that

$$((\vec{H})) \cdot \vec{E} \equiv \vec{E} \times \vec{H}$$
(147)

we obtain immediately, from (146), the third-order extension of (143) in tensor form, i.e.

$$\sigma^{(3)} = C_1 H^2((\vec{H})) + C_2 ((\vec{D} \times \vec{H}))$$
(148)

What one does with these formulae is to figure out independent and meaningful arrangements of the vectors \vec{H} and \vec{J} , so that one knows which galvanomagnetic coefficient, or combinations thereof, yields a given measurement. Since the coefficients are in turn calculated from a theoretical model, this is clearly the proper systematic way if we want to compare experiment and theory. This is mostly useful for semiconductors. For example, on the basis of the tensor forms just derived one can predict the existence of non-conventional third-order effects which, in fact, have been experimentally observed.

The only purpose of this digression has been to give an explicit example of the application of group theory to a physical problem involving crystal symmetry, and to show you how variegated the phenomenology of galvanomagnetic effects can be. This topic is discussed in detail by Beer (1963), and we shall not go any further into it.

3.1.2. The experimental arrangement: good and bad conductors

One never measures the <u>conductivity</u> of a good conductor. The thing to do is to maintain a steady current and then measure the resulting components of the electric field. This gives then the <u>resistivity</u>, as defined in Eq. (116).

On the other hand, in a poor conductor one applies a fixed electric field and measures the resulting drift of charge. For the reasons stated in 2.4.3, we do not write down an experimental definition of the conductivity but, rather, of the mobility. It would be appropriate in fact to write

$$\vec{J} = nq \vec{\mu} \cdot \vec{E} \qquad \vec{E} = \vec{\rho} \cdot \vec{J} \qquad (149)$$

as the practical form for the analysis of experimental data. Then magnetoconductivity measurements yield the elements of the tensor μ , magnetoresistivity measurements yield the elements of the tensor \vec{p} . Not mentioning more directional effects involved, of the above-mentioned kind, Figure 2 summarizes the experimental definitions of ρ , R (Hall coefficient), μ_c (conductivity mobility) and μ_H (Hall mobility).

For the low-field effects, inversion of (143) yields

$$\vec{\mathbf{E}} = \rho_0 \vec{\mathbf{J}} - R_0 \vec{\mathbf{J}} \times \vec{\mathbf{H}} + bH^2 \vec{\mathbf{J}} + c \vec{\mathbf{H}} \vec{\mathbf{H}} \cdot \vec{\mathbf{J}} + d \vec{\mathbf{D}} \cdot \vec{\mathbf{J}}$$
(150)



FIG. 2. Experimental definitions: R = Hall coefficient; θ_H = Hall angle; μ_H = Hall mobility; μ_c = conductivity mobility

where the subscript 0 means the zero magnetic field values, and (obviously ρ_0 = $\sigma_0^{-1})$

$$b = -R_0^2 \sigma_0^2 - \frac{\beta}{\sigma_0}$$

$$c = R_0^2 \sigma_0^2 - \frac{\gamma}{\sigma_0}$$

$$d = -\frac{\delta}{\sigma_0}$$

(151)

The coefficients (β, γ, δ) are those calculated by solving the Boltzmann equation. The coefficients (b, c, d) are those measured in the experiment. It is customary to define the <u>magnetoresistance</u> as the fractional change in resistivity upon application of the magnetic field. It is easy to see from (150) that, to second order,

$$\frac{\Delta \rho}{\rho_0 H^2} \equiv \frac{\rho (H) - \rho_0}{\rho_0 H^2} = b + c (\vec{j} \cdot \vec{h})^2 + d (j_x^2 h_x^2 + j_y^2 h_y^2 + j_z^2 h_z^2)$$
(152)

where j_x , j_y , j_z , h_x , h_y , h_z are the direction cosines of \vec{J} and \vec{H} . This formula, first written by Bardeen, is ready for direct description of the orientational dependence of the magnetoresistance.

For the magnetoconductivity analysis, the mobility coefficients defined in Fig.2 are directly given in terms of the calculated conductivity tensor by

 $\mu_{\rm c} = \frac{1}{\rm nq} \ \frac{\vec{u} \cdot \vec{j}}{\rm E} = \frac{1}{\rm nq} \ \vec{u} \cdot \vec{\sigma} \cdot \vec{u}$ (153)

$$\mu_{\rm H} = \frac{\rm c}{\rm H} \frac{\vec{\rm u}' \cdot \vec{\rm J}}{\vec{\rm u} \cdot \vec{\rm J}} = \frac{\rm c}{\rm H} \frac{\vec{\rm u}' \cdot \vec{\rm o} \cdot \vec{\rm u}}{\vec{\rm u} \cdot \vec{\rm o} \cdot \vec{\rm u}}$$

where \vec{u} and $\vec{u'}$ are, respectively, the unit vectors of the directions of \vec{E} and $\vec{E} \times \vec{H}$. The directional dependence is immediately obtained from the

Seitz formula, again for low-field effects. (But (153), of course, is a valid definition for any field strength.)

3.2. The Boltzmann equation in a magnetic field

We now return to Eqs (78) and (81) through (84) and assume that we can still use the same quantization scheme and that the scattering probabilities are still the same. We then have to add, on the left-hand side of (79), the Lorentz term

$$- \vec{k} \cdot \nabla_{\vec{k}} f_{\vec{k}} = - \frac{q}{\hbar c} \left(\vec{v}_{\vec{k}} \times \vec{H} \right) \cdot \nabla_{\vec{k}} f_{\vec{k}}$$
(154)

We cannot make the zero-order approximation here. This would yield

$$-\frac{q}{c}\left(\vec{v}_{\vec{k}}\times\vec{H}\right)\cdot\vec{v}_{\vec{k}}\frac{\partial f_{\vec{k}}^{\prime}}{\partial g_{\vec{k}}^{\prime}}\equiv0$$
(155)

It will be noticed that now we are not talking about successive approximations in the magnetic field, but in the true thermodynamical forces, \vec{E}' and ∇T . The Lorentz force is not a thermodynamical force. That is to say, there is no associated flow so that this flow times the Lorentz force gives a contribution to the macroscopic expression for the entropy production, as \vec{E}' and ∇T do in the left-hand side of (83). We have already remarked that the Lorentz force does not perform any work, and this fact creeps up again in (155). This implies that a magnetic field by itself does not give rise to any net flow: The carriers are just constantly turning around in their cyclotron orbits and this does not change the distribution function. To be sure, the collisions are still taking place, disrupting the life of the electrons in their stationary orbits, but under a magnetic field alone this does not result in any net rate of entropy production.

Of course, the actual stationary flows in the presence of a magnetic field and the thermodynamical forces are different from those existing when $\vec{H} = 0$, but the effect of \vec{H} is only to modify the flows set up by the thermodynamic forces. We express this fact by using just $\delta f_{\vec{k}}$, the departure from the equilibrium distribution, in (154). If this perturbed distribution carries charge, the Lorentz force will deflect part of it into transverse motion. This is the mechanism of the Hall effect which we have just considered phenomenologically. Defining again $\Phi_{\vec{k}}$ as in (77) we obtain from (154) and (155)

$$\frac{q}{\hbar c} \frac{\partial f_{\vec{k}}^{0}}{\partial \mathscr{G}_{\vec{k}}} (\vec{v}_{\vec{k}} \times \vec{H}) \cdot \nabla_{\vec{k}} \Phi_{\vec{k}} \equiv - M (\vec{H}) \Phi_{\vec{k}}$$
(156)

Here we have <u>defined</u> the "magnetic operator" $M(\vec{H})$.

Let us formally substitute this term into the right-hand side of (78). Our Boltzmann equation is then

$$T \vec{F}_{\vec{k}} \cdot \nabla \left(\frac{1}{T}\right) + \vec{G}_{\vec{k}} \cdot \vec{E}' = \left\{ L + M(\vec{H}) \right\} \Phi_{\vec{k}}$$
(157)

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Since M is not associated with any flows, we might formally regard this extra "drift" term as a sort of "collision" term, as if the electrons were constantly colliding with the lines of force of the magnetic field. For the true collisions we had the principle of microscopic reversibility, which determined the symmetry of L. But our formal collisions are funnier. A state \vec{k} is deflected into another state \vec{k} ' but, if we allow the same amount of time to elapse in thermal equilibrium under \vec{H} alone, we shall only see that the state \vec{k} ' will be deflected back into the state \vec{k} if we reverse the magnetic field. This is reflected by the following formal property of M, which is easy to prove from its definition:

$$(\mathbf{A}_{\vec{k}}, \mathbf{M}(\vec{\mathbf{H}}) \mathbf{B}_{\vec{k}}) = -(\mathbf{B}_{\vec{k}}, \mathbf{M}(\vec{\mathbf{H}}) \mathbf{A}_{\vec{k}}) = (\mathbf{B}_{\vec{k}}, \mathbf{M}(-\vec{\mathbf{H}}) \mathbf{A}_{\vec{k}})$$
(158)

In our Boltzmann equation (157), Φ_k^* is now acted on by a more complicated operator which is no longer self-adjoint. Instead

$$\left(A_{\vec{k}}, \left\{L + M(\vec{H})\right\} B_{\vec{k}}\right) = \left(B_{\vec{k}}, \left\{L + M(-\vec{H})\right\} A_{\vec{k}}\right)$$
(159)

If we now go over all the steps we took after Eq.(78), up to the calculation of \vec{J} and \vec{U} , we shall find that, because of (159), the linear transport coefficients satisfy still the Onsager reciprocity relations, but modified by the need to reverse H, i.e. in concise form:

$$K_{\alpha\beta}(\vec{H}) = K_{\beta\alpha}(-\vec{H})$$
(160)

in agreement with the correct modification of the macroscopic thermodynamical theory of irreversible processes in the presence of a magnetic field.

The various galvano-thermomagnetic effects are described in detail by Beer (1963) and Tsidil'kovskii (1962). From now on we shall restrict ourselves again to isothermal galvanomagnetic effects, for which the reciprocity relations assume the particular form we have exploited in Eq. (136).

To solve this complex integro-differential equation for a completely general model is a very difficult task indeed. The only obvious general method seems to be the variational approach mentioned in section 2, but the fact that L + M is no longer self-adjoint greatly complicates matters. There are ways of extending the formal theory, and one has again the advantage that all approximations worked out in this way are thermodynamically consistent, but the whole thing is neither so obvious (as for H = 0) nor so easily manageable when it comes to practical calculations. As usual, a great simplification is achieved by using the relaxation time approximation, which we shall do in fact. We now start our analysis from the following form of the Boltzmann equation:

$$q \vec{v}_{\vec{k}} \cdot \vec{E} = \frac{1}{\tau} \Phi_{\vec{k}} + \frac{q}{\hbar c} \vec{v}_{\vec{k}} \cdot \vec{H} \times \nabla_{\vec{k}} \Phi_{\vec{k}}$$
(161)

3.3. Elementary solutions of the Boltzmann equation in a magnetic field

We are now faced with a first-order linear differential equation in \vec{k} space. In principle, the exact solution of (161) can be written down at once by standard methods (Wilson 1954, section 8.55). But the resulting expression is hopelessly complex for an arbitrary band structure. Besides, its evaluation would be purely a strenuous tour de force which would not teach anything.

A formula equivalent to an exact solution of this equation (even of the Boltzmann equation before linearizing it in the electric field strength) can be written down directly in a more appealing physical way. This is the Chambers method, which we shall mention later on. For the time being we shall consider the cases when the solution of (161) can be easily obtained either because the model for the band structure is very tractable or because the magnetic field is not too high.

3.3.1. Simple soluble models

The simplest case is that of spherical energy surfaces. We can be guided by the following considerations:

The model is isotropic.

We know the form of \vec{J} in terms of \vec{E} and \vec{H} , from symmetry arguments. We know \vec{J} is linear in $\Phi_{\vec{k}}$, so that $\Phi_{\vec{k}}$ also depends on \vec{E} and \vec{H} in the same manner.

For H = 0 we know $\Phi_{\overrightarrow{k}}$ is reduced to (102).

Thus the solution must be of the form

$$\Phi_{\vec{k}} = \tau \, \vec{v}_{\vec{k}} \cdot q \, \vec{V} \tag{162}$$

where \vec{V} is a vector of the form

$$\vec{\mathbf{V}} = \mathbf{c}_1 \vec{\mathbf{E}} + \mathbf{c}_2 \vec{\mathbf{E}} \times \vec{\mathbf{H}} + \mathbf{c}_3 \vec{\mathbf{H}} \vec{\mathbf{H}} \cdot \vec{\mathbf{E}}$$
(163)

where c_1 , c_2 and c_3 may be functions of H^2 .

Substituting in (161) we find that, if the equation is to be satisfied for all values of $v_{\vec{t}}$ we must have

$$\vec{\mathbf{E}} = \vec{\mathbf{V}} + \boldsymbol{\omega}_{i} \tau \, \vec{\mathbf{h}} \times \vec{\mathbf{V}} \tag{164}$$

which, on account of (163), yields

$$\Phi_{\vec{k}} = \tau \vec{v}_{\vec{k}} \cdot q \frac{\vec{E} + \omega_i \tau \vec{E} \times \vec{h} + (\omega_i \tau)^2 \vec{h} \vec{h} \cdot \vec{E}}{1 + (\omega_i \tau)^2}$$
(165)

From here we evaluate immediately the coefficients of (137):

$$\lambda = \frac{2}{3} \int \frac{q^2 \tau v_{\vec{k}}^2 \left(\frac{\partial f_{\vec{k}}^2}{\partial g_{\vec{k}}}\right)}{1 + (\omega_i \tau)^2} d\vec{k}$$

$$\nu = \frac{2}{3} \int \frac{q^2 \tau (\omega_i \tau) v_{\vec{k}}^2 \left(-\frac{\partial f_{\vec{k}}^0}{\partial g_{\vec{k}}}\right)}{1 + (\omega_i \tau)^2} d\vec{k}$$
(166)
$$\xi = \frac{2}{3} \int \frac{q^2 \tau (\omega_i \tau)^2 v_{\vec{k}}^2 \left(-\frac{\partial f_{\vec{k}}^0}{\partial g_{\vec{k}}}\right)}{1 + (\omega_i \tau)^2} d\vec{k}$$

Notice that in a metal, where only the integration over the Fermi surface counts, we can take the functions of τ out of the integral and we have

$$\lambda = \frac{\sigma_0}{1 + (\omega_i \tau)^2}; \qquad \nu = \frac{\sigma_0(\omega_i \tau)}{1 + (\omega_i \tau)^2}; \qquad \xi = \frac{\sigma_0(\omega_i \tau)^2}{1 + (\omega_i \tau)^2}$$
(167)

In this case we can also write, remembering (122),

$$\vec{\mathbf{V}} = \rho_0 \vec{\mathbf{J}} = \frac{1}{\sigma_0} \vec{\mathbf{J}}$$
(168)

Hence, from (164)

$$\vec{\mathbf{E}} = \rho_0 \vec{\mathbf{J}} - \frac{1}{\mathrm{nqc}} \vec{\mathbf{J}} \times \vec{\mathbf{H}}$$
(169)

Notice that this result would not give any magnetoresistive effect, whereas the reciprocal relationship (137) does give a magnetoconductivity effect.

The next step in complication is to take still quadratic, but not spherical, energy surfaces. This is the ellipsoidal model

$$\mathscr{C}_{\overrightarrow{k}} = \frac{\hbar^2}{2m} \left[\left(\frac{m}{m_1} \right) k_1^2 + \left(\frac{m}{m_2} \right) k_2^2 + \left(\frac{m}{m_3} \right) k_3^2 \right]$$
(170)

Now we have a reciprocal mass tensor and this complicates the solution of (161). One possible way around this consists in performing a transformation

$$\mathbf{k}_{i} \rightarrow \mathbf{k}_{i}^{\dagger} = \alpha_{i}^{\frac{1}{2}} \mathbf{k}_{i} \equiv \left(\frac{\mathbf{m}}{\mathbf{m}_{i}}\right)^{\frac{1}{2}} \mathbf{k}_{i}$$
(171)

which squeezes the axes of the ellipsoid and changes into a sphere. We must be careful to transform also all the other vectors in the problem. Thus

$$\nu_{i} \rightarrow \nu_{i}^{1} = \alpha_{i}^{\frac{1}{2}} \mathbf{k}_{i}$$

$$\mathbf{E}_{i} \rightarrow \mathbf{E}_{i}^{1} = \alpha_{i}^{\frac{1}{2}} \mathbf{E}_{i}$$

$$\mathbf{H}_{i} \rightarrow \mathbf{H}_{i}^{1} = (\alpha_{j}\alpha_{k})^{-\frac{1}{2}} \mathbf{H}_{i} \quad (ijk) = cyclic order.$$
(172)

In so doing we are ensuring that the equations of motion in the primed coordinates read the same as in the isotropic case. We now solve the problem as before, and obtain, after transforming back to the unprimed coordinates,

$$\Phi_{\vec{k}} = \tau q \vec{v}_{\vec{k}} \cdot \frac{\vec{E} + \frac{q\tau}{c} \vec{\mathcal{M}}^{-1} \cdot (\vec{E} \times \vec{H}) + \left(\frac{q\tau}{c}\right)^2 \|\vec{\mathcal{M}}\| (\vec{E} \cdot \vec{H}) \vec{\mathcal{M}} \cdot \vec{H}}{1 + \left(\frac{q\tau}{c}\right)^2 \vec{H} \cdot \vec{\mathcal{M}} \cdot \vec{H} / \|\vec{\mathcal{M}}\|}$$
(173)

where $\vec{\mathcal{M}}$ is the effective mass tensor and $\|\vec{\mathcal{M}}\|$ is the determinant thereof.

It is some comfort to know that we can write down explicitly the exact solution of the Boltzmann equation, but now we must evaluate from here the resulting current and then add up the contributions from all the ellipsoids. The calculation is straightforward in principle, but very tedious in practice, and does not teach anything special.

3.2.2. The method of Jones and Zener for low fields

If the magnetic field is sufficiently low that the electrons undergo collisions much before they can complete a cyclotron orbit (i. e. collision rate \gg cyclotron frequency, or $\omega_1 \tau \ll 1$ for the isotropic model), then we can regard the system of flows for H = 0 as slightly perturbed by the addition of a magnetic field, and seek a power series expansion in some suitable dimensionless variable proportional to \vec{H} . This is just the formal inversion of (L + M) by power series

$$(L + M)^{-1} = L^{-1} (1 + L^{-1} M)^{-1} = L^{-1} + \sum_{n} (-1)^{n} (L^{-1} M)^{n}$$
 (174)

which acquires a tractable form when, in the relaxation time approximation,

$$L = -\frac{1}{\tau}$$

The resulting solution was actually first derived (by Jones and Zener) by iterating Eq. (161), which is the same. If we put

$$\vec{\Omega} \equiv \vec{v}_{\vec{k}} \times \nabla_{\vec{k}}$$
(175)

then the power series solution is

$$\Phi_{\vec{k}} = q \left\{ \tau \vec{v}_{\vec{k}} \cdot \vec{E} + \frac{q \tau}{\hbar c} \vec{H} \cdot \vec{\Omega} \left(\tau \vec{v}_{\vec{k}} \cdot \vec{E} \right) + \frac{q^2 \tau^2}{\hbar^2 c^2} (\vec{H} \cdot \vec{\Omega})^2 (\tau \vec{v}_{\vec{k}} \cdot \vec{E}) + \dots \right\}$$
(176)

Now we can tie up with our phenomenological expressions (138). Identifying the coefficients of H_k , H_k , H_q , etc. with the corresponding terms in the current calculated out of (176) we obtain explicit formulae for the evaluation of the galvanomagnetic coefficients. Since we want these to be ready for actual use in real life, and the end result does not look too obvious, we find it convenient at this stage to rely again on our symmetry arguments. Knowing the form that the final solution must have is a great help to obtain it correctly. In particular, for the case of cubic symmetry we can immediately evaluate from here the coefficients of the Seitz formula. The resulting expressions, which are complicated integrals in \vec{k} space and therefore depend on the band structure, have been used, together with (151) and (152), in many actual calculations for metals and semiconductors. The general formulae for the galvanomagnetic coefficients of (138) are given by Beer (1963). See also Wilson (1954, section 8.551).

The power series method represents the most obvious way out for low fields, and has been used repeatedly. It might be in order to reflect upon its possible range of validity. It clearly is valid for any band structure. We have here implied that it applies to the case when τ is only a function of $\mathscr{E}_{\vec{k}}$. As a matter of fact, the expansion (or iteration) procedure can also be applied if τ is a function of the vector \vec{k} , only that it will result in more complicated expressions. The real difficulty is, as already remarked, to produce explicitly a plausible model leading to a \vec{k} -dependent τ . But the power of the expansion procedure need not stop at a relaxation-time model. In fact, (174) suggests that one can use it for arbitrary scattering mechanisms. Suppose the operator L can be inverted, to a good approximation, by means of a variational calculation. Then one would have an approximate representation for L and hence for L^{-1} , which could be used in (174). The rest of the calculation would simply account for the small perturbation due to the magnetic field.

3.4. Hall effect in low fields

Now we are all set to extract some physics from our Boltzmann equations and the solutions we have been able to find. The simplest galvanomagnetic effect is the Hall effect, which we have already defined. Its physical basis is obvious: It is due to the Lorentz force acting on the moving charges which make up the current density. This would be the point of view for conductivity-type of measurements, and this is done for, say, alkali or silver halides. One measures precisely the transverse drift and uses the formula for $\mu_{\rm H}$ given in (153). But in metals and typical semiconductors one performs rather a resistive type of measurement. The experimental condition is then that there is no net transverse current, so that a transverse electric field must be set up to counterbalance the Lorentz force. This is measured externally as the Hall field, whence the Hall coefficient arises. In low fields, as the experiment is frequently done, the Hall coefficient is just a constant, independent of the magnetic field.

The Hall coefficient is not very sensitive to the geometry of the constant energy surface. Let us then make a simple isotropic model. The solution of the Boltzmann equation was worked out in (165) and (166).

3.4.1. Metals

Assuming the isotropic model, the Hall coefficient was evaluated in (169):

$$R = \frac{1}{nqc}$$
(177)

Thus, the information conveyed by R is essentially a measure of the carrier concentration. This is why it is so practical. With this sign convention we would expect R < 0 for an ordinary metal. Experimentally this turns out to be the case with metals like Li, Na, Cu, Ag, and Al. Even the actual figures are in fairly good numerical agreement with this elementary estimate. But there is a surprise with Zn and Cd. The Hall coefficient is negative! This is where the discoveries of band theory help. We know that the Fermi surface may consist of hole-like sheets. (Fig. 3).



FIG. 3. Electron-like (a) and hole-like (b) Fermi surfaces. The arrows indicate the rotation around constant energy orbits under a magnetic field normal to the plane of the drawing. The shaded regions indicate occupied states. (a) Area of Fermi surface increases with increasing energy. (b) Area of Fermi surface decreases; (a) Electron-like trajectory, leaving occupied states inside; (b) Remapping into a hole-like trajectory, leaving occupied states outside.

The topology of the Fermi surface will be seen in greater detail in the course on Fermiology. It suffices here to remark that we can rewrite the Hall coefficient as

$$R = \frac{q}{c} \frac{\tau}{m\sigma}$$
(178)

where the effective mass m is given by the second derivative of the energy. This would be <u>negative</u> for case b (Fig. 3). A metal with a Fermi surface of this kind has a <u>positive</u> Hall coefficient. The alternative convention, generally used in semiconductor nomenclature, is to think of m as positive and change the sign of q: we may talk of holes as carriers of positive charge.

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In fact, the actual Fermi surface of some metals has several sheets, some electron-like and some hole-like. The essence of this situation is most economically synthesized in the <u>two-band model</u>. We oversimplify a complicated situation in terms of two standard isotropic bands, one of electrons and one of holes, just as appears naturally in the theory of semiconductors. We shall later come back to the two-band model. All we need now is to solve the problem to first order. This is very easy. We have two contributions \vec{J}_1 and \vec{J}_2 , both calculated in the standard manner given in 3.3.1. Adding up and using the definition of R we find

$$R = \frac{q}{c} \frac{\tau_1 \sigma_1 / m_1 + \tau_2 \sigma_2 / m_2}{(\sigma_1 + \sigma_2)^2} = \frac{\sigma_1^2 R_1 + \sigma_2^2 R_2}{(\sigma_1 + \sigma_2)^2}$$
(179)

Thus, the net R results from two competing opposite signs for electrons and holes, and we can interpret in this way the appearance of experimental values of either sign.

This is very nicely displayed in the transition metals. Consider the following sequences:

 (3d)	26 Fe(+14)	27 Co(+4)	28 Ni(-4)	29 Cu(-0.8)
 (4d)	44 Ru(+2.5)	45 Rd(+0.6)	46 Pd(-0.75)	47 Ag(-0.8)
 (5d)	76 Os(?)	77 Ir(+0.35)	78 Pt(-0.2)	79 Au(-0.7)

To the left we have unfilled d-orbitals (holes). Moving to the right we gradually fill them up until we arrive at the noble metals, which in this respect are fairly close to the ideal model. We would then expect the Hall coefficient to be positive on the left (we would not even be surprised if there were a considerable quantitative departure from the prediction of the free electron model), after which it should decrease, change sign and become very close to the value predicted by (177) for the noble metals. This expectation is borne out by the experimental results given in brackets next to each metal (These numbers are R times n/q/c, so that the ideal case corresponds to -1).

Of course in a metal n is easier to find out, independently of Hall effect measurements, than in a semiconductor. It is not affected by impurities, temperature, etc. The <u>semimetals</u> (e.g. Bi) could be described as sort of metals with much fewer conduction electrons. The Fermi surface, for example, is much smaller. Thus R is larger and begins to exhibit some temperature dependence.

3.4.2. Semiconductors

The temperature dependence is here the key feature. In fact, the measurement of R is the standard way of evaluating n for a given sample and given physical conditions.

It is customary to talk about the Hall mobility (Fig.2). By definition, in low fields

$$\frac{\mu_{\rm H}\,{\rm H}}{\rm c} \equiv \tan\,\theta_{\rm H} \equiv \frac{{\rm E}_{\perp}}{{\rm E}_{\rm J}} \equiv \frac{{\rm R}\,{\rm H}\,{\rm J}}{\sigma_0^{-1}{\rm J}} = {\rm R}\,\sigma_0\,\,{\rm H}$$
(180)

Hence

$$\mu_{\rm H} = {\rm R} \sigma_0 {\rm c} \qquad {\rm R} = \frac{1}{{\rm nqc}} \left(\frac{\mu_{\rm H}}{\mu_{\rm c}} \right)$$
(181)

One says that by measuring R and σ_0 independently one can know the concentration of carriers (with sign) and their mobility. In fact the numerical agreement between the two mobilities is not perfect. Here we have the effects of statistics. The simple formulae of (167) are replaced by

$$\lambda = \frac{\mathrm{nq}^2}{\mathrm{m}} \langle \frac{\tau}{1 + (\omega_i \tau)^2} \rangle \qquad \nu = \frac{\mathrm{nq}^2}{\mathrm{m}} \langle \frac{\omega_c \tau^2}{1 + (\omega_i \tau)^2} \rangle \qquad \xi = \frac{\mathrm{nq}^2}{\mathrm{m}} \langle \frac{\omega_i^2 \tau^3}{1 + (\omega_i \tau)^2} \rangle \tag{182}$$

Hence, from (153)

$$\frac{\mu_{\rm H}}{\mu_{\rm c}} = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} \neq 1$$
(183)

In particular, for an energy dependence of τ like that of (129)

$$\frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} = \frac{\Gamma\left(\frac{5}{2}\right)\Gamma\left(2p + \frac{5}{2}\right)}{\left\{\Gamma\left(p + \frac{5}{2}\right)\right\}^2}$$
(184)

If we assume acoustic phonon scattering, for instance, p = -3/2 and (184) takes the value $3\pi/8$, which one frequently sees multiplying $(nqc)^{-1}$ in the definition of R. This numerical factor itself is of no importance. The point is to realize that in a semiconductor we must evaluate the transport coefficients by averaging over the carrier energies as in (182), and this does introduce major numerical differences when it comes to simultaneous electron and hole conduction, or to multivalley conduction (Beer, 1963; Smith, 1959). The detailed calculations are straightforward but very boring.

3.5. Magnetoresistance in low fields

The next order effect predicted by the phenomenological analysis is the dependence of the resistivity on the magnetic field. We must remember that this kind of analysis only indicates that a certain effect, or a coefficient, is allowed by general considerations like Onsager's relations, crystal symmetry, etc. This can be very helpful in indicating new undiscovered effects, or in checking the correct form of the result of a calculation. But only the physical analysis can explain the effect and only the calculation can estimate its magnitude. It may turn out, for example, that a certain coefficient is numerically zero, and then there is no such effect.

Let us consider the forward transport of charge in the presence of crossed \vec{E} and \vec{H} . By forward we mean drift along the direction of \vec{E} . Let us not restrict ourselves to a small magnetic field. In fact, let us imagine such a high magnetic field that the collisions become unimportant. Assume a solution like (165). Take the limit $(1/\tau) \rightarrow 0$. It suffices to look at the simple case of (167) (since the collisions become unimportant, details do not matter).

We find:

Forward current : Zero Transverse current: $(nq^2/m)(mc/qH) E = nq(cE/H)$

This corresponds to a transverse drift velocity numerically equal to (cE/H). But we knew this already (Appendix). By switching off the scattering, our statistical treatment reproduces the transverse velocity with which the instantaneous centre of the cyclotron orbit drifts. Now let us switch on some scattering again. The same solution of the Boltzmann equation does give a forward current. What happens is shown in Fig.4.



FIG. 4. (a) No scattering. All drift $\perp E$. (b) We switch on some scattering. This disrupts the cyclotron orbits. "Randomizes" electronic motions. The carriers start afresh after each collision. On the average it does not matter that each one carrier may start with some initial velocity. It is as if they started completely anew, from rest. The result is to stop some of the transverse drift and throw it into the forward direction. It is the existence of scattering which actually brings about any forward conduction current.

The collisions disrupt the steady orbits; the electrons start their trajectories again; in so doing they have moved forward a little. Thus, <u>if there</u> <u>is any forward current</u>, it is precisely because of the collisions. The details may be a bit more complicated with anisotropic energy surfaces or tricky Fermi surface topologies, but the situation is essentially the same.

In a conductive measurement, letting the charge flow freely, we shall always find that the presence of a magnetic field reduces the forward current, inasmuch as part of the drift is thrown into the transverse direction: there is always a <u>magnetoconductivity</u> effect. In a resistive measurement, where we force the charge to flow down the wire, the electric field is rotated, as we have already discussed, and we need very special conditions to maintain E constant (Fig. 2). We shall find a <u>magnetoresistance</u> effect, unless the cancellation between Lorentz force and the force of the Hall field results not from a balancing out between statistical averages, but from a detailed equilibrium of forces for each one individual carrier. Only then the steady flow of each particular carrier will continue going down the forward direction unperturbed and there will be no magnetoresistance effect. For this to happen all carriers must have the same inertia and the same friction, i.e., the energy surfaces must be the same for all carriers. We shall call this a <u>non-dispersive</u> system. Let us see this in terms of equations.

We take $\vec{H} \perp \vec{E}$ and use the complex notation (Appendix). The result of (167) can be concisely written as

$$J = \frac{\sigma_0}{1 + i\omega_0 \tau} E$$
(185)

Hence

$$\mathbf{E} = \rho_0 \left(1 + \mathbf{i} \,\omega_i \tau \right) \mathbf{J} \equiv \mathbf{E}_1 + \mathbf{E}_1$$
(186)

and

$$\rho(H) = \frac{E_{I}}{J} = \rho_{0}$$
(187)

There is no magnetoresistance, while

$$J_{\rm E} = \frac{\sigma_0}{1 + (\omega_{\rm T} \tau)^2} \, {\rm E} \qquad \mu \, ({\rm H}) = \frac{\mu_0}{1 + (\mu_0 \, {\rm H/c})^2} \tag{188}$$

The crux is the inversion of (185), from which (186) follows only if we do not have to perform any averaging over energy surfaces or energy distribution.

The magnetoresistance phenomenon is clearly more informative than the Hall effect. Although it does not yield directly any number like the carrier concentration, its very existence reveals that there is some form of dispersive behaviour in the system: either the scattering rate is different for different carriers, or the energy surfaces are not spherical, or both. The phenomenological variety is also greater. We can arrange various geometries for the vectors \vec{J},\vec{E} and $\vec{H},$ we can rotate the magnetic field and scan angular dependences, etc. The Hall effect is also affected by all these changes (or by most) by very little, whereas the variation of the magnetoresistance is very conspicuous and sometimes even dramatic. Broadly speaking we can make the following distinction: in low magnetic fields the main usefulness of the magnetoresistance consists in revealing something about the anisotropy of either the energy surfaces or of, say, the relaxation time. It is perhaps more directly useful for semiconductors. In high fields the magnetoresistance yields information about energy surfaces, disentangled from details of the scattering mechanisms. It is much more useful for metals, and reveals aspects of the anisotropy and the topology of the Fermi surface. (Fermi-surface topology may also be reflected in low-field phenomena, but this is much more subtle and we shall not discuss it.) Let us now consider low fields, continuing the argument along the power series expansion.
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The solution is provided by the method of Jones and Zener. All one has to do is to evaluate some integrals into which the model is directly fed. To second order one writes the final result as

$$\frac{\Delta \rho}{\rho_0} = B H^2$$
(189)

thus defining the magnetoresistance coefficient B. The low-field work consists in talking about B, which exhibits marked directional effects, as seen in Eq.(152). It is on the basis of this sort of formula that one begins to figure out different geometrical arrangements so that further experiments yield new information. Two special cases are particularly important, corresponding to $\vec{H} \parallel \vec{J}$ (B_L, L for longitudinal) and to $\vec{H} \pm \vec{J}$ (B_T, T for transverse). We have already seen that B_T vanishes unless there is some dispersive behaviour in the system, but it can be non-zero even with an entirely isotropic model. The longitudinal magnetoresistance, however, absolutely requires some anisotropy. Otherwise the carriers would simply flow along the magnetic field direction, with no Lorentz deflection, and nothing would happen.

3.5.1. Metals

The evaluation of the second-order coefficients in terms of any nontrivial model of Fermi surface is usually rather laborious (look up the formulae in Beer or Wilson and you will see). In the end one obtains an expression for B in terms of some parameters characterizing the geometry of the Fermi surface and then one seeks to explain the observed effects in terms of these parameters. For example, one might figure out an approximate representation of a non-spherical Fermi surface with, say, cubic symmetry by an expansion in cubic harmonics. The first-order term in the expansion would be

$$Y_{4}^{2}(\theta,\phi) = P_{4}(\cos\theta) + \frac{\cos^{4}\phi}{168}P_{4}^{4}(\cos\theta) = \frac{(x^{4}+y^{4}+z^{4}) - 3(x^{2}y^{2}+y^{2}z^{2}+z^{2}x^{2})}{(x^{2}+y^{2}+z^{2})^{2}}$$
(190)

Thus we might think of a surface like

$$\mathbf{k} = \alpha_0 \left(\mathscr{B}_{\overrightarrow{\mathbf{k}}} \right) + \alpha_1 \left(\mathscr{B}_{\overrightarrow{\mathbf{k}}} \right) \mathbf{Y}_4^{\mathsf{c}} (\theta, \varphi) + \cdots$$
(191)

and expect, unless the Fermi surface touches the Brillouin zone boundaries, that an expansion of this sort might be more or less adequate, especially if the anisotropy is not too large. Stopping at first order one could define one anisotropy parameter

$$A \equiv \frac{\alpha_1(\mathscr{B}_F)}{\alpha_0(\mathscr{B}_F)} \tag{192}$$

to describe the anisotropy in the shape of the Fermi surface and another one

$$A^{1} = \left[\left(\frac{d\alpha_{1}}{d\beta_{R}} \right) / \left(\frac{d\alpha_{0}}{d\beta_{R}} \right) \right]_{\sigma} F$$
(193)

to describe the anisotropy in the Fermi velocity. On doing the calculation one finds for the coefficients of (152) expressions of the form

$$b = b_{1} A^{2} + b_{2} A A^{1} + b_{3} A^{2}$$

$$c = c_{1} A^{2} + c_{2} A A^{1} + c_{3} A^{2}$$

$$d = d_{1} A^{2} + d_{2} A A^{1} + d_{3} A^{2}$$
(194)

(Thus: no anisotropy, no magnetoresistance.) In the end one evaluates B_L and B_T from here as quadratic expressions like (194), with coefficients describing angular dependence. For a given geometrical arrangement one finally arrives at the detailed comparison of observed magnetoresistance, on the one hand, and assumed Fermi surface, on the other hand. The longitudinal effect is usually much smaller than the transverse. But many experimental data have been taken in polycrystalline samples and, on averaging over orientations, B_L becomes comparable to B_T .

3.5.2. Semiconductors

Take spherical energy surfaces. Take $\vec{H} \perp \vec{E}.$ Then, using again the complex notation

$$J = \frac{nq^2}{m} \langle \frac{\tau}{1 + i\omega_o \tau} \rangle E$$
(195)

We cannot invert this relationship as easily as (185). We first have to write

$$J = \frac{nq^2}{m} \left\langle \frac{\tau}{1 + (\omega_c \tau)^2} \right\rangle E - i \frac{nq^2}{m} \left\langle \frac{\omega_c \tau^2}{1 + (\omega_c \tau)^2} \right\rangle E \equiv (a-ib) E$$
(196)

and then invert:

$$E = \frac{J}{a-ib} = \frac{a}{a^2 + b^2} J + i \frac{b}{a^2 + b^2} J$$
(197)

To second order this yields

$$\frac{\Delta\rho}{\rho_0} = \frac{\langle \tau^3 \rangle \langle \tau \rangle - \langle \tau^2 \rangle^2}{\langle \tau \rangle^2} \omega_c^2$$
(198)

This displays very nicely the effects of statistical dispersion. Because of Schwartz' inequality (198) is <u>positive definite</u>. This principle can be proved generally.

In many important cases, like n-Si and n-Ge, the magnetoresistance is not only due to statistical dispersion, but also to anisotropic energy surfaces. We have already indicated how to calculate the transport coefficients in this case. The standard business in this branch of semiconductor research consists in working with oriented single crystals and scanning angular patterns, which are then analysed with the formula given in (1952), in which the coefficients have been calculated after adding up the contributions to the total current due to the different ellipsoids. The actual calculation is rather tedious but straightforward, and it leads to expressions immediately usable for the analysis of experimental data. A great deal of very useful information has been obtained in this way.

3.6. Intermediate magnetic fields

The magnetoresistance continues increasing with H. It is customary to plot the data in the <u>Kohler diagram</u>. We have seen in section 3.3.2 that the solution in the presence of a magnetic field consists in applying an operator, which depends on $\tau \vec{H}$ to $\Phi_{\vec{K}}(H=0)$. Therefore, the currents in the presence of \vec{H} , and ultimately the magnetoresistance, depend on $\tau \vec{H}$. But τ is inversely proportional to ρ_0 . Thus: the <u>magnetoresistance</u> is a function of the form

$$\frac{\Delta \rho}{\rho_0} = F\left(\frac{H}{\rho_0}\right) \tag{199}$$

(Kohler's rule). The basis of this rule is the statement that the deflection of a carrier is proportional to H and to the time the carrier continues under the influence of H between two collisions. Of course, (199) can only hold exactly when there is no statistical dispersion in τ . Kohler's rule is therefore more useful (in fact approximately valid) for metals. The rule indicates that we can figure out what the effects would be in a higher magnetic field by decreasing the temperature. Even if the rule does not hold exactly, we can always say that $\omega_c \tau$ can be made large by increasing ω_c or by increasing τ , which involves the same idea: <u>magnetoresistance effects are favoured by low temperatures</u>. Kohler's rule is also useful in providing a way of comparing the magnetoresistance data for various metals in one universal plot. One chooses a standard temperature T_c and plots in one universal diagram the magnetoresistance versus

$$\mathrm{sH} \equiv \frac{\rho_0(\mathrm{T})}{\rho_0(\mathrm{T}_0)} \mathrm{H}$$

We have already indicated that the form of the conductivity tensor allowed by crystal symmetry suggests the existence of a variety of anisotropic phenomena. The physical basis of these phenomena can usually be understood in simple terms. For example, suppose an electric field in the (100) axis of a cubic crystal, and a magnetic field being rotated in the perpendicular plane (Fig. 5). Suppose, further, that the energy surfaces are anisotropic. The acceleration of \vec{k} , depending on $\vec{v_k} \times \vec{H}$, is always perpendicular to \vec{H} , but the actual physical drift of charge follows the acceleration of the velocity

$$\vec{\mathbf{v}}_{\vec{k}} = \left(\nabla_{\vec{k}} \vec{\mathbf{v}}_{\vec{k}}\right) \cdot \vec{k} = \frac{qc}{\hbar^2} \left(\nabla_{\vec{k}} \nabla_{\vec{k}} \delta_{\vec{k}}\right) \cdot \left(\vec{\mathbf{v}}_{\vec{k}} \times \vec{H}\right)$$
(200)

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This, of course, can have a component along \vec{H} . If an electric current is maintained in the (100) direction, then this deflection in the direction of \vec{H} must be stopped by an extra electric field, much as in the case of the ordinary Hall effect. It is as if we had a Hall effect in the same direction as \vec{H} . Knowing what to look for, it is not very difficult to go through the calculation and estimate the effect. One finds that this is zero up to second order: we must at least go up to 3rd order, which means that we must search experimentally in the intermediate-field region. To the lowest order, one finds that for a given H the magnitude of the effect should vary like sin 4 ϕ (Fig. 5). This effect has actually been observed in semiconductors and it exhibits the expected angular dependence. This is only a sample of the many different phenomena which are to be expected from a complete elucidation of all the components of the conductivity tensor in a magnetic field.



FIG.5. For \vec{H} not in a symmetry direction, actual drift \vec{J}^3 may result in the direction of \vec{H} itself, if the energy surfaces are anisotropic.

3.7. High-field effects in metals

The galvanomagnetic effects have some very distinctive and interesting features in high magnetic fields due to the fact that the scattering becomes then relatively unimportant and the carriers go round their orbits in an essentially undisturbed form. The features of the model, unmasked by the scattering, become then more apparent.

Let us explore the simplest example of a dispersive system, namely, a two-band model. Let us even assume that both types of carriers have the same m and τ . We just have the most idealized model of (negative) electrons and (positive) holes. In this discussion we shall use the following notation:

 $N_{+} = number of electrons$ $N_{+} = number of holes$ $N_{-} = N_{+} + N_{+}$ $n_{-} = N_{-} - N_{+}$ Let use consider crossed \vec{E} and \vec{H} and use the complex notation. We have an electron current

$$J_{-} = \frac{N_{-}q^{2}\tau}{m} \frac{E}{1+i(\omega_{c}\tau)}$$
(201)

and a hole current

$$J_{+} = \frac{N_{+}q^{2}\tau}{m} \frac{E}{1 - i(\omega_{c}\tau)}$$
(202)

hence a total current $J_+ + J_+$. Put

$$\sigma_{a} \equiv \frac{Nq^{2}\tau}{m} \qquad \sigma_{b} \equiv \frac{nq^{2}\tau}{m} \qquad \frac{\sigma_{a}}{\sigma_{b}} = \frac{N}{n}$$
(203)

then

$$J = \frac{\sigma_a - i(\omega_c \tau) \sigma_b}{1 + (\omega_c \tau)^2} E$$
(204)

hence

$$E_{J} = \frac{\sigma_{a} \left[1 + (\omega_{c} \tau)^{2}\right]}{\sigma_{a}^{2} + (\omega_{c} \tau)^{2} \sigma_{b}^{2}}$$
(205)

and

$$E_{\perp} = i \frac{\sigma_{b} [1 + (\omega_{c} \tau)^{2}] (\omega_{c} \tau)}{\sigma_{a}^{2} + (\omega_{c} \tau)^{2} \sigma_{b}^{2}}$$
(206)

Let us interpret the results. From (205):

$$\rho = \frac{1}{\sigma_{a}} \frac{\left[1 + (\omega_{c}\tau)^{2}\right]}{1 + (\omega_{c}\tau)^{2} (n/N)^{2}}$$
(207)

From (206):

$$R = \frac{1}{nqc} \frac{\left[1 + (\omega_c \tau)^2\right]}{(N/n)^2 + (\omega_c \tau)^2}$$
(208)

Now look at the high field limit.

$$\rho \rightarrow \frac{1}{\sigma_{\rm b}} \left(\frac{\rm N}{\rm n}\right) \quad \rm R \rightarrow \frac{1}{\rm nqc}$$
(209)

Thus, the resistivity tends to a saturation value and the Hall effect is just what we would expect from a net charge density $\rm N_{\star}$ - $\rm N_{-}$. We can take these

limits provided $n \neq 0$. Suppose there are as many electrons as holes, as is the case with divalent metals with one atom per unit cell (we are not yet considering open orbits, which we shall come to presently). Then we have n = 0 and (207) shows that ρ continues increasing like H^2 . There is no high field saturation for $N_{+} = N_{-}$. This is a very sharp contrast (saturation or not, depending on N_{+} and N_{-}). Moreover, from (208) if $N_{+} = N_{-}$ then R = 0. There is no Hall effect.

We have oversimplified the treatment. Since these theoretical predictions insist that high field studies can furnish rather direct information, let us scrutinize a little the assumptions we have made. As there is a large fraction of a full course on high field magnetoresistance in this seminar, I shall only discuss the subject in broad outline.

Let us first treat the scattering. This is easy to dispense with. Since we are interested in the high-field limit, the scattering becomes unimportant and we might as well make the simplest assumption (constant τ). Then there is the Fermi surface. This can indeed introduce major differences. Let us provisionally consider only closed Fermi surfaces. Still, the geometry can be rather complicated. Are we sure that a prediction like. say, (209) still holds for any geometry? Let us consider the situation described in Fig. 5. We have electrons and holes, contained in separate, closed surfaces of otherwise arbitrary geometry. We consider the high field limit in which we ignore the scattering. We are then confronted with the situation studied in the Appendix, only now with Bloch electrons instead of free electrons. Let us remember the quantum treatment in crossed \vec{E} and \vec{H} , because we did that rather more formally, specifying where to use canonical momenta or kinetic momenta. The object to watch is the Hamiltonian we wrote down in (A.69). We are not interested now in changing our system of quantum numbers, but we can notice one thing in this Hamiltonian. All the terms except the one containing the explicit dependence on the kinetic momentum p_v contain the mass of the particle. On going over to the semiclassical picture for Bloch electrons, these terms will change (at the very least m would go over into the effective mass) and the term in p_v will still contain the explicit dependence on the 'crystal kinetic momentum' hky. Thus, our carriers in Fig. 6 have their energy $\mathscr{E}_{\vec{\tau}}$ explicitly changed by an extra term (cE/H) $\hbar k_v$, hence a net drift velocity

$$v_{y} = \frac{1}{\hbar} \frac{\partial}{\partial k_{y}} \left(\frac{cE\hbar k_{y}}{H} \right) = \frac{cE}{H}$$
(210)

From this we get, out of the slices shown in Fig. 6, a transverse current

$$\delta J_{y} = \sum_{\pm} \iint q(\delta \nu) \frac{cE}{H} dk_{x} dk_{y}$$
(211)

where $(\delta \nu)$ is the density of states per unit area of the slices. The sign is positive for one contribution (e.g., holes) and negative for the other one (electrons). Clearly

$$\iint dk_{x} dk_{y}$$
(212)



FIG. 6. A section of a Fermi surface consisting of two closed non-intersecting surfaces. One electronlike and one hole-like. The section is normal to \vec{H} .

is just the area of the transverse section which, multiplied by $(\delta \nu)$ gives the number δN_{\pm} of carriers contained in the slice. Summing over all the slices which make up the Fermi surface we get

$$J_{y} = (N_{+} - N_{-}) q \frac{cE}{H}$$
(213)

which is the same as our previous formula for R in (209). This shows that the result was more general.

We would in fact like to write down an exact solution of the Boltzmann equation with which to evaluate in detail the elements of the conductivity tensor. We have already mentioned some methods of solution either for particular models of band structure or for low fields. If a relaxation time is assumed (and this is quite appropriate for the high-field limit) then a formal exact solution of the Boltzmann equation can be written down. It is convenient for this to describe the motion of the carriers in \vec{k} space using special coordinates appropriate to the case of a magnetic field. Consider a section (of the Fermi surface) normal to \vec{H} , and remember we are still assuming closed surfaces. Let v_1 denote the component of the element of length around the the orbit (section of the Fermi surface) contained in this plane. Then in an elementary time interval dt:

$$dk = \frac{q}{hc} v_{\perp} H dt$$
 (214)

Thus, for a closed path, the period of the orbital motion is

$$\frac{2\pi}{\omega_{\rm H}} \equiv \oint dt = \frac{c\hbar}{qH} \int \frac{dk}{v_{\perp}}$$
(215)

Here we have <u>defined</u> the frequency of the orbit, which depends on the geometry of the Fermi surface. Thus, for a fixed k_z , in the anulus

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between orbits of area $\mathcal A$ and $\mathcal A$ + d $\mathcal A$, corresponding to energies $\mathcal B$ and $\mathcal B$ + d $\mathcal B$, we have

$$d\mathcal{A} = \oint \frac{d\mathcal{B}}{\hbar v_{\perp}} dk = \frac{2\pi q H}{\hbar^2 c \omega_{H}} d\mathcal{B}$$
(216)

and

$$\omega_{\rm H} = \frac{2\pi q {\rm H}}{{\rm h}^2 {\rm c}} \left(\frac{{\rm d}}{{\rm d}} \frac{\mathscr{A}}{{\rm d}} \right)^{-1}$$
(217)

If we define the mass of the orbit $\ensuremath{\mathsf{m}_{\mathsf{H}}}$ by

$$\frac{\mathrm{qH}}{\mathrm{m}_{\mathrm{H}}\mathrm{c}} \equiv \omega_{\mathrm{H}} \tag{218}$$

then (217) provides the formula for calculating $m_{\rm H}$. For example, let us take a spherical Fermi surface:

$$\mathscr{A} = \pi \mathbf{k}^2 = \frac{2\pi \mathbf{m}}{\hbar^2} \mathscr{B} \qquad \omega_{\mathrm{H}} = \frac{2\pi \mathbf{q} \mathbf{H}}{\hbar^2 \mathbf{c}} \frac{\hbar^2}{2\pi \mathbf{m}} = \frac{\mathbf{q} \mathbf{H}}{\mathbf{m} \mathbf{c}} = \omega_{\mathbf{c}}$$
(219)

which reproduces the ordinary cyclotron frequency. You will find (217) useful in the theory of the Haas-van Alphen effect.

But we were after solving our Boltzmann equation, for which we look at (214) and (215) and define a phase variable ϕ which measures the (angular) position around the orbit. Thus, between two instants, t_0 and t_1 :

$$\varphi_1 - \varphi_0 = \omega_H \frac{c\hbar}{qH} \int_0^1 \frac{dk}{v_\perp}$$
(220)

After a complete period $\boldsymbol{\phi}$ changes by

$$\omega_{\rm H} \frac{c\hbar}{q{\rm H}} \oint \frac{q{\rm H}}{\hbar c} dt = \omega_{\rm H} \oint dt = 2\pi \qquad (221)$$

Thus its time derivative is

$$\dot{\phi} = \omega_{\rm H}$$
 (222)

We then use the coordinates (\mathscr{B}, k_z, ϕ) as a convenient set to locate an electron with phase ϕ in a section k_z of a surface of energy \mathscr{B} . Our distribution function becomes

$$f(\mathscr{B}, \mathbf{k}_{z}, \varphi) \equiv f^{0}(\mathscr{B}) + \delta f(\mathscr{B}, \mathbf{k}_{z}, \varphi)$$
(223)

The Boltzmann equation now reads

$$\omega_{\rm H} \frac{\partial (\delta f)}{\partial \varphi} + q \vec{E} \cdot \vec{v} \frac{\partial f^0}{\partial \mathscr{B}} = - \frac{\delta f}{\tau}$$
(224)

which is amazingly simple. The formal solution is

$$\delta f = -\frac{q}{\omega_{\rm H}} \frac{\partial f^0}{\partial \mathscr{B}} \vec{E} \cdot \int_{0}^{\varphi} \vec{\nabla} (\mathscr{B} \quad k_{\rm z} \quad \varphi') e^{(\varphi - \varphi')/\omega_{\rm H} t} d\varphi'$$
(225)

and the elements of the conductivity tensor:

$$\sigma_{ij} = -\frac{2q^2}{\omega_H} \int \left\{ \int_0^{\infty} v_i(\phi) e^{\phi'/\omega_H \tau} v_j(\phi + \phi') d\phi' \right\} \frac{\partial f^0}{\partial \mathscr{E}} d\vec{k}$$
(226)

This formula is valid for arbitrary Fermi surfaces. Its real usefulness consists in lending itself quite naturally to an expansion in powers of $(\underset{H}{\omega_{\tau}})^{-1}$, which is appropriate to study high field effects. An explicit example can be seen in Ziman (1960, section 12.7). One can evaluate σ_{xy} , for example, and recover (213) again. For low fields, of course, it reproduces the results directly obtained by the method of Jones and Zener. The Chambers method consists in an alternative (and direct) evaluation of the non-equilibrium distribution in rather intuitive and appealing physical terms. Hence the current is immediately written down. If the result is linearized in \vec{E} , then the Chambers formula reproduces (226).

So far we have assumed that the Fermi surface contained only closed orbits. Then we can define $\omega_{\rm H}$ and $m_{\rm H}$. But real Fermi surfaces can exhibit a different topology, and this is crucial for the galvanomagnetic effects in high fields. Consider the types of orbits of the hypothetical Fermi surface shown in Fig.7. This surface is a conceivable tight binding model for a simple cubic lattice. Imagine this unit repeated periodically in all directions.

Now suppose a magnetic field is applied in the z direction. The orbits, determined by planes with orientation π (Fig. 7) are shown in Fig.8 for different values of k_z . Orbits A are electron-like; orbits B are hole-like. Orbits C are neither type. These orbits are not necessarily closed. They run endlessly through the saddle points P in the repeated zone scheme. However, these orbits occur only for discrete values of k_z and the probability of the carrier having the right value of k_z is negligible, so that these orbits have negligible effect.

But suppose \tilde{H} is rotated in the (y, z) plane. The orbits are determined by planes with orientation, say, π^{*} (Fig. 7). Then as shown in Fig. 9, open orbits will result for a range of values of k_z and their effect will be felt in the resulting magnetoresistance. We need not go here into the details, which you will have in full later. It suffices to notice that for closed orbits the carriers go round them several times as soon as the field is sufficiently high, so that further increases of H do not introduce the carriers to new features of the Fermi surface. In fact, nothing new happens, the magnetoresistance settles down to a saturation value (unless there is exact cancel-

lation between electrons and holes). For the open orbits, on the other hand, the carriers never complete the orbit and thus go on sampling new features and the resistivity goes on changing. A detailed calculation shows that it increases like H^2 . In between there are the closed but very extended



FIG. 7. A hypothetical model of a Fermi surface.



FIG. 8. Cross sections $k_z = \text{constant}$ for different values of k_z (planes of type π) of the Fermi surface in Fig. 7. Shaded areas represent occupied states and A-- closed electron orbit $\frac{d^2k}{dd^2} > 0$ B-- closed hole orbit $\frac{d^2k}{dc^2} < 0$ C-- critical extended orbit P-- saddle points where $v_x = v_y = 0$, $\frac{dk}{dd} = 0$



FIG. 9. Cross sections of the Fermi surface shown in Fig. 7 for planes rotated about k_{χ} (planes of type π '). Orbits A and B have the same meaning as before. But orbits of type A may coalesce and give open extended orbits D. Notice that strips (1), (2), (3), etc. no longer cut equivalent parts of the Fermi surface. In general their orbits will be different; they may change in dimension or even in topology.

orbits, which may require very high fields before saturation is attained. It is clear that by systematic exploration of oriented single crystals and patient analysis of the experimental data one can ultimately unravel the topology of even very complicated Fermi surfaces. This is hard, challenging and rewarding work.

There is one fact of life that we ought to mention. Many experiments have been done with polycrystalline samples and they show a continued increase of the resistivity going rather like the first power of H. It is plausible to think that the explanation lies in the topology of the Fermi surface and in some averaging over the effects of open and closed surfaces which appear for a fixed direction of \vec{H} and variable crystal orientations. However, there is no firm ground for a quantitative theory of this averaging and it is in fact more advisable to strive to carry out a programme with single crystals. The most vigorous push in this direction has come from the Russian school (Chambers, 1960).

3.8. A semiclassical view of high field quantization effects

To conclude let us make a few remarks about quantization effects in high fields and, keeping within the spirit of this course, let us view them in a semiclassical way. Remember the formula (221) for $\omega_{\rm H}$ and the allowed sizes of the orbits in \vec{k} space (A.65). Thus, successive allowed orbits differ in area by

$$\Delta \mathscr{A} = \frac{2\pi q H}{\hbar c}$$
(227)

Let us assume high quantum number, so that

$$\frac{\mathrm{d}\mathscr{A}}{\mathrm{d}\mathscr{B}} \simeq \frac{\Delta\mathscr{A}}{\Delta\mathscr{B}} = \frac{2\pi\mathrm{q}\mathrm{H}}{\mathrm{hc}\Delta\mathscr{B}}$$
(228)

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What we are saying, in view of (217) and (228), is that a change $\Delta \mathscr{A}$ in area corresponds to a change in a quantum of energy

$$\Delta \mathscr{B} = \hbar \omega_{\mu} \tag{229}$$

just as in the simple theory for free electrons. We imply that high fields means $\omega_{\rm H}\tau\gg 1$. This means

$$\hbar\omega_{\rm H} \gg \frac{\hbar}{\tau} \tag{230}$$

The right-hand side of this inequality is a measure of the <u>collision broaden-</u> <u>ing</u> of the quantum energy levels, i.e. of the uncertainty in the energy of these levels associated with a finite lifetime τ , after which the state is destroyed by a collision. Thus, on this account, the quantum levels are sharply defined. But we still have to think of k_BT. The quantization will be blurred up unless

$$\hbar \omega_{\rm H} \ge k_{\rm B} T \tag{231}$$

For a free electron mass this requires a minimum magnetic field (in gauss) of the order of 10^4 T (T in degree Kelvin). Even if one has very expensive equipment to work at T $\simeq 1^{\circ}$ K, this would require fields which are certainly accessible but not too easily (or too cheaply). But still, this would be orders of magnitude below the degeneracy temperature of a typical metal, i.e.

$$\hbar\omega_{\rm H} \ll \mathscr{B}_{\rm F} \tag{232}$$

Outside the realm of science fiction it is reasonable to think of Fermi electrons in states of high quantum numbers. This is why even observed quantization effects can be fairly well explained in a semiclassical picture. The kind of quantum theory which could satisfy a purist is not really needed in this business to understand the observed behaviour of metals, but only to lay down the rigorous foundation of the theory. As for the actual quantization effects they are, of course, the renowned <u>oscillations</u>. If $\mathscr{B}_{\rm F}$ is an exact multiple of $\hbar\omega_{\rm H}$, then we have "allowed conduction electrons". But, as H increases a little, the allowed orbits are outside the Fermi surface, and the conductivity drops, only to go up again when the next allowed quantum level reaches the Fermi level, and so on. Thus we need

$$\frac{\mathscr{B}_{F}}{\hbar\omega_{H}} = \frac{\mathscr{B}_{F} m_{H}c}{\hbar q H}$$

to be an integer. Therefore, the period observed, as a function of $\mathrm{H}^{^{-1}}$ will be

$$\Delta \left(\frac{1}{H}\right) = \frac{q\hbar}{\mathscr{B}_{F} mc}$$
(233)

which explains the celebrated and somewhat uninteresting oscillatory behaviour of the resistivity in very high magnetic fields (Shubnikov-deHaas effect).

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The case of insulators is different. Think again of a few, very few, conduction electrons (or polarons) interacting with optical polar modes of energy $\hbar\omega_{\vec{q}}$ We can easily put all the conduction electrons in the lowest Landau level, and then we do have a thoroughly quantum region. We might expect the scattering to be enhanced every time the electrons, by absorbing a polar phonon, can jump up to a higher quantum level. Under these circumstances the electrons find a very concentrated density of final states for scattering into, and this would happen every time $\hbar\omega_{\rm H}$ is an exact submultiple of $\hbar\omega_{\vec{q}}$, which is experimentally quite feasible. The mobility would then exhibit oscillations as a function of H. Such effect has in fact been observed. This is just to show (a) how amusing the phenomenology of transport in a magnetic field can be, (b) when to take quantum theory seriously.

APPENDIX

Dynamics of free electrons in a magnetic field

In order to understand the dynamics of electrons with a complicated band structure in the presence of a magnetic field it is important to first understand the theory for free electrons. Since this, for no real reason, seems to be a rather unpopular topic, we shall summarize here the main facts.

1. Classical theory

We shall use the complex notation in the plane perpendicular to the field. Thus H will be a "scalar" multiplicative factor, r, v and E will be vectors and multiplication by i will mean rotation through $\pi/2$ about the axis of the magnetic field. The complete Lorentz force will be

$$q E - i \frac{q}{c} v H$$
 (A.1)

For E = 0

$$m\dot{v} = -i\frac{q}{c}vH; \quad v = v_0 e^{-i\omega_c t}; \quad \omega_c = \frac{qH}{mc}$$
 (A.2)

thus

$$r = i \frac{v_0}{\omega_c} e^{-i\omega_c t} \equiv r_0 e^{-i\omega_c t}$$

that is to say, a circular orbit with the cyclotron frequency ω_c . And the orbit in r space is derived from the orbit in v space by a rotation of 90° and multiplication by a scale factor.

For crossed E and H

$$\mathbf{m} \dot{\mathbf{v}} = \mathbf{q} \mathbf{E} - \mathbf{i} \frac{\mathbf{q}}{\mathbf{c}} \mathbf{v} \mathbf{H}$$
 (A.3)

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Put

$$G = \frac{q}{m}E$$
 (A.4)

then

$$\dot{v} + i\omega_c v = G$$
 (A.5)

which is solved by

$$v = iv_{\perp} - iv_{\perp} e^{-i\omega_{c}t}$$
(A.6)

(taking v(0) = 0) with

$$v_{\perp} = -\frac{cE}{H}$$
(A.7)

Taking r(0) = 0 and putting

$$x_0 = -\frac{G}{\omega_c^2} = \frac{v_\perp}{\omega_c} = -\frac{mc^2 F}{qH^2}$$
 (A.8)

we have

$$r = -x_0 + iv_1 t + x_0 e^{-i\omega_c t}$$
 (A.9)

The geometrical interpretation is given by Fig.10. Notice that v does not depend on the sign of q.



FIG. 10. Particle motion in a magnetic field.

T = kinetic energy

L = T - V Lagrangian

V = potential energy the Lagrangian equations of motion are

$$\frac{\mathrm{d}}{\mathrm{dt}}\frac{\partial \mathrm{L}}{\partial \dot{\mathrm{q}}_{\mathrm{i}}} - \frac{\partial \mathrm{L}}{\partial \mathrm{q}_{\mathrm{i}}} = 0$$



and the canonical momentum conjugate to \boldsymbol{q}_i is

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

This procedure is possible, provided the forces can be derived from a potential. If not, call F_i^M the forces which cannot be derived from a potential. Then, if a function $M(q_i, \dot{q_i})$ can be found such that

$$\mathbf{F}_{i}^{M} = \frac{\mathrm{d}}{\mathrm{dt}} \frac{\partial M}{\partial \dot{\mathbf{q}}_{i}} - \frac{\partial M}{\partial \mathbf{q}_{i}} \qquad (A.10)$$

the Lagrangian scheme goes through with L replaced by

 $L_{M} = L - M = T - V - M$ (A.11)

Let us now write down Newton's law with the familiar Lorentz force.

$$\frac{\mathrm{d}}{\mathrm{dt}} (\mathbf{m} \,\vec{\mathbf{v}}) = \mathbf{q} \left(\vec{\mathbf{E}} + \frac{1}{\mathrm{c}} \vec{\mathbf{v}} \times \vec{\mathbf{H}} \right) \tag{A.12}$$

This can easily be rewritten, in terms of the scalar and vector potentials (ϕ,\vec{A}) as

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\mathbf{m} \vec{\mathbf{v}} + \frac{\mathrm{q}}{\mathrm{c}} \vec{\mathbf{A}} \right) = \nabla (-\mathrm{q}\varphi + \frac{\mathrm{q}}{\mathrm{c}} \vec{\mathbf{v}} \cdot \vec{\mathbf{A}}) \tag{A.13}$$

Take components:

$$\frac{\mathrm{d}}{\mathrm{dt}} \left(\mathrm{m} \, \dot{\mathbf{r}}_{i} + \frac{\mathrm{q}}{\mathrm{c}} \mathbf{A}_{i} \right) = \frac{\partial}{\partial \mathbf{r}_{i}} \left(-\mathrm{q}\phi + \frac{\mathrm{q}}{\mathrm{c}} \vec{\mathbf{v}} \cdot \vec{\mathbf{A}} \right)$$
(A.14)

 \mathbf{or}

$$\frac{\mathrm{d}}{\mathrm{dt}} \left(\frac{\partial \mathrm{L}_{\mathrm{M}}}{\partial \dot{\mathrm{r}}_{\mathrm{i}}} \right) = \frac{\partial \mathrm{L}_{\mathrm{M}}}{\partial \mathrm{r}_{\mathrm{i}}} \tag{A.15}$$

satisfied by

$$L_{M} = \frac{1}{2} m v^{2} - q \phi + \frac{q}{c} \vec{v} \cdot \vec{A} \qquad (A.16)$$

Thus, the M function of our problem is

$$M = -\frac{q}{c} \vec{v} \cdot \vec{A} \qquad (A.17)$$

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Therefore, the canonical momenta conjugate to the coordinates \boldsymbol{r}_i are

$$\tilde{\mathbf{p}}_{i} = \frac{\partial \mathbf{L}_{M}}{\partial \dot{\mathbf{r}}_{i}} = \mathbf{m} \mathbf{v}_{i} + \frac{\mathbf{q}}{\mathbf{c}} \mathbf{A}_{i}$$
(A.18)

and the relation with the kinetic momentum

$$\vec{p} = m \vec{v} \tag{A.19}$$

is

$$\vec{\vec{p}} = \vec{\vec{p}} + \frac{q}{c}\vec{\vec{A}}$$

The Hamiltonian is

$$\mathcal{H} = \sum_{i} \tilde{\vec{p}}_{i} \dot{\vec{r}}_{i} - L_{M} (\vec{r}_{i}, \dot{\vec{r}}_{i})$$
$$= \tilde{\vec{p}} \cdot \vec{v} - \frac{1}{2} m \vec{v} \cdot \vec{v} - \frac{q}{c} \vec{A} \cdot \vec{v} + q\phi$$
$$(A.20)$$
$$= \frac{1}{2m} (\tilde{\vec{p}} - \frac{q}{c} \vec{A})^{2} + q\phi$$

obviously.

When passing over to quantum theory we shall have to be careful about ordering of factors in the bilinear term $\vec{p} \cdot \vec{A}$ (or $\vec{A} \cdot \vec{p}$). Think of a scalar function f. In the passage to quantum theory we shall find

$$\vec{p} \cdot \vec{A} f \rightarrow -i\hbar \nabla(\vec{A} f) = -i\hbar \vec{A} \cdot \nabla f - i\hbar f \nabla \cdot \vec{A}$$
 (A. 21)

i.e. between operators:

$$[\vec{\vec{p}}, A] = -i\hbar \nabla \cdot \vec{A}$$
 (A.22)

Thus, whether the quantum-mechanical operators \vec{p} and \vec{A} can be interchanged or not depends on whether div $\vec{A} = 0$ or not. Does this impose any important restriction? Remember that $\vec{H} = \nabla \times \vec{A}$ leaves an arbitrariness in \vec{A} , since we can add to it any gradient of a time-independent scalar function and this will not change the fields. Can we then choose \vec{A} so that div $\vec{A} = 0$? We are touching the question of gauge invariance. Let us see this still in the classical theory.

Take a scalar function $\Lambda(\vec{r})$ and change

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \nabla \Lambda(\vec{r}) \tag{A.23}$$

If Λ is also time dependent, effect a change of scalar potential

$$\varphi \rightarrow \varphi' = \varphi - \frac{1}{c} \frac{\partial \Lambda(\vec{r}, t)}{\partial t}$$
 (A.24)

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Let us take the general case. With these transformations

$$\vec{E}' = \vec{E}, \quad \vec{H}' = \vec{H}$$
 (A.25)

The fields are gauge-invariant (as physical quantities must be). Suppose then that, to begin with

$$\nabla \cdot \vec{A} + \frac{1}{c} \frac{\partial \phi}{\partial t} = g(\vec{r}, t) \neq 0$$
 (A.26)

Then, by choosing $\Lambda(\vec{r}, t)$ such that

$$\nabla \cdot (\nabla \Lambda) - \frac{1}{c^2} \frac{\partial^2 \Lambda}{\partial t^2} = -g \qquad (A.27)$$

we shall have, after the gauge transformation:

$$\nabla \cdot \mathbf{A}' + \frac{1}{c} \frac{\partial \varphi'}{\partial t} = 0$$
 (A.28)

Thus, we can always choose a gauge such that the Lorentz condition is satisfied, while physical quantities remain invariant.

II. Quantum theory

The expectation values of the quantum mechanical operators, yielding the physical quantities, will be gauge-invariant, but this leaves the possibility that the wave function may be multiplied by a phase factor. Thus (restricting ourselves to time-independent fields) the gauge transformation (A.23) effects a transformation

$$\psi \to \psi^{\dagger} = e^{i\lambda}\psi \tag{A.29}$$

We can find λ from the condition that, for any dynamical variable Q we have, in the gauges \vec{A} and \vec{A}' :

$$\langle \psi \mid \mathbf{Q}(\vec{\mathbf{A}}) \mid \psi \rangle = \langle \psi' \mid \mathbf{Q}'(\vec{\mathbf{A}}') \mid \psi' \rangle \qquad (A.30)$$

We also want to conserve the probability density and the probability current density. Thus we start from the Hamiltonian

$$\mathcal{H}(\vec{A}) = \frac{1}{2m} \left\{ \vec{p} - \frac{q}{c} A(\vec{r}) \right\}^2 + q\varphi(\vec{r}) + U(\vec{r})$$
(A.31)

where U can be any ordinary potential, apart from (\vec{A}, ϕ) . We work in the position representation, in which the <u>operators</u> $\vec{\tilde{p}}_{op}$ and \vec{r}_{op} are represented by

$$\vec{r}_{op}f = \vec{r}f; \quad \vec{p}_{op}f = -i\hbar\nabla f$$
 (A.32)

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Thus, we have to be careful and write (A.31) as

$$\mathscr{H}(\vec{A}) = -\frac{\hbar^2}{2m}\nabla^2 + q\varphi + U + \frac{ie\hbar}{2mc}(\vec{A}\cdot\nabla+\nabla\cdot\vec{A}) + \frac{q^2}{2mc}A^2$$
(A.33)

because we do not know whether, to begin with, div $\vec{A} = 0$ or not. We first look for a continuity equation

$$\frac{\partial \left|\psi\right|^{2}}{\partial t} + \nabla \cdot \vec{j} = 0$$
 (A.34)

This will give us the formula for the probability current density in the presence of \vec{A} . Using

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar} \mathscr{U}\psi; \quad \frac{\partial \psi^*}{\partial t} = -\frac{1}{i\hbar} \mathscr{U}^{\dagger}\psi^* \qquad (A.35)$$

we have

$$\frac{\partial |\psi|^2}{\partial t} = -\frac{\psi}{2i\hbar m} \left(-\frac{\hbar}{i} \nabla - \frac{q}{c} \vec{A} \right) \left(-\frac{\hbar}{i} \nabla - \frac{q}{c} \vec{A} \right) \psi^* + \frac{\psi^*}{2i\hbar m} \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \vec{A} \right) \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \vec{A} \right) \psi$$
(A. 36)

whence, after some rearrangement

~

$$\frac{a|\psi|^2}{\partial t} + \nabla \cdot \left\{ \frac{\hbar}{2\min} \left(\psi^* \nabla \psi - \psi \nabla \psi^* \right) - \frac{q}{mc} \vec{A} \psi^* \psi \right\} = 0$$
 (A.37)

The term in curly brackets gives formula for the current density in the presence of A.

Now consider the wave function ψ^{\dagger} of (A.29), which goes with the gauge transformation of (A.23). We want the formula for the current density to remain the same in the new gauge. We evaluate

$$\frac{\hbar}{\mathrm{mi}} \left(\mathrm{e}^{-\mathrm{i}\lambda} \psi^* \nabla \mathrm{e}^{\mathrm{i}\lambda} \psi - \mathrm{e}^{\mathrm{i}\lambda} \psi \nabla \mathrm{e}^{-\mathrm{i}\lambda} \psi^* \right)$$
$$- \frac{\mathrm{q}}{\mathrm{mc}} \left(\vec{A} + \nabla \Lambda \right) \mathrm{e}^{-\mathrm{i}\lambda} \psi^* \mathrm{e}^{\mathrm{i}\lambda} \psi$$
$$= \frac{\hbar}{2\mathrm{mi}} \left(\psi^* \nabla \psi - \psi \nabla \psi^* \right) + \frac{\hbar}{2\mathrm{mi}} \left(\mathrm{i}\nabla \lambda + \mathrm{i}\nabla \lambda \right) \left(\psi^* \psi \right)$$
$$- \frac{\mathrm{q}}{\mathrm{mc}} \vec{A} \psi^* \psi - \frac{\mathrm{q}}{\mathrm{mc}} \left(\nabla \Lambda \right) \psi^* \psi$$

Thus, the formula remains invariant with $\lambda = q\Lambda/\hbar c$. Summing up.

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \nabla \Lambda(\vec{r})$$

$$(A. 38)$$

$$\psi \rightarrow \psi' = e^{iq\Lambda/\hbar c} \psi$$

It is easy to verify that this value of λ also ensures the invariance of the Schrödinger equation and the kinematic velocity. For example, consider the velocity operator

 $\vec{v}_{op} = \frac{1}{m} \left(\vec{\tilde{p}}_{op} - \frac{q}{c} \vec{A} \right) \equiv \vec{v}_{op} (\vec{A})$ (A.39)

Suppose ψ is an eigenstate corresponding to eigenvalue $\vec{v}.$ Then, in the gauge \vec{A}

 $\vec{v}_{op}\psi = \vec{v}\psi \qquad (A.40)$

and, in A'

$$\vec{v}_{op}(\vec{A})\psi^{\dagger} = \frac{1}{m} \left\{ \frac{\hbar}{i} \nabla - \frac{q}{c} \vec{A} - \hbar (\nabla \lambda) \right\} (e^{i\lambda}\psi)$$
$$= \frac{\psi e^{i\lambda}}{m} \left\{ \frac{\hbar}{i} i (\nabla \lambda) - \hbar (\nabla \lambda) \right\} + e^{i\lambda} \vec{v}_{op}(\vec{A})\psi$$
$$= e^{i\lambda} \vec{v}(\vec{A})\psi = \vec{v}(\vec{A})\psi^{\dagger} \qquad (A.41)$$

that is to say, if (A.40) is satisfied, then also in the new gauge ψ ' is an eigenstate of the velocity operator with the same eigenvalue as before.

We can envisage the following picture in an abstract vector space: A gauge transformation is simply a rotation of the vectors $(\psi' = e^{i\lambda}\psi)$. Thus the operators are transformed like

$$Q(\vec{A}') = e^{i\lambda}Q(\vec{A}) e^{-i\lambda}$$
(A.42)

indeed, we have said in (A.40) and (A.41) that

$$\vec{\mathbf{v}}_{op}(\vec{\mathbf{A}}^{\,\prime})\psi^{\prime} = e^{i\lambda}\vec{\mathbf{v}}_{op}(\vec{\mathbf{A}}) e^{-i\lambda}\psi^{\prime} \qquad (A.43)$$

Thus, for the kinetic energy operator we have

$$T_{op}(\vec{A}') = \frac{m}{2} \vec{v}_{op}(\vec{A}') \cdot \vec{v}_{op}(\vec{A}') = \frac{m}{2} e^{i\lambda} \vec{v}_{op}(\vec{A}) \cdot \vec{v}_{op}(\vec{A}) e^{-i\lambda} = e^{i\lambda} T_{op}(\vec{A}) e^{-i\lambda}$$
(A.44)

Thus

$$T_{op}(\vec{A}')\psi' = e^{i\lambda}T_{op}(\vec{A}) e^{-i\lambda}e^{i\lambda}\psi = e^{i\lambda}T(\vec{A})\psi = T(\vec{A})\psi' \qquad (A.45)$$

and we again have physical invariance.

As for the total potential energy operator, $U_{op} + q\phi_{op}(\vec{r})$ since \vec{A} does not appear explicity, the gauge invariance is trivially obvious. Thus, for the total Hamiltonian

$$\mathscr{H}(\vec{A}') = e^{i\lambda} \mathscr{H}(\vec{A}) e^{-i\lambda}$$
 (A.46)

Gauge invariance arguments are involved in the wave packet treatments of the dynamics of Bloch electrons mentioned in the notes. For example, starting from the gauge

$$\vec{A} = \frac{1}{2} \quad \vec{H} \times \vec{r}$$

if we perform the translation

$$\vec{r} \rightarrow \vec{r}' = \vec{r} - \langle \vec{r} \rangle$$

where $\langle \vec{r} \rangle$ is the expectation value of the position in the packet, then this induces a gauge transformation.

$$\vec{A} \rightarrow \vec{A}' = \frac{1}{2} \vec{H} \times (\vec{r} - \langle \vec{r} \rangle) = \vec{A} + \nabla \left\{ -\frac{1}{2} \vec{r} \cdot \vec{H} \times \langle \vec{r} \rangle \right\}$$

such that, at every instant, the vector potential becomes vanishingly small on getting close to the centre of the packet. This is the procedure mentioned in the notes.

III. Quantization of the motion of a free charged particle in the presence of a magnetic field.

For $\vec{H} = (0,0 \text{ H})$ choose gauge $\vec{A} = (-y \text{ H}, 0, 0)$.

Let us recall the commutation relations between canonically conjugate variables

$$[r_i, \tilde{p}_i] = i\hbar\delta_{ii}, \text{ etc.}$$
(A.47)

(We put here $r_1 = x$, $r_2 = y$, $r_3 = z$). Then, the commutators of the kinetic momentum \vec{p} are

$$[p_{x}, p_{y}] = i \frac{qH}{c} \hbar = i m \hbar \omega_{c}$$

$$[p_{x}, p_{z}] = [p_{y}, p_{z}] = 0$$
(A.48)

Thus, since

$$\mathscr{H} = \frac{1}{2m} p^2$$

we have

$$[p_z, \mathcal{H}] = 0$$

The kinetic momentum in the direction of \vec{H} is a constant of the motion. This degree of freedom can be treated separately and it has its own spectrum of eigenvalues $p_z^2/2m$ where p_z is not quantized by the magnetic field (e.g., in a crystal p_z can take the allowed values of $\hbar k_z$ as for H = 0). The z dependence of the eigenfunctions is simply given by plane waves

Write

$$\mathcal{H} \equiv \mathcal{H}_{\perp} + \mathcal{H}_{\parallel} \equiv \frac{1}{2} \left\{ \left(\frac{\mathbf{p}_{\mathbf{x}}}{\sqrt{\mathbf{m}}} \right)^2 + \left(\frac{\mathbf{p}_{\mathbf{y}}}{\sqrt{\mathbf{m}}} \right)^2 \right\} + \frac{\mathbf{p}_{\mathbf{z}}^2}{2\mathbf{m}}$$
(A.49)

0

Consider \mathcal{H}_{l} . It has the form

$$\frac{1}{2}(P^2 + Q^2), \quad \text{with } [P,Q] = i\hbar\omega_c$$

This is formally the problem of the harmonic oscillator Hamiltonian, with eigenvalues (Landau levels)

$$\mathbf{E}_{\perp}(\mathbf{n}) = \left(\mathbf{n} + \frac{1}{2}\right) \hbar \omega_{c}$$

Thus, the spectrum of eigenvalues of (A.49) is

$$\mathbf{E}(\mathbf{n},\mathbf{p}_{z}) = \left(\mathbf{n} + \frac{1}{2}\right) \hbar \omega_{c} + \frac{1}{2m} \mathbf{p}_{z}^{2}$$

We started out with three degrees of freedom and now we have two quantum numbers. What happens? It happens that we have a degeneracy in (x, y). Let us look at the equations of motion in the (x, y) plane.

$$\dot{\mathbf{p}}_{\mathbf{x}} = \frac{\mathbf{i}}{\hbar} \left[\mathcal{H}_{\mathbf{x}}, \mathbf{p}_{\mathbf{x}} \right] = \omega_{c} \mathbf{p}_{\mathbf{y}} = \mathbf{m} \omega_{c} \mathbf{v}_{\mathbf{y}} = \mathbf{m} \omega_{c} \dot{\mathbf{y}}$$

$$(A.50)$$

$$\dot{\mathbf{p}}_{\mathbf{y}} = \frac{\mathbf{i}}{\hbar} \left[\mathcal{H}_{\mathbf{x}}, \mathbf{p}_{\mathbf{y}} \right] = -\omega_{c} \mathbf{p}_{\mathbf{x}} = -\mathbf{m} \omega_{c} \mathbf{v}_{\mathbf{x}} = -\mathbf{m} \omega_{c} \dot{\mathbf{x}}$$

Thus

$$\dot{x} = -\frac{1}{m\omega_{c}}\dot{p}_{y}$$

$$\dot{y} = \frac{1}{m\omega_{c}}\dot{p}_{x}$$
(A.51)

Define the operators

$$x_0 = x + \frac{1}{m\omega_c} p_y$$

$$(A.52)$$

$$y_0 = y - \frac{1}{m\omega_c} p_x$$

Then

$$\dot{\mathbf{x}}_{0} = \mathbf{0} = [\mathcal{Y}_{\perp}, \mathbf{x}_{0}]; \quad \dot{\mathbf{y}}_{0} = \mathbf{0} = [\mathcal{Y}_{\perp}, \mathbf{y}_{0}]$$
(A.53)

Thus, x_0 and y_0 are constants of motion. They are the operators of the co-ordinates of the centre of the cyclotron orbits. However, we cannot precisely locate the centre of the orbit as in the classical case. Consider the following commutators

$$[x_0, y_0] = -i \frac{\hbar}{m \omega_c}$$
 (A.54)

and

$$[\dot{\mathbf{x}}, \dot{\mathbf{y}}] = \frac{\mathbf{i} \hbar \omega_c}{\mathbf{m}} \tag{A.55}$$

and notice that

$$[\dot{x}, \dot{y}] = [v_x, v_y] = (i\omega_c)^2 [x_0, y_0]$$
 (A.56)

Now remember that in the general theory [q, p] = in means that the product of the uncertainties is

$$\Delta q \Delta p \ge \frac{1}{2} \hbar$$

It is convenient to define a characteristic length b by

$$b^2 = \frac{\hbar c}{|q|H} = \frac{\hbar}{m|\omega_c|}$$

Then $[x_0, y_0] = ib^2$ and $[v_v, v_x] = i(b\omega_c)^2$ mean that

$$\Delta x_0 \Delta y_0 \ge \frac{1}{2} b^2$$
, $\Delta v_y \Delta v_x \ge \frac{1}{2} (b\omega_c)^2$

We cannot dermine x_0 and y_0 (or, equivalently, v_x and v_y) simultaneously; the commutators give us a measure of the uncertainty involved. Now, with our choice of gauge, the Hamiltonian does not contain x or z explicitly. Therefore

$$[p_x, \mathcal{H}] = [p_z, \mathcal{H}] = 0$$
 (A. 57)

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Thus, with this gauge, the dependence of the wave function on x gives also a plane wave term

For an orbit "centered about" the point (x_0, y_0) we shall try some function of $(y - y_0)$. Now if we consider an eigenvalue of v_y , this determines the eigenvalue of x and then y_0 is completely undetermined. Indeed, all wave functions of the form

$$\{i(x p_x + z p_x)/\hbar\} Y_n(y - y_0)$$

are degenerate, i.e., they correspond to the same energy (A.49) for all values of y_0 . To sum up: The presence of two non-commuting constants of motion $(x_0 \text{ and } y_0)$ brings about an infinite degeneracy (unless the motion in the (x, y) plane were limited by finite extension, in which case the degeneracy would be finite); the energy eigenvalues depend only on two quantum numbers.

Consider now the operator

$$\rho_0^2 = x_0^2 + y_0^2 \tag{A.58}$$

whose eigenvalues give the square of the distance from the origin of coordinates to the centre of the allowed orbits. Clearly,

$$[\rho_0^2, \mathcal{H}_1] = 0$$
 (A.59)

Thus, ρ_0^2 is a constant of motion. Now

$$\rho_0^2 = \frac{1}{2} \left\{ \left(\sqrt{2} x_0^2 + \left(\sqrt{2} y_0^2 \right)^2 \right\}; \quad \left[\sqrt{2} x_0^2, \sqrt{2} y_0^2 \right] = 2 \text{ i } b^2. \quad (A.60)$$

Therefore, the eigenvalues of ρ_0 are

$$\rho_0^2 (n^1) = (2n^1 + 1) b^2 \qquad (A.61)$$

How about the allowed "sizes" of the orbits? Consider the operator

$$\rho^{2} = (x - x_{0})^{2} + (y - y_{0})^{2} = \frac{2mc^{2}}{q^{2}H^{2}} \mathcal{H}_{\perp}$$
(A.62)

Its eigenvalues labelled by the same quantum number as in (A.49) are:

$$\rho^{2}(n) = \frac{2mc^{2}}{q^{2}H^{2}} \left(n + \frac{1}{2}\right) \frac{\hbar |q| H}{mc} = \left(n + \frac{1}{2}\right) 2b^{2}$$
(A.63)

Thus, we obtain this picture: The orbits can be centred on points contained in concentric circles of radius $b\sqrt{2n'+1}$ and the size of the allowed orbits

(i.e. of the radius thereof) is $b\sqrt{2n+1}$. Now in \vec{k} space, recalling the definition of b and using the same complex notation as before, in the plane perpendicular to \vec{H} :

$$\dot{k} = -\frac{i}{b_{-}^2}\dot{r}$$
 (A.64)

i.e., a rotation by $-\pi/2$ and a scaling by a factor b^{-2} . Therefore, the original quantization scheme is modified in the following way: The k_z component is unaffected, but the continuous density of states in (k_x, k_y) is now changed drastically, the allowed (k_x, k_y) orbits can have radii equal to $b^{-1}\sqrt{2n+1}$ and areas

$$\mathscr{A}_{n} = (2n+1) \frac{\pi |\mathbf{q}| \mathbf{H}}{hc}$$
(A.65)

You will find these notions useful as a background to the theory of the de Haas-van Alphen effect, which you will see in the course on Fermi surfaces.

The case of crossed \vec{E} and \vec{H} is easily treated in the same manner. For \vec{E} in the x direction and \vec{H} in z direction, let us choose

$$\vec{A} = (0, xH, 0)$$
 (A.66)

Then

$$\mathscr{A}(\vec{A}) = \frac{1}{2m} \left\{ p_x^2 + (p_y - \frac{q}{c} x H)^2 + p_z^2 \right\} - qEx$$
 (A.67)

Define

$$Q = \frac{q H}{c} x - p_y - \frac{mcE}{H}$$
(A.68)

Then

$$\mathscr{H}(\vec{A}) = \frac{1}{2m} (p_x^2 + Q^2) - \frac{cE}{H} p_y - \frac{1}{2} m \left(\frac{cE}{H}\right)^2 + \frac{p_z^2}{2m}$$
 (A.69)

with

$$\left[\frac{\mathbf{p}_{\mathbf{x}}}{\sqrt{\mathbf{m}}}, \frac{\mathbf{Q}}{\sqrt{\mathbf{m}}}\right] = i\hbar\omega_{\mathbf{c}}$$
(A.70)

Also,

$$[\mathbf{p}_{v}, \mathcal{H}(\vec{A})] = 0 \tag{A.71}$$

Thus we can write down at once the spectrum of eigenvalues:

$$E(n, p_y, p_z) = \left(n + \frac{1}{2}\right) \hbar \omega_c - \frac{cE}{H} p_y - \frac{1}{2} m \left(\frac{cE}{H}\right)^2 + \frac{p_x^2}{2m} \qquad (A.72)$$

where p_y and p_z are now the <u>eigenvalues</u> of the corresponding operators in (A.69). Notice that the quantization scheme is now different from that obtained for E = 0.

The meaning of the first and last term is obvious. As for the others, let us look again at the coordinates of the (instantaneous) centre of the orbit. For instance

$$\dot{\mathbf{x}}_{0} = \frac{\mathbf{i}}{\hbar} \left[\mathcal{H}, \mathbf{x}_{0} \right]$$
(A. 73)

but now

$$x_0 = x + \frac{c}{qH} (p_y - \frac{q}{c} Hx) = \frac{c}{qH} p_y$$
 (A.74)

Hence

$$\dot{x}_0 = 0$$
 (A.75)

The x coordinate of the centre of the orbit is constant. For the other one

$$\dot{y}_{0} = \frac{i}{\hbar} \left[qEx, \frac{c}{qH} p_{x}\right] = \frac{i}{\hbar} \frac{cE}{H} \left[x, p_{x}\right] = -\frac{cE}{H}$$
(A.76)

Therefore the y coordinate is shifting with the precise (constant) velocity - cE/H, i.e. p_v takes just one eigenvalue

$$p_{y} = -\frac{mcE}{H}$$
(A.77)

and therefore we evaluate the second and third terms in (A. 72):

$$-\frac{cE}{H}p_{y} - \frac{1}{2}m\left(\frac{cE}{H}\right)^{2} = \frac{1}{2}m\left(\frac{cE}{H}\right)^{2}$$
(A.78)

which is precisely the expected kinetic energy of the motion along the y axis. Needless to say, we have recovered the classical trajectories.

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FOURIER TRANSFORMS AND CORRELATION FUNCTIONS

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Abstract

1. Properties of Fourier transforms. 2. Fourier transforms in structural crystallography. 3. Fourier transforms in lattice dynamics. 4. Fourier transforms and inelastic neutron scattering.

1. PROPERTIES OF FOURIER TRANSFORMS

Since the reader might, after the preceding papers, be in a mood to appreciate something simple, which does not introduce new ideas or many new concepts, but which will, I hope, throw light from a different angle on some of the topics already encountered, I have decided to discuss Fourier transforms and some of their properties. Fourier transforms appear in the discussion of any problem involving the scattering of radiation by condensed matter, and the determination of the structure in space and time of condensed matter from the momentum and energy changes of the radiation which it scatters.

When the quantum energy of the incident radiation is large compared with the energy of excited states of interest in the solid (for me, condensed matter is solid matter) we have essentially elastic scattering, as in the scattering of X-rays by a crystal. In units of the amplitude scattered by a single classical electron, the amplitude and phase of the radiation scattered by an electron distribution $\rho(\vec{r})$ is

$$\mathbf{F}(\vec{\mathbf{K}}) = \int \rho(\vec{\mathbf{r}}) \exp^{i\vec{\mathbf{K}}\cdot\vec{\mathbf{r}}} d^{3}\mathbf{r}$$
(1.1)

where

$$\vec{K} = -\vec{k} + \vec{k}_0 \text{ (with } \vec{k} = \vec{k}_0 \text{)}$$
(1.2)

is the change in wave vector of the scattered radiation. At this stage I am following the notation used in X-ray crystallography, where $F(\vec{K})$ is called the structure factor. Solid state physicists often misuse the term, and apply it to $|F(\vec{K})|^2$ which is of course the quantity that can be measured experimentally, while $F(\vec{K})$ cannot be directly measured. Since Eq. (1.1) expresses the fact that $F(\vec{K})$ is the Fourier transform of $\rho(\vec{r})$, $\rho(\vec{r})$ must be the inverse Fourier transform of F(K), thus

$$\rho\left(\vec{r}\right) = \int F\left(\vec{K}\right) e^{-i\vec{K}\cdot\vec{r}} \frac{d^{3}K}{(2\pi)^{3}}$$
(1.3)

(See for example, Stuart [1]). $d^3 K$ is an element of volume in the Fourier space or reciprocal space in which \vec{K} is a vector. (The factor $(2\pi)^{-3}$ introduces a troublesome asymmetry between expressions (1.1) and (1.3) which would not be there if we used $k = 1/\lambda$ rather than $k = 2\pi/\lambda$ for the wave number, but this would introduce a factor 2π in the exponential, in conformity with the usage of all crystallographers but contrary to the usage of all physicists. This is a simple test to distinguish a crystallographer from a physicist).

Before going on to some of the physical applications of Fourier transforms I want to remind you of some of their properties.

(a) It is advantageous to refer \vec{K} to a set of axes reciprocal to those to which \vec{r} is referred. Note that we are not yet concerned with periodic distributions. Thus with

$$\vec{r} = x_1 \vec{a}_1 + x_2 \vec{a}_2 + x_3 \vec{a}_3$$

$$\vec{K} = y_1 \vec{b}_1 + y_2 \vec{b}_2 + y_3 \vec{b}_3$$
(1.4)

where

and

$$\vec{b}_1 = \frac{2\pi \vec{a}_2 \times \vec{a}_3}{v} \text{ etc., and } v = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$$
(1.5)

we have

$$\vec{\mathbf{r}} \cdot \vec{\mathbf{K}} = 2\pi \prod_{i=1}^{3} \mathbf{x}_i \mathbf{y}_i$$
(1.6)

(1.7)

and

$$\frac{d^{3}K}{(2\pi)^{3}} = \frac{1}{v} dy_{1} dy_{2} dy_{3}$$

This means, incidentally, that if we know the Fourier transform of a distribution, we also have the Fourier transform of any other distribution which can be derived by a homogeneous distortion of the first. The transform remains the same when expressed in fractional coordinates of reciprocal axes.

(b) From Eq. (1) the transform of a spherically-symmetric distribution is

$$\mathbf{F}(\mathbf{K}) = \int_{0}^{\infty} 4\pi \mathbf{r}^{2} \rho(\mathbf{r}) \frac{\sin \mathbf{K}\mathbf{r}}{\mathbf{K}\mathbf{r}} d\mathbf{r}$$
(1.8)

This will be recognised as the form factor or atomic scattering factor for X-rays. As $K \rightarrow 0$ it reduces to Z, the atomic number of the atom.

(c) Some examples:

$$\rho(\mathbf{r}) = \left(\frac{p}{\pi}\right)^{3/2} e^{-pr^2}$$
(1.9)

then

$$= F(K) = e^{-\frac{K^2}{4p}}$$
(1.10)

The Fourier transform of a Gaussian is also a Gaussian and there is a reciprocal relation between their widths.

As $p \to \infty$, (1.9) becomes a δ -function satisfying $\int \delta(r) d^3r = 1$, and F(K) = 1. This is the well known result for the Fourier transform of a δ -function.

. If

$$\rho(\mathbf{r}) = \frac{1}{r}$$
, we have $F(K) = \frac{4\pi}{K^2}$ (1.11)

This result is used frequently in scattering by a Coulomb potential.

If $\rho(\vec{r})$ is unity inside a parallelepiped of dimensions $X_1\vec{a}_1, X_2\vec{a}_2, X_3\vec{a}_3$ and zero outside, the transform is

$$F(\vec{K}) = V_{i=1}^{3} \frac{\sin \pi X_{i} y_{i}}{\pi X_{i} y_{i}}$$
(1.12)

where V is the volume of the parallelepiped. The one-dimensional form of this expression is, of course, familiar from the theory of Fraunhofer diffraction.

(d) There is not time to discuss the symmetry of Fourier transforms in any detail, but it can be shown that any orthogonal transformation of the distribution without change of origin results in the same operation on the transform. It is easy to show that if

$$\rho'(\vec{r}) = \rho(\vec{r} - \vec{r_0})$$

$$F'(\vec{K}) = e^{i\vec{K} \cdot \vec{r_0}} F(\vec{K})$$
(1.13)

(e) When two distributions are added, their transforms add. The operation corresponding to multiplication in one space is convolution in the other space. This requires some discussion. Define the inverse transform of $F_1(\vec{K}) F_2(\vec{K})$ by

$$\rho_{12}(\vec{\mathbf{r}}) = \int_{\mathbf{K}} \mathbf{F}_{1}(\vec{\mathbf{K}}) \mathbf{F}_{2}(\vec{\mathbf{K}}) e^{-i\vec{\mathbf{K}}\cdot\vec{\mathbf{r}}} \frac{d^{3}\mathbf{K}}{(2\pi)^{3}}$$
(1.14)

We wish to find ρ_{12} in terms of ρ_1 and ρ_2 .

$$\rho_{12}(\vec{\mathbf{r}}) = \int_{K} F_{1}(\vec{K}) \left\{ \int_{r'} \rho_{2}(\vec{\mathbf{r}}') e^{i\vec{K}\cdot\vec{\mathbf{r}'}} d^{3}\mathbf{r'} \right\} exp^{-i\vec{K}\cdot\vec{\mathbf{r}'}} \frac{d^{3}K}{(2\pi)^{3}}$$
$$= \int_{r'} \rho_{2}(\vec{\mathbf{r}'}) \left\{ \int_{K} F_{1}(\vec{K}) e^{-i\vec{K}(\vec{\mathbf{r}\cdot\mathbf{r}'})} \frac{d^{3}K}{(2\pi)^{3}} \right\} d^{3}\mathbf{r'}$$
$$= \int_{r'} \rho_{2}(\vec{\mathbf{r}'}) \rho_{1}(\vec{\mathbf{r}}\cdot\vec{\mathbf{r}'}) d^{3}\mathbf{r'} = \rho_{1}(\vec{\mathbf{r}}) * \rho_{2}(\vec{\mathbf{r}'}) \qquad (1.15)$$

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This is the convolution theorem. In particular we can use it to show that the transform of $|F(\vec{K})|^2$ is

$$\left| \vec{\mathbf{F}}(\vec{\mathbf{K}}) \right|^{2} \leftrightarrow \int_{\mathbf{r}'} \rho(\vec{\mathbf{r'}}) \rho(\vec{\mathbf{r'}} + \vec{\mathbf{r'}}) d^{3}\mathbf{r'}$$
(1.16)

This is an important result; we have already noted that in X-ray scattering it is $|F(\vec{K})|^2$ which is accessible to measurement. What we can get from it by Fourier transformation is the auto-correlation function of the distribution.

(f) It is useful to know the Fourier transform of a lattice, taking the latter to be a set of δ -functions of unit weight at the points

$$\vec{r}_{\ell} = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 + \ell_3 \vec{a}_3$$
(1.17)

with $-\frac{1}{2}N_1 < \ell_1 < \frac{1}{2}N_1$ etc. defining the extent of the lattice. Then

$$\rho_{\rm L}(\vec{\mathbf{r}}) = \sum_{\ell} \delta(\vec{\mathbf{r}} - (\ell_1 \vec{\mathbf{a}}_1 + \ell_2 \vec{\mathbf{a}}_2 + \ell_3 \vec{\mathbf{a}}_3)) = \sum_{\ell} \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{\ell})$$
(1.18)

and

$$F_{L}(\vec{K}) = \sum_{\ell} e^{i\vec{K}\cdot\vec{r}_{\ell}}$$
(1.19)

Using fractional co-ordinates as before, this reduces to

$$F_{L}(\vec{K}) = \prod_{i=1}^{3} \frac{\sin N_{i}\pi y_{i}}{\sin \pi y_{i}}$$
(1.20)

This function peaks at integral values of y_i , that is at the points of the reciprocal lattice. In the limit where $N_1, N_2, N_3 \rightarrow \infty$ we get the following result. Integrate the above function over reciprocal space, near a reciprocal lattice point, for which incidentally we use \vec{K}_h just as we used $\vec{r_\ell}$ for a point of the lattice in (direct) space:

$$\int_{\vec{K} \text{ near } \vec{K}_{h}} F_{L} (\vec{K}) d^{3}K = \frac{(2\pi)^{3}}{v} \int_{-\frac{1}{2}}^{+\frac{1}{2}} \frac{\sin N_{1} \pi y_{1}}{\sin \pi y_{1}} \frac{\sin N_{2} \pi y_{2}}{\sin \pi y_{2}} \frac{\sin N_{3} \pi y_{3}}{\sin \pi y_{3}} dy_{1} dy_{2} dy_{3}$$
$$= \frac{(2\pi)^{3}}{v} \qquad (1.21)$$

where v now is the volume of the unit cell of the (direct) lattice. Thus in the limit of large N = $N_1 N_2 N_3$ the transform becomes a δ -function of weight $(2\pi)^3/v$, repeated at every point of the reciprocal lattice,

$$\vec{\mathbf{K}}_{h} = \mathbf{h}_{1}\vec{\mathbf{b}}_{1} + \mathbf{h}_{2}\vec{\mathbf{b}}_{2} + \mathbf{h}_{3}\vec{\mathbf{b}}_{3}$$
(1.22)

That is

$$F_{L}(\vec{K}) = \frac{(2\pi)^{3}}{v} \sum_{h} \delta(\vec{K} - \vec{K}_{h}) \qquad (1.23)$$

when

 $\rho_{\rm L} (\vec{\mathbf{r}}) = \sum_{\ell} \delta (\vec{\mathbf{r}} - \vec{\mathbf{r}}_{\ell})$

2. FOURIER TRANSFORMS IN STRUCTURAL CRYSTALLOGRAPHY

The principles of crystal structure analysis can be given concise expression in terms of Fourier transforms. Structure analysis nowadays is largely left to the chemists and molecular biologists, but many of the concepts are useful in considering analogous situations involving, for example, inelastic scattering of neutrons, which physicists still regard as their domain - although the chemists are beginning to move in.

Let us forget about thermal motion meantime and simply take the density to be the same in every unit cell, $\rho(\vec{r})$. As before, the transform of $\rho(\vec{r})$ is $F(\vec{K})$. The electron distribution on the crystal is then

$$\rho_{\rm c}(\vec{\rm r}) = \sum_{\ell} \rho(\vec{\rm r} - \vec{\rm r}_{\ell})$$
(2.1)

If we write this as

$$\rho_{c}(\vec{r}) = \sum_{\ell} \int_{r'} \delta(\vec{r'} - \vec{r}_{\ell}) \rho(\vec{r} - \vec{r'}) d^{3}r' \qquad (2.2)$$

we see that it is the result of convoluting the distribution $\rho(\vec{\mathbf{r}})$ with the distribution $\sum_{\ell} \delta(\vec{\mathbf{r}} \cdot - \vec{\mathbf{r}}_{\ell})$. Consequently by the convolution theorem, the

transform of the crystal is the transform of $\rho\left(\vec{r}\right)$ multiplied by the transform of the lattice

$$F_{c}(\vec{K}) = F(\vec{K})F_{L}(\vec{K})$$

$$= \frac{(2\pi)^{3}}{v}\sum_{h}F(\vec{K})\delta(\vec{K} - \vec{K}_{h}) \qquad (2.3)$$

The transform of the crystal is therefore the structure factor of one unit cell, sampled at reciprocal lattice points. If every unit cell of the crystal is identical, there is nothing in reciprocal space except at the reciprocal lattice points. We can now get an alternative expression for $\rho_c(\vec{r})$ using

$$\rho_{\rm c}\left(\vec{r}\right) = \int F_{\rm c}\left(\vec{K}\right) e^{-i\vec{K}\cdot\vec{r}} \frac{\mathrm{d}^{3}K}{(2\pi)^{3}}$$
(2.4)

Substituting from (2.3) in (2.4) we get

$$\rho_{c}(\vec{r}) = \frac{1}{v} \sum_{h} F(\vec{K}_{h}) e^{-i\vec{K}_{h} \cdot \vec{r}}$$
(2.5)

This is a well known result, the electron density in a crystal is given by a three-dimensional Fourier series. Each Fourier coefficient is just the transform of the density in one unit cell, sampled at a reciprocal lattice point which is the wave vector of the Fourier term. In practice this series cannot immediately be evaluated since experimental measurement of the intensities of the Bragg reflections gives $|F(\vec{K}_h)|^2$ - the condition

$$\vec{k} + \vec{k}_0 = \vec{K}_h$$
(2.6)

incidentally, being simply the expression of Bragg's law, and corresponding to the fact that intensity can be found only when $\vec{K} = \vec{K}_h$.

However it is always possible to evaluate the function

$$P_{c}(\vec{r}) = \frac{1}{v} \sum_{h} |F(\vec{K}_{h})|^{2} e^{-i \vec{K}_{h} \cdot \vec{r}}$$
(2.7)

which reduces to a cosine series since $F(-\vec{k}_h) = F^*(\vec{k}_h)$, $\rho(\vec{r})$ being entirely real (unless the wavelength of incident X-rays is near an absorption edge for some atoms in the crystal). Using the methods outlined earlier it is easy to show that

$$P_{c}(\vec{r}) = \int_{r'} \rho_{c}(\vec{r'}) \rho_{c}(\vec{r} + \vec{r'}) d^{3}r' \qquad (2.8)$$

the integral being over one unit cell of the crystal. This function is known as the Patterson function, after its discoverer (1935). It is widely used in crystal structure analysis.

The scattering of X-rays is principally by the core electrons. It is very difficult to determine the distribution of valence electrons or the state of ionisation of an atom by X-ray diffraction. Consequently, for our present purpose it is an excellent approximation to take

$$\rho (\vec{\mathbf{r}}) = \sum_{\kappa=1}^{n} \rho_{\kappa} (\vec{\mathbf{r}} - \vec{\mathbf{r}}_{\kappa})$$
(2.9)

where $\rho_{\kappa}(\mathbf{r})$ is the spherically-symmetric distribution in the κ -th atom, centred at $\vec{\mathbf{r}}_{\kappa}$. The structure factor is then given by

$$F(\vec{K}) = \sum_{\kappa=1}^{n} f_{\kappa}(K) e^{-i \vec{K} \cdot \vec{r}_{\kappa}}$$
(2.10)

where $f_{\kappa}(K)$ is the form factor of the κ -th atom. Consequently we have

$$\left| \mathbf{F}(\vec{\mathbf{K}}_{h}) \right|^{2} = \sum_{\boldsymbol{\kappa}\boldsymbol{\kappa}'} \mathbf{f}_{\boldsymbol{\kappa}}(\mathbf{K}) \mathbf{f}_{\boldsymbol{\kappa}'}(\mathbf{K}) e^{i \vec{\mathbf{K}} \cdot (\vec{\mathbf{r}}_{\boldsymbol{\kappa}} - \vec{\mathbf{r}}_{\boldsymbol{\kappa}'})}$$
(2.11)

Comparing (2.11) with (2.10), we readily reach the conclusion that an alternative expression for $P_c(\vec{r})$ is

$$P(\vec{r}) = \sum_{\ell} P_{\kappa\kappa'}(\vec{r} - (\vec{r}_{\kappa} - \vec{r}_{\kappa'}))$$

$$P_{c}(\vec{r}) = \sum_{\ell} P(\vec{r} - \vec{r}_{\ell}) \qquad (2.12)$$

where $P_{\kappa\kappa'}(\vec{r'})$ is got by convoluting the distributions $\rho_{\kappa}(\vec{r'})$ and $\rho_{\kappa'}(\vec{r'})$. In words, the Patterson function or auto-correlation function has a peak for every atom pair, in a position which is the vector distance between the atom pair. We might call it a vector map. It can be shown that, just as

$$\int \rho_{\kappa}(\mathbf{r}) d^3 \mathbf{r} = Z_{\kappa}$$
, the atomic number (2.13)

$$\int \mathbf{P}_{\kappa\kappa'}(\mathbf{r}) \,\mathrm{d}^3 \mathbf{r} = Z_{\kappa} Z_{\kappa'} \tag{2.14}$$

The weight of a peak in the vector map is thus proportional to the product of the corresponding two atomic numbers. If a crystal contains both light and heavy atoms, peaks representing vectors between heavy atoms will dominate in the vector map. The total number of peaks in one unit cell of the vector map is in general n^2 , but of these n occur at the origin and represent the interactions of atoms with themselves.

We have already remarked that $\rho_c\left(\vec{r}\right)$ cannot be evaluated directly from the experimental data since the phase of $F(\vec{K}_h)$ is unknown, but we can always evaluate $P_c(\vec{r})$ since it involves $|F(\vec{K}_h)|^2$. Can we reconstruct $\rho_{c}\left(\vec{r}\right)$ from a knowledge of $P_{c}\left(\vec{r}\right)$, in other words, can a crystal structure be directly determined from X-ray data alone? The answer in principle is yes, when certain conditions are satisfied which unfortunately are seldom satisfied in practice. Figure 1a is supposed to represent a centrosymmetric (two-dimensional) structure in which atoms are represented by points. Figure 1b is the corresponding vector set of points, those at $\pm 2\vec{r_1}$ etc. have unit weight and those at $\pm (\vec{r_1} - \vec{r_2})$ etc. have double weight. Now set down Fig. 1b twice with origins separated by the vector to any peak of unit weight, say $2\vec{r_1}$. The result is shown in Fig. 1c, coincidences in the superposition map out the original set of points. This is generally true, a set of points can be recovered from the corresponding vector set of points. While we have illustrated this for a non-periodic structure the result remains true for a periodic structure. The difficulty in practice is that peaks in a vector map overlap one another and superpose by accident. I present this result to you as an interesting curiosity, possibly there are applications in other branches of physics and I shall mention one in lattice dynamics if time permits later.

and

so



FIG.1c. The vector set put down with its origin at $\vec{r_1}$, giving the dots on the diagram, and at $\vec{r_1}$ to give the circles. Coincidences map out the original fundamental set, with the correct origin

Similar principles apply in a discussion of X-ray scattering by a liquid, which we take to be monatomic. The spherically-symmetric function

$$P(\mathbf{r}) = \int |F(K)|^2 \frac{\sin Kr}{Kr} \frac{4\pi K^2 dK}{(2\pi)^3}$$
(2.15)

depends on the number of interatomic distances lying between r and r + dr. Each such vector is represented not by a point but by a peak given by

$$P_{\kappa\kappa}(r) = \int f^{2}(K) \frac{\sin Kr}{Kr} \frac{4\pi K^{2} dK}{(2\pi)^{3}}$$
(2.16)

Since the peak at the origin is of no interest we subtract it out to get

$$P^{1}(\mathbf{r}) = \int \left\{ |F(K)|^{2} - N f_{\kappa}^{2}(K) \right\} \frac{\sin Kr}{Kr} \frac{4\pi K^{2} dK}{(2\pi)^{3}}$$
(2.17)

Apart from the difference of notation, this is Eq. (1.11) given by Professor March in the present book [2].

I pointed out earlier that in discussing X-ray scattering by a crystal we had taken the density to be the same in each unit cell. One type of density variation involves electronic excitations and leads to inelastic incoherent scattering designated Compton scattering. Scattering by phonons also takes place as shown by Professor Leibfried in the present book [3]. The zero-phonon or elastic scattering is unchanged by temperature except that each atomic scattering factor $f_{\kappa}(K)$ is replaced by

$$f_{\kappa}(K) e^{-W_{\kappa}(K)}$$
(2.18)

The Debye-Waller factor $\exp(-W_{\kappa}(\vec{K}))$ involves $W_{\kappa}(\vec{K})$ and in the harmonic approximations this is given by

$$W_{\kappa}(\vec{K}) = \frac{1}{2Nm_{\kappa}} \sum_{qj} \left| \vec{K} \cdot \vec{e}(\vec{q}j) \right|^{2} \frac{(\vec{n}(\vec{q}j) + \frac{1}{2})\hbar\omega(\vec{q}j)}{\omega^{2}(\vec{q}j)}$$
(2.19)

This is not essentially different from Leibfried's equation (6.32). An alternative form of this expression is

$$W_{\kappa}(\vec{K}) = \frac{1}{2} (\vec{K} \cdot \vec{u}_{\ell\kappa})^2$$
(2.20)

where $\vec{u}_{\ell\kappa}$ is the displacement of the atom of type κ from its equilibrium position $\vec{r}_{\ell} + \vec{r}_{\kappa}$, and the average is taken over all values of ℓ . We are usually content to take $W_{\kappa}(\vec{K})$ to be isotropic, but this is not necessarily so even for an atom in a cubic crystal if it occupies some general position in the unit cell. The form of Eqs (2.18) and (2.20) shows that the effect of thermal vibration is to give an average density for the atom of type κ which is $\rho_{\kappa}(\mathbf{r})$ convoluted with the transform of $W_{\kappa}(\vec{K})$. In the harmonic approximation this is a Gaussian of different widths in three mutually perpendicular directions. These directions are determined by the interatomic forces of the structure concerned, if we denote distances
measured in the respective directions by $z_1 \ z_2 \ z_3$ the transform of $W_{\kappa}(\vec{K})$, normalised so as to give the probability that the atom centre is in the volume element $dz_1 \ dz_2 \ dz_3$ is

$$p(z_1 z_2 z_3) = ((2\pi)^{3/2} u_1 u_2 u_3)^{-1} e^{-\frac{1}{2} \left(\frac{z_1^2}{u_1^2} + \frac{z_2^2}{u_2^2} + \frac{z_3^2}{u_3^2} \right)}$$
(2.21)

where u_1^2 is clearly the mean square displacement in the z_1 -direction. Correspondingly,

$$W(\vec{K}) = \frac{1}{2} (u_1^2 K_1^2 + u_2^2 K_2^2 + u_3^2 K_3^2)$$
(2.22)

where $K_1K_2K_3$ are the components of \vec{K} in the same system of axes. Six parameters are therefore involved, three being the axes of the "ellipsoid of thermal vibration" and three specifying the orientation of this ellipsoid, for each type of atom. This is a refinement which solid state physicists are usually prepared to ignore, in fact they are usually content to work out $W(\vec{K})$ using the Debye approximation for the frequency distribution. For molecular crystals the anisotropy of Debye-Waller factors can give information about their dynamics since in many instances the contribution of "internal" modes, which deform valence bonds, is small, and Debye-Waller factors are determined by "lattice" modes in which the molecule behaves as a rigid unit which can translate and librate. Obviously there are then relations between the Debye-Waller factors of the individual atoms of the molecule (see, for example, Pawley [4]), and these can be determined experimentally in the course of a crystal structure analysis.

Even when the harmonic approximation is not valid, it remains true that the transform of the Debye-Waller factor determines the average electron distribution, or strictly speaking the average nuclear distribution of an atom, which the electrons are usually presumed to follow. (See, for example, Dawson [5]).

3. FOURIER TRANSFORMS IN LATTICE DYNAMICS

From this point it is convenient to adopt a notation which prevents proliferation of symbols. Thus $\phi(\vec{K})$ is used for the transform of $\phi(\vec{r})$ etc., except that from force of habit we shall continue to use $F(\vec{K})$ and $\rho(\vec{r})$ as before for charge distributions.

Let us begin by considering the energy of a static assembly of points which interact with a potential ϕ (r). We then have for the total energy

$$\phi = \frac{1}{2} \sum_{j \neq j'} \phi \left(\overrightarrow{r_j} - \overrightarrow{r_{j'}} \right)$$
(3.1)

$$=\frac{1}{2}\sum_{j\neq j'}\int \phi(\vec{K}) e^{i\vec{K}\cdot(\vec{r_{j}}-\vec{r_{j'}})\frac{d^{3}K}{(2\pi)^{3}}}$$
(3.2)

Introducing the structure factor appropriate to a distribution of points,

$$F(\vec{K}) = \sum_{j=1}^{n} e^{i \vec{K} \cdot \vec{r}_{j}}$$
(3.3)

we see that

$$\phi = \frac{1}{2} \int \phi (\mathbf{K}) \left(\left| \mathbf{F}(\vec{\mathbf{K}}) \right|^2 - n \right) \frac{\mathrm{d}^3 \mathbf{K}}{(2\pi)^3}$$
(3.4)

The presence of a structure factor in this expression hints at the connection between energy and scattering properties. The term -n subtracts out the interaction of each point with itself which would otherwise be included. This type of result is particularly useful when we have to deal with Coulomb interaction. The potential at a distance r from a distribution $\rho(\vec{r})$ is

$$\phi(\vec{\mathbf{r}}) = \int_{\mathbf{r}'} \frac{\rho(\mathbf{r}')}{|\vec{\mathbf{r}} - \vec{\mathbf{r}'}|} d^3 \mathbf{r}'$$
(3.5)

This convolutes the functions $\rho(\vec{r})$ and r^{-1} , so that

$$\phi(\vec{K}) = \frac{4\pi F(\vec{K})}{K^2}$$
(3.6)

which is a frequently used result.

The energy of an extended distribution of charge $\rho(\vec{r})$ is

$$\phi = \frac{1}{2} \int \rho \left(\vec{\mathbf{r}} \right) \phi \left(\vec{\mathbf{r}} \right) d^3 \mathbf{r}$$
(3.7)

By suitable manipulation of the convolution theorem, Eq. 1.15, we find that ϕ is also given by

$$\phi = \frac{1}{2} \int \mathbf{F}^*(\vec{K}) \phi(\vec{K}) \frac{\mathrm{d}^3 \mathbf{K}}{(2\pi)^3}$$
$$= \frac{1}{2} \int \frac{4\pi \left| \mathbf{F}(\vec{K}) \right|^2}{\mathbf{K}^2} \frac{\mathrm{d}^3 \mathbf{K}}{(2\pi)^3} \tag{3.8}$$

Applying this result to a crystal, we readily find that the energy per unit cell (including the self-energy) is

$$\phi = \frac{1}{2v} \sum_{h} \left| \frac{4\pi}{K_{h}^{2}} \left| F\left(\vec{K}_{h} \right) \right|^{2}$$
(3.9)

Suppose for example we wish to evaluate the Madelung energy of a crystal, taking the ions to be point charges Z_{κ} at \vec{r}_{κ} . The electrostatic energy between point charges is the same as that between spherically-symmetric charge distributions which do not overlap, so we replace each point charge by

 $Z_{\kappa} \left(\frac{p}{\pi}\right)^{3/2} \exp\left(-pr^{2}\right)$

Then, using Eq. (1.10),

$$\mathbf{F}(\vec{\mathbf{K}}_{h}) = e^{-\frac{\mathbf{K}_{h}}{4p}} \sum_{\kappa} Z_{\kappa} e^{i\vec{\mathbf{K}}_{h}\cdot\vec{\mathbf{r}}}$$
(3.10)

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The expression (3.9) can then be evaluated without difficulty. It includes the self-energy which can be shown to be $(p/2\pi)^{\frac{1}{2}} Z_{\kappa}^2$ per atom. The basis of the related Ewald method of evaluating lattice sums is that one secures rapid convergence of the series by choosing a relatively small value of p and making a correction for the effect of charge overlap, which turns out to involve a rapidly convergent series in the direct lattice.

We turn now to a consideration of how the energy varies with atomic displacements. To simplify the notation we take the crystal to be composed of atoms all of one kind, although the method can readily be extended to the general case. Using α , β , γ for three mutually perpendicular directions and writing the displacement of the atom in the ℓ 'th unit cell as

$$\vec{u}_{\ell} = \vec{u}(\vec{q}) e^{i\vec{q}\cdot\vec{r}_{\ell} - \omega(\vec{q})t}$$
(3.11)

so that the usual normalising factors are all incorporated in the amplitude $\vec{u}(\vec{q}),$ the equations of motion lead to

$$m \omega^{2}(\vec{q}) u_{\alpha}(\vec{q}) = \sum_{\beta} M_{\alpha\beta}(\vec{q}) u_{\beta}(\vec{q}) \qquad (3.12)$$

Assuming the existence of an interatomic potential ϕ (r) one readily deduces (see for example these proceedings Leibfried [3]) that

$$M_{\alpha\beta}(q) = -\sum_{\ell} \left(\frac{\partial^2 \phi(r)}{\partial x_{\alpha} \partial x_{\beta}} \right)_{r=r_{\ell}} (e^{\vec{i}q + \vec{r_{\ell}} - 1})$$
(3.13)

The term $\ell = 0$ makes no contribution, but the atom at the origin is correctly included, the -1 in the bracket originating from the fact that the force constant "between an atom and itself" is minus the sum of the force constants between the atom and all other atoms. Putting

$$N_{\alpha\beta}(\vec{q}) = -\sum_{\ell} \left(\frac{\partial^2 \phi(\mathbf{r})}{\partial x_{\alpha} \partial x_{\beta}} \right)_{\mathbf{r}=\mathbf{r}_{\ell}} e^{i \vec{q} \cdot \vec{r}_{\ell}}$$
(3.14)

we see that

$$M_{\alpha\beta}(\vec{q}) = N_{\alpha\beta}(\vec{q}) - N_{\alpha\beta}(0) \qquad (3.15)$$

Substituting for $\phi(\mathbf{r})$ in terms of $\phi(\mathbf{K})$ in Eq. (3.14) we get

$$N_{\alpha\beta} (q) = \sum_{\ell} \int K_{\alpha} K_{\beta} \phi (K) e^{-i\vec{K}\cdot\vec{r}_{\ell}} e^{i\vec{q}\cdot\vec{r}_{\ell}} \frac{d^{3}K}{(2\pi)^{3}}$$
$$= \frac{(2\pi)^{3}}{v} \int K_{\alpha} K_{\beta} \phi (K) \sum_{h} \delta (\vec{K} - \vec{q} - \vec{K}_{h}) \frac{d^{3}K}{(2\pi)^{3}}$$
$$= \frac{1}{v} \sum_{h} (\vec{K}_{h} + \vec{q})_{\alpha} (\vec{K}_{h} + \vec{q})_{\beta} \phi (\vec{K}_{h} + \vec{q}) \qquad (3.16)$$

We finally have therefore that

$$\mathbf{M}_{\alpha\beta}\left(\vec{\mathbf{q}}\right) = \frac{1}{\mathbf{v}}\sum_{\mathbf{h}} \left\{ \left(\vec{\mathbf{K}}_{\mathbf{h}} + \vec{\mathbf{q}}\right)_{\alpha} \left(\vec{\mathbf{K}}_{\mathbf{h}} + \vec{\mathbf{q}}\right)_{\beta} \phi\left(\vec{\mathbf{K}}_{\mathbf{h}} + \vec{\mathbf{q}}\right) - \left(\vec{\mathbf{K}}_{\mathbf{h}}\right)_{\alpha} \left(\mathbf{K}_{\mathbf{h}}\right)_{\beta} \phi\left(\mathbf{K}_{\mathbf{h}}\right) \right\}$$
(3.17)

This result was apparently first derived by Pines [6]. A variant of it applicable only to Coulomb interaction has however been known for a long time. In practice Eq. (3.17) is sometimes the most convenient way of evaluating the $M_{\alpha\beta}(\vec{q})$, which when used in Eq. (3.12) lead to phonon frequencies and eigenvectors. A good example is the problem of calculating phonon frequencies in an alkali metal, using the pseudo-potential idea as applied by Harrison and others (see, for example, Ref. [7]).

We can use these considerations to develop a very oversimplified theory of phonons in an alkali metal. Consider two identical spherically symmetric positive charge distributions $\rho_c(\vec{r})$ and $\rho_c(\vec{r} - \vec{R})$, where c now denotes 'core'. The form factor of each will be denoted $f_c(K)$, and $f_c(0) = Ze$, the total charge in each. The interaction energy is readily found to be

$$\phi(\mathbf{R}) = \int \frac{4\pi f_c^2(\mathbf{K})}{\mathbf{K}^2} e^{-i\vec{\mathbf{K}}\cdot\vec{\mathbf{R}}} \frac{d^3\mathbf{K}}{(2\pi)^3}$$
(3.18)

and the transform of this is obviously

$$\phi(\mathbf{K}) = \frac{4\pi f_{\rm c}^2(\mathbf{K})}{\mathbf{K}^2} \tag{3.19}$$

If the two positive charge distributions are immersed in a gas of free electrons, the transform of the screened potential is found to be

$$\phi(\mathbf{K}) = \frac{4\pi \mathbf{f}_{\mathbf{C}}^{2}(\mathbf{K})}{\mathbf{K}^{2} \epsilon(\mathbf{K})}$$
(3.20)

Here ϵ (K) is just the special case for $\omega = 0$ of the dielectric function ϵ (K, ω) discussed by Professor Lundqvist [8]. An expression for ϵ (K) was first obtained by Bardeen in the Hartree approximation 30 years ago. If we now substitute expression (3.20) for ϕ (K) in Eq. (3.17) we have the matrix elements which, via Eq. (3.12), will give phonon frequencies and eigenvectors. The question of how f_c (K) is to be determined is one we shall not pursue, we note however that ρ_c (r) is just the charge distribution which will produce the appropriate localised pseudopotential, and that f_c (K)/ ϵ (K) is the transform of the charge distribution in what Professor Ziman has called a 'neutral pseudoatom'[9].

To show how this works let us derive the Bohm-Staver formula for the velocity of sound in a metal. From Eq. (3.12) we have for a wave travelling in the (100) direction with longitudinal polarisation that

$$m\omega^2(q) = M_{\alpha\alpha}(q) \qquad (3.21)$$

If ϕ (K) falls off sufficiently fast that only the term h = 0 contributes to the series 3.17 we find from (3.17) that

$$M_{\alpha \alpha}(q) = \frac{q^2 \phi(q)}{v} \text{ for } q \to 0$$
 (3.22)

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Now following Ziman [10], we find that

$$\epsilon (q) = \frac{6\pi Z e^2}{vq^2 E_f} \text{ for } q \to 0$$
(3.23)

where $f_c(0)$ = Ze is the total charge in a core, or the conduction electron charge per atom, and E_f is the Fermi energy. Consequently

$$q^{2}\phi(q) = \frac{4\pi f_{c}^{2}(q)}{\epsilon(q)}$$
$$= \frac{2}{3} q^{2} v Z E_{f} \text{ for } q \rightarrow 0 \qquad (3.24)$$

From equations (3, 21) and (3, 22) we then have

$$S = \frac{\omega}{q} = \left(\frac{2ZE_f}{3m}\right)^{\frac{1}{2}}$$
(3.25)

for the velocity of sound. Note that m is an atomic mass, not the mass of the electron!

4. FOURIER TRANSFORMS AND INELASTIC NEUTRON SCATTERING

The discussion in this section follows that of Lomer and Low [11], but makes considerable use of analogy with earlier results. Taking a nucleus of scattering length b = 1 as the unit, the density appropriate to neutron scattering is evidently

$$\rho(\vec{\mathbf{r}}) = \sum_{j} b_{j} \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{j}) \qquad (4.1)$$

(only coherent scattering will be considered). Taking the incident neutron wave function as

$$\psi_0 = e^{i(\mathbf{k}_0 \cdot \mathbf{r} - \omega_0 \mathbf{t})}$$
(4.2)

it is very plausible that (in the units we are using) the scattered wave function is

$$\psi_{s}(t) = \int \rho(\vec{r}, t) e^{i\vec{K}\cdot\vec{r}}d^{3}r$$
 (4.3)

A detailed proof is in [11]. We next evaluate the Fourier transform of this over some long period τ ,

 $f(\omega) = \frac{1}{\tau} \int_{0}^{\tau} \psi_{s} (t) e^{-i\omega t} dt$ (4.4)

where $\hbar\left(\omega_{0}-\omega\right)$ will be the scattered neutron energy. The scattered intensity in a range $\Delta\omega$ is evidently

 $\sum \left| f\left(\omega \right) \right| ^{2}$

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where the sum is over the discrete energy values allowed by the finite time τ of analysis. The number of terms is $\tau \Delta \omega/2\pi$, so that

$$\sum_{\sigma} |f(\omega)|^2 = \frac{\tau \Delta \omega}{2\pi} \left| \frac{1}{\tau} \int_{0}^{\tau} \int_{r} \rho(\vec{r}t) e^{i(\vec{K} \cdot \vec{r} - \omega t)} d^3 r dt \right|^2$$
(4.5)

Thus taking account of the way in which neutron flux is defined, the flux in an energy range $\hbar\,\Delta\omega$ and solid angle $\Delta\Omega$ is

$$\sum \, \left| f\left(\omega \right) \right|^2 \! \Delta \, \Omega \, \hbar \, k / m_n$$

so that

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\,\Omega \mathrm{d}\,\omega} = \frac{\mathrm{k}}{\mathrm{k}_0} \frac{1}{2\pi\,\tau} \left| \int_0^{\tau} \int_{\mathbf{r}} \rho\left(\vec{\mathbf{r}}, t\right) \,\mathrm{e}^{\mathrm{i}\,(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}-\omega t)} \mathrm{d}^3 \,\mathrm{rdt} \right|^2 \tag{4.6}$$

$$= \frac{k}{k_0} \frac{1}{2\pi\tau} \left| F(\vec{K}, \omega) \right|^2, \text{ say.}$$
(4.7)

the quantity $(1/2\pi\tau) |F(\vec{K},\omega)|^2$ is always written as $S(\vec{K}\omega)$ by practitioners of the art of neutron scattering. Now just as (Eq.1.16)

$$\left|\mathbf{F}\left(\vec{\mathbf{K}}\right)\right|^{2} \nleftrightarrow \int_{\mathbf{r}'} \rho\left(\vec{\mathbf{r}'}\right) \rho\left(\vec{\mathbf{r}}+\vec{\mathbf{r}'}\right) d^{3}\mathbf{r'}$$
(4.8)

so
$$2\pi S(\vec{K},\omega) \equiv \frac{1}{\tau} \left| F(\vec{K},\omega) \right|^2 \leftrightarrow \frac{1}{\tau} \int_{t=0}^{\tau} \int_{r} \rho(\vec{r'}t') \rho(\vec{r+r'},t+t') d^3r' dt'$$
 (4.9)

where \Leftrightarrow as before means "is the transform of". The time of observation τ which relates $|F(\vec{K},\omega)|^2$ and $|S(\vec{K},\omega)|$ appears unexpectedly. However just as $|F(K)|^2$ of relation (4.8) is always proportional to V, the volume of the scatterer (for actual physical systems), so $|F(\vec{K},\omega)|^2$ is proportional to both V and τ . We do not object to $d^2\sigma/d\Omega d\omega$ being proportional to V, but we normalise it to be independent of τ as $\tau \to \infty$. Thus in the definition of $F(\vec{K},\omega)$ (Eqs. (4.6) and (4.7)) we let the range of the $\pm \infty$.

tion of $F(\vec{K}, \omega)$ (Eqs (4.6) and (4.7)) we let the range of t be $\pm \infty$. Writing $\langle \rangle$ for an average over t', the important relation (4.9) written as an equation becomes

$$S(\vec{K}, \omega) = \frac{1}{2\pi} \int \langle \int_{\vec{r}} \rho(\vec{r'}, t') \rho(\vec{r} + \vec{r'}, t + t') d^{3}r' \rangle$$

$$\times e^{i(\vec{K} \cdot \vec{r} - \omega t)} d^{3}r dt \qquad (4.10)$$

In words, $S(\vec{K}, \omega)$ and therefore the scattering cross section, is the Fourier transform of a space-time correlation function.

Let us confirm a result we assumed earlier to be intuitively obvious, in discussing the Debye-Waller factor, and find on what the elastic scattering depends. If we simply put $\omega = 0$ in Eq. (4.6) we run into

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trouble with factors of τ , because the elastic scattering is not spread over any finite number of terms $\tau \Delta \omega / 2\pi$, but depends only on $|(f(0))|^2$. We find that

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\omega=0} = |f(0)|^2 = \left|\int \langle \rho(\mathbf{r}t) \rangle e^{i\overrightarrow{K}\cdot\overrightarrow{r}} \mathrm{d}^3\mathbf{r}\right|^2 \qquad 4.11$$

where $\langle \rangle$ denotes an average over infinite t, in agreement with our earlier assumption. Thus elastic scattering depends on the persistence of at least some part of the scattering density in an unchanging pattern, as in a crystal.

In X-ray scattering, or the scattering of neutrons of comparatively high energy, $k\approx k_0$ and

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \int \frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \mathrm{d}\omega} \,\mathrm{d}\,\omega = \int \mathbf{S}\left(\vec{\mathbf{K}},\,\omega\right) \mathrm{d}\,\omega \tag{4.12}$$

From Eq. (4.10) we find that

$$\int S(\vec{K}, \omega) d\omega = \int \langle \int_{r'} \rho(\vec{r'}, t') \rho(\vec{r} + \vec{r'}, t') d^3r' \rangle e^{\vec{iK} \cdot \vec{r}} d^3r$$
(4.13)

We can call this the transform of the average snapshot of the correlation function – not the same thing as the snapshot of the average, which gives the elastic scattering! We need not dwell on the fact that the transform of S (K, ω) is a space-time correlation function, as discovered by van Hove – this has emerged from our discussion at an early stage. A difficulty we have not faced up to as yet is that in writing Eq. 4.1 we have an expression involving operators rather than ordinary vectors. $\vec{r_j}$ is not an observable. Before we need tackle this, we give an alternative form of S (\vec{K} , ω) which is useful. Introducing a time-dependent structure factor, which will therefore also be an operator,

$$F(\vec{K}, t) = \sum_{j} b_{j} e^{i\vec{K} \cdot \vec{r_{j}}(t)}$$
(4.14)

one finds after some manipulation that

$$S(\vec{K}, \omega) = \frac{1}{2\pi} \int \langle F(-\vec{K}, t') F(\vec{K}, t+t') \rangle \exp(-i\omega t) dt$$
(4.15)

The average $\langle \rangle$ must now be interpreted as giving

$$S(\vec{K}, \omega) = \frac{1}{2\pi} \int \sum_{n} w_{n} \langle n | F(-\vec{K}, 0) F(\vec{K}, t) | n \rangle \exp(-i\omega t) dt \qquad (4.16)$$

with the sum taken over all states $|n\rangle$ of the system in equilibrium at temperature T.w_n is the population factor

$$w_{n} = \frac{e^{-\beta E_{n}}}{\sum_{n} e^{-\beta E_{n}}} \quad \text{where } \beta = (k_{B}T)^{-1}$$
(4.17)

If we write $F(\vec{K}, t) = \exp(iHt/\hbar) F(\vec{K}, 0) \exp(-iHt/\hbar)$ and follow through a derivation given by Professor Lundqvist[8] in his lectures (Eqs 9.2 and 9.3) we find an alternative expression

$$S(\vec{K},\omega) = \sum w_{n} |\langle m|F(\vec{K}, 0)|n \rangle|^{2} \delta(\omega - (\omega_{m} - \omega_{n}))$$
(4.18)

where $|n\rangle$ is an initial state with energy level $\hbar\omega_n$ and $|m\rangle$ is a final state. This is the expression for $S(\vec{K},\omega)$ which can be derived directly from second-order perturbation theory and is usually the starting point of a discussion of its properties. From the relative probabilities of transition probabilities with increase or decrease in energy of the system in response to an external perturbation, we have

$$\sum_{m \le n} = e^{-\beta \hbar \omega} \sum_{m > n}$$
(4.19)

where $\sum_{m \le n}$ denotes the sum in (4.18) evaluated over states such that $\omega_m < \omega_n$,

i.e. for neutron energy gain. Hence

$$S(\vec{K}, -\omega) = e^{-\theta \hbar \omega} S(\vec{K}, \omega)$$
 (4.20)

Finally, let us recast Eq. (4.15) in a form which applies to neutron scattering by a crystal. Eq. (4.15) is

$$S(\vec{K}, \omega) = \frac{1}{2\pi} \int \sum_{jj'} b_j b_{j'} \langle e^{-i\vec{K}\cdot\vec{r}_j(0)} e^{i\vec{K}\cdot\vec{r}_{j'}(t)} \rangle \exp(-i\omega t) dt \qquad (4.21)$$

In a crystal we can replace the index j by ℓ and κ to identify the unit cell and type of atom and write

$$\vec{\mathbf{r}}_{j} = \vec{\mathbf{u}}_{\ell\kappa} + \vec{\mathbf{r}}_{\ell\kappa}$$
(4.22)

where $\vec{r}_{\ell\kappa}$ is independent of time. If we now make use of the result which applies in the harmonic approximation,

$$\langle \exp^{i\vec{K}\cdot\vec{u}} \rangle = \exp^{-\frac{1}{2}\langle (\vec{K}\cdot\vec{u})^2 \rangle}$$
 (4.23)

Eq. (4.21) reduces to

$$S(\vec{K},\omega) = \frac{1}{2\pi} \int \sum_{\substack{\ell \ \ell' \\ \kappa \kappa'}} b_{\kappa} e^{-W_{\kappa}} b_{\kappa'} e(2W_{\ell \ \ell' \kappa \kappa'})$$

$$e^{-i\omega t} dt e^{i\vec{K} \cdot (\vec{\ell}_{\ell' \kappa'} \vec{\tau}_{\ell \kappa'})}$$
(4.24)

where

$$2W_{\ell\ell'\kappa\kappa'}(t) = \vec{K} \cdot \vec{u}_{\ell\kappa}(0) \vec{K} \cdot \vec{u}_{\ell'\kappa'}(t)$$
(4.25)

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and the definition of the Debye-Waller factor $\exp(-W_{\kappa})$ is as given before. We omit this factor from Eq. (4.26) since it can be considered to be incorporated in the modified scattering length b_{κ} . On expanding $\exp(2W_{\ell'\kappa\kappa'})$ as a power series, we get successive terms which are just the cross sections of the crystal for zero-phonon (elastic), one-phonon etc. processes. Thus the cross-section for one-phonon scattering is

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = \frac{\mathrm{k}}{2\pi\mathrm{k}_{0}}\sum_{\substack{\ell \ \ell', \\ \kappa\kappa'}} \mathrm{b}_{\kappa} \mathrm{b}_{\kappa'} \int \langle \vec{\mathrm{K}} \cdot \vec{\mathrm{u}}_{\ell\kappa} (0) \vec{\mathrm{K}} \cdot \vec{\mathrm{u}}_{\ell'\kappa'} (t) \rangle$$
$$e^{-\mathrm{i}\omega t} \quad \mathrm{d}t \ e^{\mathrm{i}\vec{\mathrm{K}}} \cdot \vec{\mathrm{r}}_{\ell'\kappa'} - \vec{\mathrm{r}}_{\ell\kappa}) \tag{4.26}$$

This can be evaluated by introducing phonon co-ordinates along the lines indicated by Professor Leibfried [3].

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LINEAR RESPONSE, GENERALIZED SUSCEPTIBILITY AND DISPERSION THEORY

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Abstract

1. Linear response to a dynamical disturbance – Theory. 1.1. Response function and generalized susceptibility. 1.2. Reactive and absorptive part of a susceptibility. Definition. 1.3. Kramers and Kronig dispersion relations. 1.4. Formal expression of the response function. 1.5. Symmetries. 1.6. Absorption and interpretation of $X''(\omega)$. 1.7. A Kubo formula. 1.8. Fluctuation dissipation theorem. 1.9. Moments and sum rules. 1.10. Classical case. Additional sum rules. 1.11. Spectral representations and energy levels of the unperturbed system. 1.12. Density fluctuations, f sum rule and longitudinal sum rule. 2. Linear response to a dynamical disturbance – applications and examples. 2.1. Classical oscillator. 2.2. Conductivity tensor. 2.3. Einstein relation. 2.4. Nyquist theorem.

1. LINEAR RESPONSE TO A DYNAMICAL DISTURBANCE. THEORY

1.1. Response function and generalized susceptibility

The system to which we apply an external force at a given time is assumed to be initially in a state of thermodynamic equilibrium. The unperturbed system is characterized by a density operator D which is nonnegative definite with:

$$Tr D = 1$$
 (1.1)

The mean value of any operator B related to the system is given by:

$$\langle B \rangle = Tr (DB)$$
 (1.2)

and therefore D determines the state of the system completely.

For a classical system, D would be a probability distribution in a phase space, rather than an operator, and each observable B would be a function defined in this space. In the classical limit, the formalism is not fundamentally different; consequently, we shall deal mainly with quantum systems, but the results will often be extended to classical systems by passing to the limit $\hbar = 0$.

When the system is at thermal equilibrium, the density operator must be:

$$D = Z^{-1} e^{-\theta H}$$
(1.3)

where H is the effective Hamiltonian and Z the partition function. Actually, if, for example, the system consists of a set of identical particles and if the number of particles is not fixed we must put:

$$H = \mathcal{H} - \mu N \tag{1.4}$$

where \mathcal{H} is the true Hamiltonian, μ the chemical potential and N the number of particles.

Let us now apply a time-dependent external disturbance to the system. In this case, the Hamiltonian H is replaced by the time-dependent Hamiltonian H(t):

$$H{t} = H + v{t}$$
 (1.5)

where v {t} is supposed to be a small perturbation. Since we are only interested in linear responses, we may assume without loss of generality that v {t} has the simple form:

$$v \{t\} = -a(t) A$$
 (1.6)

where A is a constant operator, and a(t) a function of time representing a generalized external force and vanishing for remote times. Actually, it is convenient to assume that a(t) vanishes exponentially when t goes to infinity:

$$\exists \epsilon \text{ with } \epsilon > 0 \rightarrow \lim_{t \to -\infty} e^{-\epsilon t} a(t) = 0$$
 (1.7)

As a consequence of the perturbation, the average of the operator B becomes time-dependent and its mean value, at time t, will be denoted by $\langle B(t) \rangle_{v}$. The linear relation between this quantity and the small perturbing potential can be written in the form:

$$\langle B(t) \rangle_{v} - \langle B \rangle = \int_{-\infty}^{+\infty} X_{BA}(t-t') a(t') dt'$$
 (1.8)

where X_{BA} (t) is assumed to be a bounded function of t:

 $\left|X_{BA}(t)\right| < C \tag{1.9}$

This mathematical assumption expresses the fact that the system reacts in a rather smooth way to any percussion, i.e. any strong instantaneous perturbation.

Thus, X $_{\text{BA}}\left(t\right)$ defines a linear response. Owing to causality requirements, we have, however,

$$X_{BA}(t) = 0$$
 $t < 0$ (1.10)

Therefore, the preceding equation must be written:

$$\langle B(t) \rangle_{v} - \langle B \rangle = \int_{-\infty}^{t} X_{BA}(t-t') a(t') dt'$$
 (1.11)

This relation takes a very simple form if we use Fourier transforms. For this purpose, it is useful to associate a function $X_{BA}(z)$ of the complex variable z = z' + iz'' with $X_{BA}(t)$; for z'' > 0 this function is defined by the following (Lebesgue) integral:

$$X_{BA}(z) = \int_{-\infty}^{\infty} X_{BA}(t) e^{izt} dt \equiv \int_{0}^{\infty} X_{BA}(t) e^{izt} dt \qquad (1.12)$$

As $X_{BA}(t)$ is assumed to be bounded, the integral converges uniformly in any domain $z^{"} \ge \epsilon > 0$ and therefore defines an analytic function $\chi_{RA}(z)$ of z in the upper part of the complex plane of z (i.e. z" > 0).

Actually, by putting $z = \omega + i\epsilon$, we can write:

$$X_{BA}(\omega + i\epsilon) = \int_{-\infty}^{+\infty} X_{BA}(t) e^{-\epsilon t} e^{i\omega t} dt \qquad (1.13)$$

which shows that for a given value of ϵ , $\chi_{BA}(\omega + i \epsilon)$ can be considered as the Fourier transform in ω of the function $X_{RA}(t) \exp(-\epsilon t)$. By passing to the limit $\epsilon \rightarrow 0$, we can define a function (or, in special cases, a distribution) $X_{BA}(\omega)$:

$$X_{BA}(\omega) \equiv X_{BA}(\omega + i0) \equiv \lim_{\epsilon \to 0} X_{BA}(\omega + i\epsilon)$$
(1.14)

which is the boundary value of the analytic function $\chi_{BA}(z)$ on the real axis.

Conversely, we have:

$$X_{BA}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} X_{BA}(\omega) e^{-i\omega t} d\omega \qquad (1.15)$$

With the same kind of notation, the Fourier transform $\alpha(\omega)$ of a(t) can be defined by:

$$\alpha(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} e^{-0t} a(t) dt \equiv \lim_{\epsilon \to 0} \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-\epsilon t} a(t) \quad (1.16)$$

Thus, a(t) is equal to:

$$a(t) = \int_{-\infty}^{+\infty} \alpha(\omega) e^{-i\omega t} e^{+0t} d\omega$$
(1.17)

In the same way, the function $\langle B(t) \rangle - \langle B \rangle$ can be expressed in terms of its spectral distribution:

$$\langle B(t) \rangle_{\bullet} - \langle B \rangle = \int_{-\infty}^{+\infty} \beta(\omega) e^{-i\omega t + 0t} dt$$
 (1.18)

where $\beta(\omega)$ is given by:

$$\beta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left[\langle \mathbf{B}(\mathbf{t}) \rangle_{\mathbf{v}} - \langle \mathbf{B} \rangle \right] e^{i\omega t + 0t} dt \qquad (1.19)$$

Then Eqs (1.8) and (1.9) can be written in the simple form:

$$\beta(\omega) = \chi_{BA}(\omega) \alpha(\omega) \qquad (1.20)$$

Thus, $\chi_{BA}(\omega)$ can be regarded as a generalized susceptibility.

At this point, we must remark that the appearance of broken symmetries may sometimes obscure our simple picture. Let us consider, for example, a ferromagnetic system at a temperature below the Curie point. In the absence of any magnetic field, the average magnetic moment is zero, but if we apply to the system a very small magnetic field \vec{b}_0 , a finite magnetic moment appears. Thus, the influence of this infinitesimal field changes, in a drastic way, the nature of the density operator. However, for a given value of \vec{b}_0 , we can define a magnetic susceptibility $\chi(\omega, \vec{b}_0)$ which describes the variations of the magnetic moment produced by adding (for instance in the same direction) a small field $\vec{b}(t)$ to \vec{b}_0 . Thus, a magnetic susceptibility for a zero field can be defined as the limit of $\chi(\omega, \vec{b}_0)$ when $\vec{b}_0 \rightarrow 0$. The same kind of behaviour is to be expected when strong modifications of the state of a system can result from its interaction with infinitesimal symmetrybreaking external sources.

1.2. Reactive and absorptive part of a susceptibility. Definition

The response function $X_{BA}(t)$ can always be written in the form:

$$X_{BA}(t) = X_{BA}'(t) + iX_{BA}''(t)$$
 (1.21)

where by definition we have:

$$X_{BA}^{\dagger}(-t) = X_{AB}^{\dagger}(t)$$
 (1.22)

$$X_{BA}^{n}(-t) = -X_{AB}^{n}(t)$$
 (1.23)

In fact, $X_{BA}^{\boldsymbol{1}}(t)$ and $X_{BA}^{\boldsymbol{\eta}}(t)$ are also defined by:

$$X_{BA}^{T}(t) = \frac{1}{2} \left[X_{BA}(t) + X_{AB}(-t) \right]$$
 (1.24)

$$X_{BA}^{"}(t) = -\frac{i}{2} \left[X_{BA}(t) - X_{AB}(-t) \right]$$
 (1.25)

For reasons which will be given later on, $X_{BA}^{t}(t)$ and $X_{BA}^{t}(t)$ will be called the reactive and the absorptive part of the response function, respectively. (Note that $X_{BA}^{t}(t)$ is real and $X_{BA}^{t}(t)$ is purely imaginary.)

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In the same way, we define $\chi_{BA}^{\,\prime}(\omega)$ and $\chi_{BA}^{\,\prime\prime}(\omega)$ by (see Eq.(1.13))

$$X_{BA}^{\prime}(\omega) = \int_{-\infty}^{+\infty} X_{BA}^{\prime}(t) e^{-0|t|} e^{i\omega t} dt \qquad (1.26)$$

$$X_{BA}^{*}(\omega) = \int_{-\infty}^{+\infty} X_{BA}^{*}(t) e^{-0|t|} e^{i\omega t} dt \qquad (1.27)$$

Thus, we have:

$$X_{BA}^{*}(\omega) = \frac{1}{2} \left[X_{BA}(\omega) + X_{AB}(-\omega) \right]$$
(1.28)

$$\chi_{BA}^{n}(\omega) = -\frac{i}{2} \left[\chi_{BA}(\omega) - \chi_{AB}(-\omega) \right]$$
(1.29)

These quantities satisfy symmetry conditions:

$$X'_{BA}(\omega) = X'_{AB}(-\omega) = \left[X'_{AB}(\omega)\right]^{*}$$
(1.30)

$$\chi_{BA}^{\mathbf{n}}(\omega) = -\chi_{AB}^{\mathbf{n}}(-\omega) = \left[\chi_{AB}^{\mathbf{n}}(\omega)\right]^{\times}$$
(1.31)

Thus, in the space of the operators A or B, $\chi^{\,\prime}\left(\omega\right)$ and $\chi^{\,\prime\prime}(\omega)$ may be considered Hermitian.

Incidentally, we remark that $\chi_{AA}^{\dagger}(\omega)$ and $\chi_{AA}^{\dagger}(\omega)$ are both real. In this case, we have:

$$X'_{AA}(\omega) = \int_{0}^{\infty} \cos \omega t \ X_{AA}(t) \ e^{-0t} \ dt \qquad (1.32)$$

$$X_{AA}^{"}(\omega) = \int_{0}^{\infty} \sin \omega t X_{AA}(t) e^{-0t} dt \qquad (1.33)$$

and, conversely:

$$X'_{AA}(t) = \frac{1}{\pi} \int_{0}^{\infty} \cos \omega t X'_{AA}(\omega) d\omega \qquad (1.34)$$

$$X_{AA}^{"}(t) = -\frac{i}{\pi} \int_{0}^{\infty} \sin \omega t X_{AA}^{"}(\omega) d\omega \qquad (1.35)$$



FIG.1. Integration contour %.

1.3. Kramers and Kronig dispersion relations

The causal nature of the response function implies relations between $X_{BA}^{'}(\omega)$ and $X_{BA}^{''}(\omega)$. These dispersion relations are derived by expressing the analytic function $X_{BA}(z)$ in terms of its boundary value $X_{BA}(\omega)$.

This result is usually obtained by writing $X_{B_A}(z)$ as a Cauchy integral on the contour \mathscr{C} of Fig.1. This contour consists of a fraction of a line parallel to the real axis (at a distance ϵ above it) and of a fraction of a circle centered at the origin (radius R).

$$\chi_{BA}(z) = \frac{1}{2\pi i} \int_{\mathscr{A}} \frac{\chi_{AB}(x)}{x - z} dx \qquad (1.36)$$

Now the Lebesgue lemma [1] says that $\chi(\omega + i\epsilon)$ which is the Fourier transform of the "good" function $X_{BA}(t) \exp(-\epsilon t)$ goes to zero when $|\omega| \rightarrow 0$. On the other hand, since $X_{BA}(t)$ is bounded in the domain $z^{"} > \epsilon$, Phragmén-Lindelöf theorem [2] can be applied and it shows that in the domain $z^{"} > \epsilon$, the preceding conditions imply the uniform convergence of $\chi_{BA}(z)$ to zero when $|z| \rightarrow \infty$.

Let us then keep ϵ fixed and let R increase. We see that, as a consequence of the preceding remark, the integral on the circle must vanish in the limit $R \rightarrow \infty$. Therefore, in this limit, Eq. (1.35) becomes:

$$\chi_{BA}(z) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\chi_{BA}(\omega + i\epsilon)}{\omega + i\epsilon - z} d\omega$$
(1.37)

The same result can be obtained by direct application of the following theorem given by Titchmarsh [3].

Theorem

Let $\Phi(z)$ be an analytic function regular for y > 0 and let

$$\int_{-\infty}^{+\infty} \left| \Phi(x+iy)^2 \right| dx$$

exist and be bounded. Then, as $y \rightarrow 0$, $\Phi(x+iy)$ converges in mean toward a function $\Phi(x)$ and also $\Phi(x+iy) \rightarrow \Phi(x)$ for almost all x. For y > 0:

$$\Phi(z) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\Phi(u)}{u-z} du$$
 (1.38)

In order to apply this theorem, we put:

$$z = x + iy + i\epsilon \quad y \ge 0 \tag{1.39}$$

$$X_{BA}(z) \equiv X_{BA}(x + iy + i\epsilon) = \Phi(x + iy)$$
(1.40)

On the other hand, as $\chi_{BA}(z'+iz'')$ is the Fourier transform in z' of $X_{BA}(t) \exp(-z''t)$, Parseval's theorem leads to the following condition for $z'' \ge \epsilon$:

$$\int_{-\infty}^{+\infty} \left| X_{BA}(z^{\dagger} + iz^{\dagger}) \right|^2 dz^{\dagger} = 2\pi \int_{-\infty}^{+\infty} \left| X_{BA}(t) \right|^2 e^{-2z^{\ast}t} dt \le \frac{\pi \varphi^2}{z^{\ast}} \le \frac{\pi \varphi^2}{\epsilon}$$
(1.41)

Thus, Titchmarsh's theorem can be directly applied and we obtain Eq. (1.37) again.

In order to express $\chi_{BA}(z)$ in terms of $\chi_{BA}(\omega)$ which is a quantity of physical interest, we consider now the limit $\epsilon \to 0$. We note that if the function $\chi_{BA}(t)$ is square integrable, Titchmarsh's theorem can be applied for $\epsilon = 0$. Then, $\chi_{BA}(\omega)$ is also a function of square integrable modulus and we have:

$$\chi_{BA}(z) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\chi_{BA}(\omega + i0)}{\omega + i0 - z} d\omega \equiv \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\chi_{BA}(\omega)}{\omega - z} d\omega$$
(1.42)

Incidentally, we verify that the integral on the right hand side of this equation is convergent. However, if the square of $X_{BA}(t)$ is not integrable, the preceding equation can be given a meaning if we consider $X_{BA}(\omega)$ to be a distribution.

Finally, dispersion relations are obtained when z becomes real $(z^n \rightarrow + 0)$. We get:

$$\chi_{BA}(\omega) \equiv \chi_{BA}(\omega+i0) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\chi_{BA}(\omega')}{\omega' - \omega - i0} d\omega' \qquad (1.43)$$

Making use of the relation

$$\frac{1}{\omega^{1}-\omega-i0} = \frac{\mathscr{P}}{\omega^{1}-\omega} + i\pi\,\delta\,(\omega^{1}-\omega) \qquad (1.44)$$

Eq.(1.43) can be written in the simple form:

$$\chi_{BA}(\omega) = \frac{1}{i\pi} \int_{-\infty}^{+\infty} \frac{\chi_{BA}(\omega')}{\omega' - \omega} d\omega' \qquad (1.45)$$

This equation can be written more explicitly by separating the Hermitian and the anti-Hermitian part of $\chi_{BA}(\omega)$ (see Eqs (1.28) and (1.29)).

This operation leads to the Kramers-Kronig relations:

$$\chi_{BA}^{\prime}(\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\chi_{BA}^{\prime}(\omega^{\prime})}{\omega^{\prime} - \omega} d\omega^{\prime} \qquad (1.46)$$

$$\chi_{BA}^{"}(\omega) = -\frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\chi_{BA}^{*}(\omega^{*})}{\omega^{*} - \omega} d\omega^{*}$$
(1.47)

which are very useful for the interpretation of many experiments.

Thus, we see that the total response $\chi_{BA}(\omega)$ can be expressed in terms of $\chi_{BA}^{*}(\omega)$ or $\chi_{BA}^{*}(\omega)$, only. However, in general, the function $\chi_{BA}^{*}(\omega)$ (which corresponds to the absorptive part of the response function) is more localized than $\chi_{BA}^{*}(\omega)$. For this reason, it is interesting to express $\chi_{BA}(\omega)$ in terms of $\chi_{BA}^{*}(\omega)$ only. Actually, from the Kramers-Kronig relations, we deduce:

. .

$$X_{BA}(\omega) = \frac{1}{i\pi} \int_{-\infty}^{+\infty} \frac{X_{BA}^{"}(\omega)}{\omega' - \omega - i0} d\omega' \qquad (1.48)$$

We may remark also that (for z" > 0):

$$X_{BA}(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\chi_{BA}^{*}(\omega)}{\omega - z} d\omega \qquad (1.49)$$

a relation which can be derived easily from Eq. (1.42) by using relation (1.46).

1.4. Formal expression of the response function. Kubo formula

For a quantum system in a state of equilibrium the density operator D is a constant in any representation (Heisenberg, Schrödinger, or interaction representation). On the other hand, the formal expressions giving the response function $\chi_{BA}(\omega)$ in terms of H, A and B may be derived by using any representation. However, it may be simpler to use the interaction representation as will be done here.

First, we shall define the time-dependent operators A(t) and B(t) by putting:

$$A(t) = e^{i\frac{Ht}{\hbar}} A e^{-i\frac{Ht}{\hbar}}$$
(1.50)

$$B(t) = e^{i\frac{Ht}{\hbar}} B e^{-i\frac{Ht}{\hbar}}$$
(1.51)

In the interaction representation, the density operator D(t) is given by its initial value and the equation:

$$i\hbar\dot{D}(t) = \left[e^{i\frac{Ht}{\hbar}} v \{t\} e^{-i\frac{Ht}{\hbar}}, D(t) \right] = - [A(t), D(t)] a(t) \quad (1.52)$$

On the other hand, we have:

$$\langle B(t) \rangle_{v} - \langle B \rangle \approx Tr \left([D(t) - D] B(t) \right)$$
 (1.53)

Now, we may put:

$$D(t) = D + \delta D(t) \qquad (1.54)$$

where $\delta D(t)$ is given in the linear approximation by:

$$\delta D(t) = i\hbar^{-1} \int_{-\infty}^{t} [A(t'), D] a(t') dt'$$
 (1.55)

This expression is rather formal, but a really meaningful result is obtained by using this expression in Eq.(1.53):

$$\langle B(t) \rangle_{v} - \langle B \rangle = i\hbar^{-1} \int_{-\infty}^{t} dt' a(t') Tr ([A(t'), D] B(t))$$
 (1.56)

By using the cyclic invariance of the trace, we obtain:

$$\langle B(t) \rangle_{v} - \langle B \rangle = i\hbar^{-1} \int_{-\infty}^{t} dt' a(t') \operatorname{Tr} \left(D[B(t), A(t')] \right)$$
 (1.57)

=
$$i\hbar^{-1}\int_{-\infty}^{t} \langle [B(t), A(t')] \rangle a(t') dt'$$
 (1.58)

By comparing this expression with the definition (1.11), we get finally:

$$X_{BA}(t-t') = i\hbar^{-1} \langle [B(t), A(t')] \rangle \Theta(t-t')$$
 (1.59)

where $\Theta(t)$ is the step function $(\Theta(0) = \frac{1}{2}, \Theta(x) = +1$ for $x > 0, \Theta(x) = 0$ for x < 0). Incidentally, we see immediately that this function satisfies the causality requirements (Eq.(1.10)). On the other hand, the response function must be real since B(t) and A(t') are Hermitian, which implies that the mean value of their commutator is purely imaginary. Finally, the fact that the response function depends only on the difference (t-t') is immediately evident since we have:

$$X_{BA}(t-t^{\dagger}) = -\frac{\Theta(t-t^{\dagger})}{i\hbar} \langle [B(t), A(t^{\dagger})] \rangle = -\frac{\Theta(t-t^{\dagger})}{i\hbar Z} \operatorname{Tr} \left(e^{-\beta H} [B(t), A(t^{\dagger})] \right)$$

$$= -\frac{\Theta(t-t^{\dagger})}{i\hbar Z} \operatorname{Tr} e^{-\beta H} [e^{iH(t-t^{\dagger})} B e^{-iH(t-t^{\dagger})}, A] = -\frac{\Theta(t-t^{\dagger})}{i\hbar} \langle [B(t-t^{\dagger}), A] \rangle$$
(1.60)

The Hermitian and anti-Hermitian parts of the response function have very simple expressions; according to Eq. (1.59) and the definitions (1.24) and (1.25) we have $(\epsilon(t) = -1 + 2\Theta(t))$:

$$X_{BA}^{'}(t-t') = i(2\hbar)^{-1} \epsilon(t-t') \langle [B(t), A(t')] \rangle$$
 (1.61)

$$X_{BA}^{"}(t-t') = (2\hbar)^{-1} \langle [B(t), A(t')] \rangle$$
 (1.62)

Incidentally, we remark that $X_{BA}(t-t^{i})$ can be written in terms of $X_{BA}^{ii}(t-t^{i})$ or $X_{BA}^{ii}(t-t^{i})$ alone:

$$X_{BA}(t-t') = 2i\Theta(t-t') X_{BA}''(t-t') = 2\Theta(t-t') X_{BA}'(t-t')$$
(1.63)

Actually, the first relation coincides with the dispersion relation (1.48).

1.5. Symmetries

The reality of the response function implies relations between the real and the imaginary parts of $X_{BA}(\omega)$:

$$\operatorname{Re} X_{BA}(\omega) = \operatorname{Re} X_{BA}(-\omega) \qquad (1.64)$$

$$\operatorname{Im} X_{BA}(\omega) = -\operatorname{Im} X_{BA}(-\omega) \qquad (1.65)$$

and also, as we have seen, between the Hermitian and the anti-Hermitian parts of $\chi_{RA}(\omega)$ (Eqs(1.30) and (1.31)):

$$\chi_{BA}^{i}(\omega) = \chi_{AB}^{i}(-\omega) = [\chi_{AB}^{i}(\omega)]^{*}$$
 (1.66)

$$\chi^{''}_{BA}(\omega) = -\chi^{''}_{AB}(-\omega) = [\chi^{''}_{AB}(\omega)]^{*}$$
(1.67)

Additional symmetry properties can be found by time reversal. Let θ be this transformation. The Hamiltonian H is, in general, invariant with respect to time reversal; however, if a magnetic field \vec{b} is applied to the system, then, the time reversal operation changes \vec{b} into $-\vec{b}$. On the other hand, the operators A and B have often simple symmetry properties under time reversal such as:

 $\theta A \theta^{-1} = \epsilon_{A} A \qquad \theta B \theta^{-1} = \epsilon_{B} B$ (1.68)

and for any operator $\mathcal O,$ the time reversal operator θ satisfies also the relation

.

$$\operatorname{Tr} \theta \mathcal{Q} \theta^{-1} = \operatorname{Tr} \mathcal{Q}^{\dagger} \tag{1.69}$$

Consequently, the time reversal invariance of the system can be expressed as follows:

$$X_{BA}(t-t',\vec{b}) \equiv -\Theta(t-t')Z^{-1} \operatorname{Tr} \left(\frac{e^{-\beta H(\vec{b})}}{i\hbar} \left[B(t), A(t')\right]\right)$$
(1.70)

$$= -\Theta(t-t^{\dagger})Z^{-1} \operatorname{Tr} \left(\theta[A(-t^{\dagger}), B(-t)] \frac{e^{-\beta H(\overline{b})}}{-i\hbar} \theta^{-1} \right)$$
(1.71)

where $H(\vec{b})$ is the Hamiltonian considered to be a function of \vec{b} (Z is invariant under time reversal). The last equation can be written $(\theta i \theta^{-1} = -i)$

$$X_{BA}(t-t', \vec{b}) = -\epsilon_{A} \epsilon_{B} \Theta(t-t') Z^{-1} \operatorname{Tr} \left([A(t'), B(t)] \frac{e^{-\beta H(-\vec{b})}}{i\hbar} \right)$$
(1.72)

$$= -\epsilon \mathop{\epsilon}_{A \ B} \Theta(t-t') Z^{-1} \operatorname{Tr} \left(\frac{e^{-\beta H(-\overline{b})}}{-i\hbar} \left[B(t), A(t') \right] \right)$$
(1.73)

Finally, we get:

$$X_{BA}(t-t', \vec{b}) = \epsilon_A \epsilon_B X_{AB}(t-t', -\vec{b})$$
(1.74)

or, by using Fourier transforms:

$$\chi_{BA}(\omega, \vec{b}) = \epsilon_{A} \epsilon_{B} \chi_{AB}(\omega, -\vec{b})$$
(1.75)

1.6. Absorption and interpretation of $\chi^{"}(\omega)$

Our aim is to calculate the energy produced in a system by the external perturbation $v{t}$. This energy is of course always positive and due to absorption in the system. But dissipative effects are non-linear. For this reason and in order to preserve interference terms, it will be assumed in this section that the perturbing potential is a sum of terms:

$$v{t} = -\sum_{j} a_{j}(t) A_{j}$$
 (1.76)

For the sake of simplicity the response function corresponding to A_j and A_l will be simply written X_{jl} (t). In Heisenberg representation, we have:

$$i\hbar \frac{dH}{dt} = [H, H\{t\}] = [H, v\{t\}] = -\sum_{j} a_{j}(t) [H, A_{j}]$$
 (1.77)

All the operators in this equation are assumed to be time-dependent. This means that we have:

$$i\hbar \frac{d}{dt} \langle H \rangle_{v} = -\sum_{j} a_{j}(t) \langle [H, A_{j}] \rangle_{v} \qquad (1.78)$$

The static part $\langle [H,A_j] \rangle$ vanishes for a system in thermal equilibrium. Therefore from (1.57), we get:

$$i\hbar \frac{d}{dt} \langle H \rangle_{v} = -i\hbar^{-1} \sum_{j\ell} a_{j}(t) \int_{-\infty}^{t} \langle [H, A_{j}(t)], A_{\ell}(t')] \rangle a_{\ell}(t') dt'$$
$$= -\sum_{j\ell} a_{j}(t) \int_{-\infty}^{t} \frac{\partial}{\partial t} \langle [A_{j}(t), A_{\ell}(t')] \rangle a_{\ell}(t') dt' \qquad (1.79)$$

Therefore by using definition (1.59), we obtain:

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle H \rangle_{\mathbf{v}} = \sum_{j\ell} \int_{-\infty}^{+\infty} a_{j}(t) \frac{\partial}{\partial t} X_{j\ell}(t-t') a_{\ell}(t') \mathrm{d}t' \qquad (1.80)$$

For reasons of simplicity, we assume that the perturbation is monochromatic (but real); therefore we put:

$$\mathbf{a}_{j}(t) = \frac{1}{2} \left[\mathbf{a}_{j} \mathbf{e}^{-i\omega t} + \mathbf{a}_{j}^{*} \mathbf{e}^{i\omega t} \right]$$
(1.81)

Then, the preceding expression becomes:

$$\frac{\mathrm{d}}{\mathrm{dt}} \left\langle \mathrm{H} \right\rangle_{v} = \frac{i\omega}{4} \sum_{j\ell} \left(a_{j} e^{-i\omega\tau} + a_{j}^{*} e^{i\omega\tau} \right) \left[a_{\ell} e^{-i\omega\tau} \chi_{j\ell}(\omega) - a_{\ell}^{*} e^{i\omega\tau} \chi_{j\ell}(-\omega) \right]$$
(1.82)

Now, we can drop the periodic terms which are irrelevant here and calculate the average flow of energy:

$$\frac{\overline{d}}{dt} \langle H \rangle_{v} = -\frac{i\omega}{4} \sum_{j\ell} \left[a_{j}^{*} a_{\ell} \chi_{j\ell}(\omega) - a_{\ell}^{*} a_{j} \chi_{j\ell}(-\omega) \right]$$
(1.83)

Then, by using definition (1.29), we obtain finally:

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \mathrm{H} \rangle_{\mathbf{v}} = \frac{1}{2} \sum_{j\ell} a_{j}^{*} a_{\ell} \ \omega \chi_{j\ell}^{\mathbf{u}}(\omega) \qquad (1.84)$$

This result shows that $\chi_{j\ell}^{"}\left(\omega\right)$ can really be identified with the dissipative part of $\chi_{i\ell}\left(\omega\right).$

1.7. A Kubo formula

Another formal expression of the response function has been given by Kubo [4]. In order to derive it, we write $X_{RA}(t)$ in the following form which

results from the cyclical invariance of the trace of a product of operators; in doing so we start from Eq.(1.60):

$$X_{BA}(t) = \frac{\Theta(t)}{i\hbar Z} \operatorname{Tr} \left(\left[e^{-\beta H}, A \right] B(t) \right)$$
(1.85)

Now, we use the following identity:

$$\left[e^{-\beta H}, A\right] = \int_{0}^{\beta} e^{-\beta H} e^{\lambda H} \left[A, H\right] e^{-\lambda H} d\lambda \qquad (1.86)$$

which can be easily proved by multiplying both sides by $\exp\left(\beta H\right)$ and differentiating. Thus,

$$[e^{-\beta H}, A] = i\hbar \int_{0}^{\beta} e^{-\beta H} \dot{A}(-i\hbar\lambda) d\lambda \qquad (1.87)$$

Finally, by introducing this expression in Eq.(1.85) we obtain Kubo's formula:

$$X_{BA}(t) = \Theta(t) \int_{0}^{\beta} \langle \dot{A}(-i\hbar\lambda) B(t) \rangle d\lambda$$
$$= -\Theta(t) \int_{0}^{\beta} \langle A(-i\hbar\lambda) \dot{B}(t) \rangle d\lambda \qquad (1.88)$$

1.8. Fluctuation dissipation theorems

The natural fluctuations occurring in a system at equilibrium are related to the dissipation effects resulting from an interaction of the system with external forces. Of course, this connection proves to be very important and, though it has been clarified only rather recently [5], it has been recognized and used a long time ago (Einstein relation, Nyquist theorem [6]) in special cases.

The time-dependent fluctuation function $\boldsymbol{F}_{\text{BA}}(t)$ is defined by the anti-commutator:

$$F_{BA}(t-t') = \frac{1}{2} \langle \{ (B(t) - \langle B \rangle), (A(t') - \langle A \rangle) \} \rangle$$
 (1.89)

Our aim is to establish a relation between the Fourier transform $\Phi_{BA}(\omega)$ of $F_{BA}(t)$ and the dissipative part of the susceptibility $\chi_{BA}^{"}(\omega)$.

$$\Phi_{BA}(\omega) = \int_{-\infty}^{+\infty} F_{BA}(t) e^{i\omega t - 0|t|} dt \qquad (1.90)$$

For this purpose, we introduce the function $S_{BA}(t)$ and its Fourier transform $\Sigma_{BA}(\omega)$:

$$S_{BA}(t) = \langle (B(t) - \langle B \rangle) (A - \langle A \rangle) \rangle = \langle (B - \langle B \rangle) (A(-t) - \langle A \rangle) \rangle$$
(1.91)

$$\Sigma_{BA}(\omega) = \int_{-\infty}^{+\infty} S_{BA}(t) e^{i\omega t - 0|t|} dt \qquad (1.92)$$

By using these definitions, we see immediately that:

$$X_{BA}^{"}(t) = (2\hbar)^{-1} [S_{BA}(t) - S_{AB}(-t)]$$
 (1.93)

$$\mathbf{F}_{BA}(t) = \frac{1}{2} \left[\mathbf{S}_{BA}(t) + \mathbf{S}_{AB}(-t) \right]$$
(1.94)

But on the other hand:

$$\langle A(-t)B \rangle = Z^{-1} \operatorname{Tr} \left(e^{-\beta H} e^{-i\frac{Ht}{\hbar}} A e^{i\frac{Ht}{\hbar}} B \right)$$

$$= Z^{-1} \operatorname{Tr} \left(e^{-\beta H} e^{i\frac{\hbar}{\hbar}H(t-i\hbar\beta)} B e^{-i\frac{\hbar}{\hbar}H(t-i\hbar\beta)} A \right)$$

$$= \langle B(t-i\hbar\beta) A \rangle$$

$$(1.95)$$

Consequently we obtain

$$S_{AB}(-t) = S_{BA}(t-i\hbar\beta)$$
(1.96)

and, therefore, we have:

$$X''_{BA}(t) = (2\hbar)^{-1} [S_{BA}(t) - S_{BA}(t-i\hbar\beta)]$$
 (1.97)

$$F_{BA}(t) = \frac{1}{2} \left[S_{BA}(t) + S_{BA}(t - i\hbar\beta) \right]$$
(1.98)

Let us now take the Fourier transforms of these expressions. If we assume that

1) $\langle (A(t) - \langle A \rangle) (B - \langle B \rangle) \rangle \rightarrow 0$ for $t \rightarrow \infty$

2)
$$\langle (A(t) - \langle A \rangle) (B - \langle B \rangle) \rangle$$
 is analytic in the domain $0 < \text{Im } t < \beta h$

we can write:

$$\int_{-\infty}^{+\infty} e^{i\omega t} S_{AB}(-t) dt \equiv \int_{-\infty}^{+\infty} e^{i\omega t} S_{BA}(t-i\hbar\beta) dt$$
$$= e^{-\beta\hbar\omega} \int_{-\infty}^{+\infty} e^{i\omega t} S_{BA}(t) dt = e^{-\beta\hbar\omega} \sum_{BA}(\omega)$$
(1.99)

Therefore, we obtain in this case:

$$X_{BA}^{(1)}(\omega) = (2\hbar)^{-1} (1 - e^{-\beta\hbar\omega}) \Sigma_{BA}(\omega)$$
 (1.100)

$$\Phi_{\rm BA}(\omega) = \frac{1}{2} (1 + e^{-\beta \hbar \omega}) \Sigma_{\rm BA}(\omega)$$
 (1.101)

Thus, we are led to the fluctuation dissipation theorem:

$$X''_{BA}(\omega) = \hat{n}^{-1} th (\beta \hbar \omega/2) \Phi_{BA}(\omega)$$
 (1.102)

1.9. Moments and sum rules

The corresponding classical formula is, of course, obtained by passing to the limit $\hbar\to 0;$ in this way we obtain:

$$X''_{BA}(\omega) = \frac{1}{2} \beta \omega \Phi_{BA}(\omega) \qquad (1.103)$$

Note that, if A = B, $\chi_{BA}^{"}(\omega)$ and $\Phi_{BA}(\omega)$ are real.

As an interesting application of the preceding theorem, we have also:

$$\hbar \int_{-\infty}^{+\infty} \coth\left(\frac{\beta\hbar\omega}{2}\right) e^{-i\omega(t-t')} \chi_{AA}^{"}(\omega) d\omega = \int_{-\infty}^{+\infty} e^{-i\omega(t-t')} \Phi_{AA}(\omega) d\omega = 2\pi F_{AA}(t-t')$$
(1.104)

which leads to the sum rule (for t = t'):

$$\int_{-\infty}^{\infty} \operatorname{coth}\left(\frac{\beta \hbar \omega}{2}\right) \chi_{AA}^{"}(\omega) \, d\omega = 2\pi \, \tilde{h}^{-1} \langle \left(A - \langle A \rangle\right)^{2} \rangle \qquad (1.105)$$

or for a classical system

$$\int_{-\infty}^{+\infty} \chi_{AA}^{n}(\omega) \frac{d\omega}{\omega} = \pi \beta \left\langle \left(A - \left\langle A \right\rangle \right)^{2} \right\rangle$$
(1.106)

.

This equation can be generalized by taking derivatives of Eq.(1.104) with respect to t and t'. Thus, we get (when the equation has a meaning):

$$\int \omega^{2n} \coth \left(\frac{\beta \hbar \omega}{2}\right) X_{AA}^{"}(\omega) d\omega = 2\pi \hbar^{-1} \langle \left(A^{(n)}(t)\right)^2 \rangle \qquad (1.107)$$

where $A^{(n)}(t)$ is the nth order time derivative of A(t) (t is arbitrary). In the classical limit, we have also:

$$\int_{-\infty}^{+\infty} \omega^{2n-1} \chi_{AA}^{\dagger}(\omega) d\omega = \pi \beta \left\langle \left(A^{(n)}(t)\right)^2 \right\rangle$$
 (1.108)

We note that if the potentials acting on the particles of the system are regular, all the moments of $\chi^{"}_{AA}(\omega)$ exist since the mean values appearing on the right-hand side of (1.107) are finite. But, of course, this is not true in the case of Coulomb interactions.

1.10. Classical case. Additional sum rules

In the classical case, useful relations are obtained also between the reactive part of the susceptibility and the fluctuations by using the Kramers-Kronig relation (1.46):

$$\chi_{AA}^{\dagger}(\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\chi_{AA}^{\dagger}(\omega^{\dagger})}{\omega^{\dagger} - \omega} d\omega^{\dagger}$$
(1.109)

Thus, by putting $\omega = 0$ in this equation and by taking into account the symmetry properties of $\chi_{AA}^{i}(\omega)$ and $\chi_{AA}^{m}(-\omega)$ we deduce from Eq.(1.106):

$$X_{AA}(0) = X_{AA}'(0) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \omega^{-1} X_{AA}''(\omega) d\omega = \beta \langle (A(t) - \langle A \rangle)^2 \rangle$$
(1.110)

On the other hand, by examining the behaviour of $\chi'_{AA}(\omega)$ for large values of ω , we obtain also an interesting relation (see Eq.(1.108) for n = 1):

$$\lim_{\omega \to \infty} \omega^2 \chi'_{AA}(\omega) = -\frac{1}{\pi} \int_{-\infty}^{+\infty} \omega \chi''_{AA}(\omega) d\omega = -\beta \langle (\dot{A}(t))^2 \rangle \qquad (1.111)$$

If this equation has a meaning, we can infer from the convergence of the integral that $\lim_{\omega \to \infty} \omega^2 \chi^{"}_{AA}(\omega) = 0$. Thus, we get finally:

$$\lim_{\omega \to \infty} \omega^2 \chi_{AA}(\omega) = \lim_{\omega \to \infty} \omega^2 \chi_{AA}^{\dagger}(\omega) = -\beta \langle (\dot{A}(t))^2 \rangle \qquad (1.112)$$

1.11. Spectral representations and energy levels of the unperturbed system

The meaning of all the preceding relations may become more evident by using explicit representations in terms of the eigenstates and eigenenergies of the system. Thus we have immediately (see Eq.(1.91)):

$$S_{BA}(t) = Z^{-1} \left(\sum_{mn} e^{-\beta E_n} e^{i(E_n - E_m)t/\hbar} \langle n | A | m \rangle \langle m | B | n \rangle - \sum_{n} e^{-\beta E_n} \langle n | A | n \rangle \sum_{m} e^{-\beta E_m} \langle m | B | m \rangle \right)$$
(1.113)

Hence, we get the Fourier transform:

$$\Sigma_{BA}(\omega) = \hbar Z \sum_{mn}^{-1} \sum_{mn} e^{-\beta E_n} \delta (\hbar \omega - (E_m - E_n)) \langle n | A | m \rangle \langle m | B | n \rangle$$
(1.114)

and by using Eqs (1.100) and (1.101) we obtain:

$$\chi_{BA}^{n}(\omega) = \frac{1}{2} Z^{-1} \sum_{mn} (e^{-\beta E_{n}} - e^{-\beta E_{m}}) \delta(\hbar\omega - (E_{m} - E_{n})) \langle n | A | m \rangle \langle m | B | n \rangle$$
(1.115)

$$\Phi_{BA}(\omega) = \frac{\hbar}{2} Z^{-1} \sum_{mn} (e^{-\beta E_n} + e^{-\beta E_m}) \delta(\hbar\omega - (E_m - E_n)) \langle n | A | m \rangle \langle m | B | n \rangle$$
(1.116)

In the same way, it is easy to find an explicit representation for $X_{BA}(\omega)$, since we have according to Eqs (1.63) and (1.97):

$$X_{BA}(t) = 2i\Theta(t) X_{BA}^{"}(t)$$

= $i\hbar^{-1}\Theta(t) \sum_{mn} (e^{-\beta E_n} - e^{-\beta E_m}) e^{i(E_n - E_m)t/\hbar} \langle n | A | m \rangle \langle m | B | n \rangle$ (1.117)

Therefore we obtain the following expression:

$$X_{BA}(\omega) = -Z^{-1}\sum_{mn} (e^{-\beta E_n} - e^{-\beta E_m}) \frac{\langle n | A | m \rangle \langle m | B | n \rangle}{\hbar \omega - (E_m - E_n) + i0}$$
(1.118)

which shows the relationship between the excitations of a system and the response function.

1.12. Density fluctuations, f sum rule and longitudinal sum rule

The general theory is frequently applied to the study of large systems consisting of a set of identical particles of mass m interacting between each other and with the medium in which they move. In this case, the Hamiltonian can be written in the form:

$$H = \frac{1}{2m} \sum_{s=1}^{N} \vec{P}_{s}^{2} + U(r_{1}...r_{N})$$
(1.119)

where $U(r_1...r_N)$ is an operator which depends on the medium and on the positions $r_1...r_N$ of the particles under consideration; on the other hand, \vec{P}_s is the momentum of the sth particle. The form of this Hamiltonian implies an interesting relation, the f sum-rule, which plays an important role in the theory of conductivity and will be derived now.

First, we introduce the density operator $n{\vec{r}}$ and the current operator $\vec{j}{\vec{r}}$:

$$n\{\vec{r}\} = \sum_{s} \delta(\vec{r} - \vec{r}_{s}) \qquad (1.120)$$

$$\vec{j}\{\vec{r}\} = \frac{1}{2m} \sum_{s} (\vec{P}_{s} \ \delta(\vec{r} - \vec{r}_{s}) + \delta(\vec{r} - \vec{r}_{s})\vec{P}_{s}) \qquad (1.121)$$

and their Fourier transforms:

$$n(\vec{k}) = \sum_{s} e^{i\vec{k}\cdot\vec{r}_{s}}$$
(1.122)

$$\vec{j}(\vec{k}) = \frac{1}{2m} \sum_{s} (\vec{P}_{s} e^{i\vec{k}\cdot\vec{r}_{s}} + e^{i\vec{k}\cdot\vec{r}_{s}} \vec{P}_{s}) \qquad (1.123)$$

which are related by:

$$[H, n(\vec{k})] = \hbar \vec{k} \cdot \vec{j}(\vec{k})$$
 (1.124)

a relation which implies the conservation of particles; in fact, if we define:

$$n(\vec{k},t) = e^{i\frac{Ht}{\hbar}}n(\vec{k}) e^{-i\frac{Ht}{\hbar}}$$
 (1.125)

$$\vec{j}(\vec{k},t) = e^{i\frac{Ht}{\hbar}} \vec{j}(\vec{k}) e^{-i\frac{Ht}{\hbar}}$$
(1.126)

these time-dependent operators satisfy the conservation equation:

$$\frac{d}{dt}n(\vec{k},t) = \frac{i}{h} [H, n(\vec{k},t)] = i\vec{k}\cdot\vec{j}(\vec{k},t)$$
(1.127)

Now, we note that:

$$[\vec{j}(\vec{k}), n(-\vec{k})] = -\frac{N}{m} \hbar \vec{k}$$
 (1.128)

With the help of Eq.(1.124), we deduce:

$$[[H, n(\vec{k})], n(-\vec{k})] = -\frac{N}{m} h^2 k^2$$
 (1.129)

LINEAR RESPONSE

For a system at temperature T the mean value of the left-hand side can be expressed in terms of the eigenstates $|n\rangle$ of H:

$$\langle [[H, n(\vec{k})], n(-\vec{k})] \rangle = Z^{-1} \sum_{\ell m} e^{-\beta E_{\ell}} (E_{\ell} - E_{m}) \langle \ell | n(\vec{k}) | m \rangle \langle m | n(-\vec{k}) | \ell \rangle$$
$$+ \langle \ell | n(-\vec{k}) | m \rangle \langle m | n(\vec{k}) | \ell \rangle) \qquad (1.130)$$

In the right-hand side of this expression, both terms are even in \vec{k} ; therefore, by comparing this expression with Eq.(1.129), we obtain:

$$2 Z^{-1} \sum_{\ell m} e^{-\beta E_{\ell}} (E_{m} - E_{\ell}) |\langle \ell | n(k) | m \rangle|^{2} = \frac{N}{m} \hbar^{2} k^{2}$$
(1.131)

It is customary to define the oscillator strength of the level $|n\rangle$ by:

$$f_{\ell}(\vec{k},T) = \frac{2m}{NZ\hbar^{2}k^{2}} \sum_{m} e^{-\beta E_{\ell}} (E_{m} - E_{\ell}) |\langle \ell | n(k) | m \rangle|^{2}$$
(1.132)

and thus, we get the f sum rule:

$$\sum_{k} f_{k}(\vec{k}, T) = 1$$
 (1.133)

This relation can be expressed in a slightly different form which is also very useful. In agreement with definition (1.62), we put:

$$X_{j_{\alpha}j_{\beta}}^{"}(\vec{r} - \vec{r}', t - t') = (2\hbar)^{-1} \langle [j_{\alpha}\{\vec{r}, t\}, j_{\beta}\{\vec{r}', t'\}] \rangle \qquad (1.134)$$

where

$$\vec{j}\{\vec{r},t\} = e^{i\frac{Ht}{\hbar}}\vec{j}\{\vec{r}\} e^{-i\frac{Ht}{\hbar}}$$
 (1.135)

and its Fourier transform:

$$X_{j_{\alpha}j_{\beta}}^{\mathbf{n}}(\vec{k},\omega) = \int d^{3}\mathbf{r} e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} \int dt e^{i\omega(t-t')} X_{j_{\alpha}j_{\beta}}^{\mathbf{n}}(\vec{r}-\vec{r}',t-t')$$
$$= (2\hbar\Omega)^{-1} \int dt e^{i\omega(t-t')} \langle [j_{\alpha}(\vec{k},t), j_{\beta}([\vec{k},t')] \rangle^{'} \qquad (1.136)$$

 $(\Omega = volume of the sample).$

Our aim is to find a sum rule which is just another version of the f sum rule for the susceptibility $\chi_{j_{\alpha}j_{\beta}}^{n}(\vec{k},\omega)$.

In a homogeneous medium, we can separate $\chi_{j_{\alpha}j_{\beta}}^{*}(\vec{k},\omega)$ into a longitudinal and a transversal part; by definition we have

$$\chi_{j_{\alpha}j_{\beta}}^{"}(\vec{k},\omega) = \frac{k_{\alpha}k_{\beta}}{k^{2}}\chi_{jj}^{"L} + \left(\delta_{\alpha\beta} - \frac{k_{\alpha}k_{\beta}}{k^{2}}\right)\chi_{jj}^{"T}$$
(1.137)

Therefore:

$$\chi_{jj}^{\dagger L}(\vec{k},\omega) = (2\hbar k^2 \Omega)^{-1} \int dt \ e^{i\omega(t-t')} \langle [\vec{k} \cdot \vec{j}(\vec{k},t), \vec{k} \cdot \vec{j}(-\vec{k},t')] \rangle \qquad (1.138)$$

This expression can be transformed by using the continuity equation (1.127):

$$\chi_{jj}^{\mu}(\vec{k},\omega) = i (2\hbar k^2 \Omega)^{-1} \int dt \ e^{i\omega(t-t')} \langle [\vec{k}\cdot\vec{j}(\vec{k},t), \ \vec{n}(-\vec{k},t')] \rangle$$
(1.139)

$$= - \omega (2\hbar k^2 \Omega)^{-1} \int dt \left\langle [\vec{k} \cdot \vec{j} (\vec{k}, t), n(-\vec{k}, t')] \right\rangle$$
(1.140)

Thus, we derive the longitudinal sum rulė:

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \, \omega^{-1} \chi_{jj}^{\mu L}(\vec{k},\omega) = -(2\hbar k^2 \Omega)^{-1} \langle [\vec{k} \cdot \vec{j} \, (\vec{k}), n(-\vec{k})] \rangle \qquad (1.141)$$

which by using Eq. (1.128) becomes:

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \, \omega^{-1} \, \chi_{jj}^{\mu L}(\vec{k}, \omega) = \frac{n}{2m}$$
(1.142)

(where $n = N/\Omega$ is the density of particles).

Or by application of the Kramers-Kronig relation (1.46) and of the symmetry conditions (1.66) and (1.67):

$$\chi_{jj}^{L}(\vec{k},0) = \chi_{jj}^{L}(\vec{k},0) = \frac{n}{m}$$
 (1.143)

2. LINEAR RESPONSE TO A DYNAMICAL DISTURBANCE. EXAMPLES AND APPLICATIONS

2.1. Classical oscillator

As a simple illustration of the theory, we consider now the case of a simple classical oscillator driven by an external force. The coordinate x(t) of the oscillating mass m satisfies the equation:

$$m \ddot{x}(t) + \gamma \dot{x}(t) + m \omega_0^2 x(t) = f(t)$$
 (2.1)

where m is the mass, $m\omega_0^2$ the spring constant, γ a friction coefficient and f(t) an external force which can be regarded as resulting from a perturbing potential:

$$v \{t\} = -xf(t)$$
 (2.2)

The preceding equation and the usual assumption $x(-\infty) = 0$ determines the variations of x(t) completely:

$$x(t) = \int_{-\infty}^{t} X_{xx}(t-t') f(t') dt'$$
 (2.3)

Now, we get:

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \varphi(\omega) d\omega \qquad (2.4)$$

$$\mathbf{x}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \xi(\omega) d\omega \qquad (2.5)$$

and thus the preceding equation can be transformed into:

$$\xi(\omega) = \chi_{xx}(\omega) \varphi(\omega) \qquad (2.6)$$

But Eq.(2.1) gives:

$$[m(\omega_0^2 - \omega^2) - i\gamma\omega] \xi(\omega) = \varphi(\omega)$$
 (2.7)

and therefore, we have:

$$X_{xx}(\omega) = \frac{1}{m(\omega_0^2 - \omega^2) - i\gamma\omega}$$
(2.8)

This function has two poles; two regimes are possible:

a)
$$\gamma < 2m \omega_0$$
 (weakly damped oscillator).

then the roots are given by:

$$\omega = \pm \omega_1 - i\omega_2 \qquad \omega_1 > 0 \qquad \omega_2 > 0 \qquad (2.9)$$

b) $\gamma > 2m \omega_0$ (strongly damped oscillator);

then

$$\omega = -i(\omega_1 \pm \omega_2) \qquad \omega_1 > \omega_2 > 0 \qquad (2.10)$$

In any case, the roots have negative imaginary parts and therefore, in agreement with the causality requirements $\chi_{xx}(\omega)$ is analytic in the half plane Im $\omega > 0$.

The Kronig-Kramers relation (see Eq.(1.45)):

$$X_{xx}(\omega) = \frac{1}{i\pi} \int_{-\infty}^{+\infty} \frac{\chi_{xx}(\omega)}{\omega' - \omega} d\omega' \qquad (2.11)$$

turns out to be obvious because we can write:

$$\frac{\mathscr{P}}{\omega-\omega^{\dagger}} = \frac{1}{2} \left(\frac{1}{\omega^{\dagger}-\omega+i0} + \frac{1}{\omega^{\dagger}-\omega-i0} \right)$$
(2.12)

on the right-hand side of Eq.(2.11), close the contour upwards and calculate the residue at the pole $\omega' = \omega + i0$; this residue is of course $\chi_{xx}(\omega)$. The real and imaginary parts of $\chi_{xx}(\omega)$ are given by:

$$X'_{xx}(\omega) = \frac{m(\omega_0^2 - \omega^2)}{m^2(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$
(2.13)

$$\chi_{\mathbf{xx}}^{"}(\omega) = \frac{\gamma \omega}{m^2 (\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$
(2.14)

and we verify immediately the symmetry conditions of section 1.4. The shapes of the curves corresponding to these functions are very characteristic for small values of γ ; they are represented in Fig.2.





FIG.2b. $\chi^{**}(\omega)$ for small values of γ .

The work W(t) done by the external force f(t) is given by:

$$\frac{\mathrm{d} W(t)}{\mathrm{d}t} = \mathbf{\dot{x}}(t) \ \mathbf{f}(t) = \int_{-\infty}^{\infty} \mathbf{f}(t) \ \mathbf{\dot{X}}_{\mathbf{xx}}(t-t') \ \mathbf{f}(t') \ \mathrm{d}t'$$
$$= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega't} \ \mathbf{f}(t) \ e^{i\omega't'} \ \mathbf{f}(t') \ \omega' \ \mathbf{X}_{\mathbf{xx}}(\omega') \ \mathrm{d}\omega' \ \mathrm{d}t' \qquad (2.15)$$

Thus, if we put:

$$f(t) = \frac{1}{2} (f e^{-i\omega t} + f^* e^{i\omega t})$$
 (2.16)

we get:

$$\frac{\mathrm{d}W(t)}{\mathrm{d}t} = \frac{\omega}{2} \chi_{xx}^{"}(\omega) \mathrm{ff}^{*} \qquad (2.17)$$

in agreement with the general results of section 1.5: this result reminds us that $\chi^{\prime}_{xx}(\omega)$ is the absorptive part and $\chi^{\prime}_{xx}(\omega)$ the reactive part of the susceptibility.

Let us now examine how the fluctuation dissipation theorem applies to this case. Our system is classical but the friction γ is just a phenomenological coefficient and no real Hamiltonian corresponds to the equation of motion (2.1). The oscillating mass may however be regarded, for example, as a ball moving in a viscous medium. In this case, there exists a Hamiltonian for the whole system consisting of the ball and of the medium in which it oscillates, and γ describes the response of the medium. Then the fluctuation dissipation theorem should be valid for the whole system. Equations (1.110) and (1.112) are written in this case:

$$X_{xx}(0) = \beta \langle x^2(t) \rangle$$
 (2.18)

$$\lim_{\omega \to \infty} \omega^2 \chi_{xx}(\omega) = -\beta \langle \dot{x}^2(t) \rangle$$
 (2.19)

But, on the other hand, from (2.8), we get:

$$X_{xx}(0) = \frac{1}{m\omega_0^2} \lim_{\omega \to \infty} \omega^2 X_{xx}(\omega) = -\frac{1}{m}$$
(2.20)

From the comparison of these expressions, we get finally:

$$\frac{1}{2} m \omega_0^2 \langle \mathbf{x}^2(t) \rangle = \frac{1}{2} m \langle \dot{\mathbf{x}}^2(t) \rangle = \frac{1}{2} \text{KT}$$
(2.21)

This is exactly Boltzmann's equipartition theorem, and this result appears rather remarkable if we consider the phenomenological nature of γ .

We note also that all these results would remain unchanged if the friction forces were frequency-dependent and represented by a coefficient $\gamma(\omega)$ provided that:

$$\gamma(0) = 0 \qquad \lim_{\omega \to \infty} \omega^{-1} \gamma(\omega) = 0 \qquad (2.22)$$

2.2. Conductivity tensor

The behaviour of the system consisting of a sample of matter interacting with an electromagnetic field is determined by two kinds of equations.

Firstly, the fields satisfy two groups of Maxwell equations which, in the reciprocal space and with proper units. can be written:

 $(\vec{h}(\vec{k},\omega))$ is the electric field. $\vec{b}(\vec{k},\omega)$ is the magnetic induction)

 $\vec{k} \cdot \vec{b} (\vec{k}, \omega) = 0$

$$\begin{bmatrix} \vec{k} \times \vec{h} (\vec{k}, \omega) - \omega \vec{b} (\vec{k}, \omega) = 0 \qquad (2.23) \end{bmatrix}$$

I)

$$\vec{k} \times \vec{b}(\vec{k}, \omega) + \omega \vec{h}(\vec{k}, \omega) = -i \vec{J}(\vec{k}, \omega) \qquad (2.25)$$

$$\vec{k} \cdot \vec{h} (\vec{k}, \omega) = \rho (\vec{k}, \omega) \qquad (2.26)$$

(2, 24)

(2.25)

(2.26)

where $\rho(\vec{k}, \omega) = en(\vec{k}, \omega)$.

Secondly, there are the "material equations" which give the current and the density of charge appearing in the material as a result of its interaction with the electromagnetic field. Thus $\vec{J}(\vec{k},\omega)$ and $\rho(\vec{k},\omega)$ are functions of $\vec{h}(\vec{k},\omega)$ and $\vec{b}(\vec{k},\omega)$. However, $\rho(\vec{k},\omega)$ is not independent of $\vec{J}(\vec{k},\omega)$ since we have the continuity relation:

$$\omega \rho(\vec{k}, \omega) - \vec{k} \cdot \vec{J}(\vec{k}, \omega) = 0 \qquad (2.27)$$

On the other hand, $\vec{b}(\vec{k},\omega)$ can be expressed in terms of $\vec{h}(\vec{k},\omega)$ by means of Eq.(2.23) which implies also Eq.(2.24). Thus, the response of the material to an electromagnetic stimulation is completely determined by the conductivity which relates $\vec{J}(\vec{k},\omega)$ to $\vec{h}(\vec{k},\omega)$. In an homogeneous medium (and a crystal, for example, can be considered homogeneous for wave lengths which are long compared with the interatomic distances), we can write:

$$J_{\alpha}(\vec{k},\omega) = \sum_{\beta} \sigma_{\alpha\beta}(\vec{k},\omega) h_{\beta}(\vec{k},\omega) \qquad (2.28)$$

where $\sigma_{\alpha\beta}(\vec{k},\omega)$ is the conductivity tensor.

In order to emphasize this point, we can assume, for example, that the medium is isotropic and expand $\sigma_{\alpha\beta}(\vec{k},\omega)$; for small values of \vec{k} and ω we find in this way:

$$\sigma_{\alpha\beta}(\vec{k},\omega) = \rho^{-1} \quad \delta_{\alpha\beta} - i\omega \mathscr{A} \delta_{\alpha\beta} + i\mathscr{B} \omega^{-1} (k_{\alpha}k_{\beta} - k^{2} \delta_{\alpha\beta})$$
$$\mathscr{C} \omega \sum_{\gamma} \epsilon_{\alpha\beta\gamma}k_{\gamma} + i(\Lambda\omega)^{-1} \delta_{\alpha\beta} \qquad (2.29)$$

where ρ is the resistivity, \mathscr{A} the electric polarizability (with $\mathscr{A} = \epsilon - 1$ where ϵ is the dielectric constant), \mathscr{B} a magnetic constant (with $\mathscr{B} = 1 - \mu^{-1}$ where μ is the magnetic permeability), \mathscr{C} a constant of rotatory power (with $\epsilon_{\alpha\beta\gamma}$ completely antisymmetric with respect to the indices and $\epsilon_{xyz} = 1$), and Λ the London constant (if the system is a superconductor).

Thus, we see how all the simple electromagnetic properties of an isotropic medium are related to the form of $\sigma_{\alpha\beta}(\vec{k},\omega)$.

The conductivity tensor $\sigma_{\alpha\beta}(\vec{k},\omega)$ can be expressed in a formal way by means of a Kubo formula which often serves as a starting point for further investigations. The complete Hamiltonian can be written:

$$H\{t\} = \frac{1}{2m} \sum_{s=1}^{N} \left[\vec{P}_{s} - \frac{e}{c} \vec{A} \{\vec{r}_{s}, t\}\right]^{2} + e \sum_{s=1}^{N} V\{\vec{r}_{s}, t\} + U(r_{1}...r_{N})$$
(2.30)

We note now that it is always possible to choose a gauge such that:

$$V\{\vec{r},t\} = 0$$
 (2.31)

On the other hand, since we are interested in the linear response only, we may write:

$$H \{t\} \simeq H + v\{t\}$$
 (2.32)

where H is the unperturbed Hamiltonian and $v\left\{t\right\}$ the perturbation:

$$v\{t\} = -\frac{e}{2mc} \sum_{s} [\vec{\vec{P}}_{s} \cdot \vec{A} \{\vec{\vec{r}}_{s}, t\} + \vec{A} \{\vec{\vec{r}}_{s}, t\} \cdot \vec{\vec{P}}_{s}] = -\frac{e}{c} \int \vec{j} \{\vec{r}\} \cdot \vec{A} \{\vec{r}, t\} d^{3}\vec{r} \qquad (2.33)$$

where $j\{r\}$ is given by (1.121). On the other hand, the total current is given by:

$$\vec{J}\{\vec{r}\} = e \ j\{\vec{r}\} - \frac{e^2}{mc} \ n\{\vec{r}\} \ \vec{A}\{\vec{r},t\}$$
 (2.34)

By assuming that the system is homogeneous, we may write, in first approximation:

$$J_{\alpha}\{\vec{r},t\} = \frac{e^2}{c} \int_{-\infty}^{t} dt' \int d^3 \vec{r}' X_{j_{\alpha}j_{\beta}}(\vec{r} \cdot \vec{r}', t - t') A_{\beta}\{\vec{r}',t'\} - \frac{e^2}{mc} n A_{\beta}\{\vec{r},t\}$$
(2.35)

Now, we can use the relation:

$$\vec{h}\{\vec{r},t\} = -\frac{1}{c} \frac{\partial}{\partial t} \vec{A}\{\vec{r},t\} \qquad \vec{A}\{\vec{r},t\} = -c \int_{-\infty}^{t} \vec{h}\{\vec{r},t'\} dt' \qquad (2.36)$$

or its Fourier transform:

$$\vec{A}(\vec{k},\omega) = \frac{c}{i\omega - 0} \vec{h}(\vec{k},\omega)$$
(2.37)

By comparing Eqs (2.28) and (2.33), we get:

$$\sigma_{\alpha\beta}(\vec{k},\omega) = \frac{e^2}{i\omega - 0} \left[\chi_{j_{\alpha}j_{\beta}}(k,\omega + i0) - \frac{n}{m} \delta_{\alpha\beta} \right]$$
(2.38)

In particular, if we denote the longitudinal part of any vector $\vec{g}(\vec{k})$ by the symbol $\vec{g}^{L}(\vec{k})$ with:

$$\vec{g}^{L}(\vec{k}) = \vec{k}(\vec{k} \cdot g(\vec{k}))/k^{2}$$
 (2.39)

we can write:

$$\vec{J}^{L}(\vec{k},\omega) = \sigma^{L}(\vec{k},\omega) \vec{h}^{L}(\vec{k},\omega)$$
(2.40)

with

$$\sigma^{L}(\vec{k},\omega) = \frac{e^{2}}{i\omega - 0} \left[\chi^{L}_{jj}(\vec{k},\omega + i0) - \frac{n}{m} \right]$$
(2.41)

where $\chi_{jj}^{L}(\vec{k},\omega)$ is defined as $\chi_{jj}^{"L}(\vec{k},\omega)$ in Eq.(1.137).

Then the sum rule (1.143) expresses the fact that, for a normal system, the d.c. conductivity ($\omega = 0$, $\vec{k} = 0$) is finite. However, it must be noted that, for free electrons, although the f sum rule remains valid for $\vec{k} \neq 0$, the d.c. conductivity is infinite. This anomaly can be related to the fact that in this case:

$$\lim_{\mathbf{h}\to 0} \chi_{jj}^{\mathbf{L}}(\vec{\mathbf{k}},\omega) \neq \chi_{jj}(0,\omega) = 0 \qquad (2.42)$$

Another simple expression of the longitudinal conductivity can be obtained by using the Kubo formula of section 1.7. From Eqs (2.35) and (2.36), we deduce after partial integration with respect to t':

$$\vec{J}^{L}\{\vec{\mathbf{r}},t\} = e^{2} \int_{-\infty}^{t} dt^{\dagger} \int d^{3} \mathbf{r}^{\dagger} \int_{-\infty}^{t'} dt^{\ast} X^{L}_{jj}(\vec{\mathbf{r}}-\vec{\mathbf{r}}^{\dagger},t-t^{\ast}) \vec{\mathbf{h}}^{L}\{\vec{\mathbf{r}}^{\dagger},t^{\dagger}\}$$
(2.43)

by using Eq. (2.36) and the f sum rule (see Eq. (1.142):

$$\int_{-\infty}^{t} X_{jj}^{L}(\vec{\mathbf{r}} - \vec{\mathbf{r}}', t - t') dt' = \frac{n}{m} \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}')$$
(2.44)

Or, from Eq.(1.88):

$$\vec{J}^{L}\{\vec{r},t\} = e^{2} \int_{-\infty}^{t} dt' \int_{0}^{\beta} d\lambda \langle j^{L}\{\vec{r'}, -i\hbar\lambda\} j^{L}\{\vec{r}, t-t'\} \rangle h^{L}\{\vec{r'}, t'\}$$

$$= e^{2} \int_{-\infty}^{t} dt^{\dagger} \int_{0}^{\beta} d\lambda \langle j^{L} \{ \vec{r}^{\dagger}, t^{\dagger} - i\hbar\lambda \} j^{L} \{ \vec{r}, t \} \rangle \vec{h}^{L} \{ \vec{r}^{\dagger}, t^{\dagger} \}$$
(2.45)

which gives:

$$\sigma^{L}(\mathbf{k},\omega) = e^{2} \int e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} d^{3}\mathbf{r} \int_{0}^{\infty} dt e^{i\omega t} \int_{0}^{\beta} d\lambda \langle \mathbf{j}^{L}\{\vec{\mathbf{r}'},-i\hbar\lambda\} \mathbf{j}^{L}\{\vec{\mathbf{r}},t\} \rangle$$
$$= \Omega^{-1} e^{2} \int_{0}^{\infty} dt e^{i\omega t} \int_{0}^{\beta} d\lambda \langle \mathbf{j}^{L}(-\vec{\mathbf{k}},-i\hbar\lambda) \mathbf{j}^{L}(\vec{\mathbf{k}},t) \rangle \qquad (2.46)$$

2.3. Einstein relation

The well known Einstein relation which connects the mobility of a set of particles with their diffusion constant D:

$$\mu = e D/KT \tag{2.47}$$

is a simple consequence of Eq.(2.45), in the classical limit (h = 0). In fact, if we denote by v_s the velocity of the s^{th} particle along an arbitrary axis, we may write:

$$\mu = (en)^{-1} \sigma^{L} (0, 0) = N^{-1} e\beta \int_{0}^{\infty} dt \sum_{ss'} \langle v_{s}(0) v_{s}'(t) \rangle$$
$$= e\beta \int_{0}^{\infty} dt \langle v(0) v(t) \rangle \qquad (2.48)$$

where v(t) is the velocity of any particle (the mean density is $n = N/\Omega$ and $\beta = 1/KT$). On the other hand: (for $\mathcal{F} \gg 1$)

$$\int_{0}^{\infty} dt \langle \mathbf{v}(0) | \mathbf{v}(t) \rangle = \frac{1}{2\mathcal{F}} \int_{0}^{\mathcal{F}} dt \int_{0}^{\mathcal{F}} dt^{\dagger} \langle \mathbf{v}(t) | \mathbf{v}(t^{\dagger}) \rangle$$
$$= \frac{1}{2\mathcal{F}} \langle (\mathbf{x}(\mathcal{F}) - \mathbf{x}(0))^{2} \rangle \qquad (2.49)$$

But a particle, which is at the origin at t = 0 has a probability $p(\vec{r}, t)$ of being at \vec{r} at time t which is given by:

$$p(\vec{r}, t) = (4\pi Dt)^{-\frac{3}{2}} e^{-\frac{t^2}{4Dt}}$$
 (2.50)

Therefore:

$$\langle \left(\mathbf{x}(t) - \mathbf{x}(0) \right)^2 \rangle = \int \mathbf{x}^2 \mathbf{p}(\vec{\mathbf{r}}, t) \, d^3\mathbf{r} = 2\mathrm{D}t$$
 (2.51)

Thus, from Eqs (2.48), (2.49) and (2.51), we can deduce Eq.(2.47).


FIG.3. A circuit with a resistance R and a block box of independence $Z(\omega)$,

2.4. Nyquist theorem

The thermal noise of a resistance [7] can be calculated by direct application of the fluctuation dissipation theorem. Thus, let us consider a resistance connected to a black box of impedance $Z(\omega)$ (see Fig. 3) which will be assumed to be purely reactive $(Z(\omega) = iZ"(\omega))$ with $Z"(\omega)$ real. The conductivity of the loop consisting of the resistance and of the black box will be given by:

$$\sigma(\omega) = \frac{1}{i\omega} \left[x_{JJ}(\omega) - x_{JJ}(0) \right]$$
(2.52)

This formula is completely equivalent to Eq.(2.41) and can be derived in the same way. Here $J(\omega)$ is the Fourier transform of the total current:

$$J(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} J\{t\} dt$$

and $X_{II}(\omega)$ is the Fourier transform of:

$$X_{JJ}(t-t') = \hbar^{-1} \langle [J\{t\}, J\{t'\}] \rangle \Theta (t-t')$$
 (2.53)

On the other hand, by definition, we have:

$$\sigma(\omega) = \frac{1}{R + Z(\omega)} = \frac{R - iZ''(\omega)}{R^2 + [Z''(\omega)]^2}$$
(2.54)

Therefore, by comparing Eqs (2.52) and (2.54), we get $(X_{II}^{"}(0) = 0)$;

$$\omega^{-1} X_{JJ}^{"}(\omega) = \frac{R}{R^{2} + [Z^{"}(\omega)]^{2}}$$
(2.55)

We can now apply the fluctuation dissipation theorem Eq.(1.102) or, more conveniently, its classical form given by Eq. (1.103) because in all cases of practical interest $\beta\hbar\omega \ll 1$. Thus, we get:

$$\Phi_{JJ}(\omega) = 2\beta^{-1} \frac{R}{R^2 + [Z''(\omega)]^2}$$
(2.56)

LINEAR RESPONSE

On the other hand, according to Eqs (1.89) and (1.90), we have:

$$\langle \{J(\omega) J(-\omega^{\dagger})\} \rangle = \int dt \ e^{i\omega t} \int dt^{\dagger} \ e^{-i\omega t^{\dagger}} \langle \{J\{t\}, J\{t^{\dagger}\}\} \rangle$$
$$= 2 \int dt \int dt^{\dagger} \ e^{i(\omega t - \omega^{\dagger} t^{\dagger})} F_{JJ}(t - t^{\dagger}) \qquad (2.57)$$
$$= 4\pi \ \delta(\omega - \omega^{\dagger}) \Phi_{JJ}(\omega)$$

 $J(\boldsymbol{\omega})$ can be considered here to be classical (i.e., a c-number) and therefore:

$$\langle J(\omega) J(-\omega') \rangle = 2\pi \,\delta(\omega - \omega') \,\Phi_{JJ}(\omega)$$
 (2.58)

By comparing with Eq.(2.56), we finally obtain the Nyquist theorem:

$$\langle J(\omega) J(-\omega^{\dagger}) \rangle = 4\pi \operatorname{KT} \frac{R}{R^2 + [Z''(\omega)]^2} \delta(\omega - \omega^{\dagger})$$
 (2.59)

The meaning of this theorem can be better understood if we simulate the effect of the thermal noise which produces current fluctuations in the black box. For this purpose, we may add:

a) either a current generator (current J_0) of infinite impedance in parallel with the resistance R (Fig. 4a).

b) or a voltage generator (e.m.f.E $_0$) in series with the resistance (Fig.4b).

It is trivial to show that J_0 or E_0 must be given by:

$$\langle J_0(\omega) J_0(-\omega') \rangle = 4\pi \text{ KT R}^{-1} \delta(\omega - \omega')$$
 (2.60)

$$\langle E_0(\omega) E_0(-\omega') \rangle = 4\pi \text{ KT R } \delta(\omega - \omega')$$
 (2.61)

These results indicate clearly that the thermal noise comes only from the resistance and does not depend on the purely reactive black box at all.



FIG.4a. Current generator in parallel with a resistance.



FIG.4b. Voltage generator in series with the resistance.

DES CLOIZEAUX

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PART II

DYNAMICAL LATTICE PROPERTIES

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PHASE TRANSITIONS AND CRITICAL PHENOMENA

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Abstract

Fundamental thermodynamic, microscopic and statistical concepts.
 Linear response, normal modes, fluctuations.
 Specific microscopic models.
 Molecular field approximation (MFA).
 Ornstein-Zernike theory of fluctuations.
 The spherical model.
 The Onsager refinement of the MFA.
 The random phase approximation (RPA).
 Nature of the phase transition.

1. FUNDAMENTAL THERMODYNAMIC, MICROSCOPIC, AND STATISTICAL CONCEPTS

Statistical mechanics gives the relations between the thermodynamic properties of a system and its microscopic description. We list here for easy reference some of the fundamental concepts.

<u>Thermodynamics</u>: All thermodynamic properties of a system can be derived from its thermodynamic potential. The choice of the proper potential depends on the system considered. The main types of systems are:

1) No interaction of the system with its environment except with constant external fields X_i constant energy E and particle number N. Proper thermodynamic potential is the entropy

$$S = S(E, X, N)$$
 (1.1)

The thermodynamic properties of the system - its temperature T, extensive variables x belonging to the forces X, chemical potential μ - are given by the partial derivatives of S:

$$dS = \frac{1}{T} dE + \frac{x}{T} dX - \frac{\mu}{T} dN \qquad (1.2)$$

It is often more convenient to solve (1.1) for E:

$$E = E(S, X, N)$$
 (1.1')

$$dE = TdS - x dX + \mu dN \qquad (1.2')$$

2) System in energy exchange with a heat bath at temperature T; constant forces X and particle number N. Proper thermodynamic potential is the free energy

$$F(T, X, N) = E - TS$$
 (1.3)

$$dF = -SdT - xdX + \mu dN$$
(1.4)

3) System in energy and particle exchange with a bath at temperature T and chemical potential μ . Proper thermodynamic potential is the "identically vanishing potential"

$$\Omega(T, X, \mu) = F - \mu N = E - \mu N - TS$$
(1.5)

$$d\Omega = -SdT - x \, dX - Nd\mu \tag{1.6}$$

Conventionally, the internal energy U is defined for a system with given values of the extensive variables x; it is related to our E by the contact transformation

$$U(x) = E + x X; \quad \frac{\partial U}{\partial x} = X$$
 (1.7)

and our E is called the enthalpy. Corresponding relations hold for the other thermodynamic potentials. For the systems we are going to consider we find it, however, more convenient to include the interaction term - xX with the external force X in the definition of the energy, since we then get a closer correspondence with the microscopic description, where we always include the interaction with external fields X in the Hamiltonian. The only exception is the case of freely moving particles in a box of volume V, where it is easier to consider V as the independent variable (the identically vanishing potential is, in this case, $\Omega(T, V, X, \mu)+pV$), instead of introducing an external potential which is zero in V and jumps to an infinite value at the surface of V.

All the thermodynamic potentials have the important property that they have a minimum (except for the entropy which has a maximum) in the state of thermodynamic equilibrium of the system to which they belong. This extremal property leads to a very convenient variational principle formulation of statistical mechanics.

<u>Microscopic description</u>: In quantum mechanics, the microscopic state of a system is described by a vector in Hilbert space, and physical observables correspond to Hermitian operators in Hilbert space. In the Heisenberg representation, the state vector is constant, and the operators depend on time. The microscopic properties of a system can be derived from its Hamiltonian \mathscr{H} ; the equation of motion of an observable A is

$$\frac{\mathrm{dA}}{\mathrm{dt}} = \frac{\partial A}{\partial t} + \frac{1}{\mathrm{in}} [A, \mathcal{H}]$$
(1.8)

If \mathcal{H} does not depend explicitly on time, it is the operator of the energy of the system. The expectation value of the observable A in a state described by the vector ψ is

$$\langle A \rangle_{\mu} = (\psi, A\psi)$$
 (1.9)

In classical mechanics, the microscopic state of a system is described by a point in phase space Γ ; physical observables and especially the Hamiltonian are functions in Γ , and the equations of motion are obtained from (1.8) by replacing the commutator by the Poisson bracket:

$$\frac{1}{i\hbar}[A, B] \rightarrow \{A, B\} = \sum_{r} \frac{\partial(A, B)}{\partial(q_{r}, p_{r})} \equiv \sum_{r} \left(\frac{\partial A}{\partial q_{r}} \frac{\partial B}{\partial p_{r}} - \frac{\partial A}{\partial p_{r}} \frac{\partial B}{\partial q_{r}} \right)$$
(1.10)

PHASE TRANSITIONS

<u>Statistics</u>: The properties of a thermodynamic system are considered as statistical averages over an ensemble of microscopic systems. The statistical distribution of the microscopic systems in the ensemble is (for the case of quantum systems) described by the statistical operator (density matrix) ρ . This is a Hermitian operator with the properties:

All eigenvalues
$$\rho_n$$
 satisfy $0 \le \rho_n \le 1$; (1.11)

$$\sum \rho_n \equiv tr \rho = 1$$
 (1.12)

In an ensemble described by the statistical operator ρ with eigenvalues ρ_n and eigenvectors ψ_n , each of its members is in one of the states ψ_n , and ρ_n gives the probability distribution over these states.

The equation of motion of the statistical operator is in Schrödinger representation

$$\frac{\partial \rho}{\partial t} = -\frac{1}{i\hbar} \left[\rho, \mathcal{H} \right]$$
(1.13)

The statistical average (thermodynamic expectation value) of an observable A over the ensemble is

$$\langle A \rangle = \sum \rho_n (\psi_n, A\psi_n) \equiv \operatorname{tr} \rho A$$
 (1.14)

The connection to thermodynamics is effected by Boltzmann's hypothesis which relates the entropy of a thermodynamic system to the statistical properties of the ensemble:

$$S = -k \langle \log \rho \rangle = -k tr \rho \log \rho \qquad (1.15)$$

The various types of thermodynamic systems considered above are related to corresponding types of ensembles:

1) Microcanonical ensemble: All eigenvectors ψ_n belonging to non-vanishing eigenvalues ρ_n lie in a subspace of Hilbert space which is spanned by the eigenvectors of the Hamiltonian with energy eigenvalues in an interval δE around energy E, and particle number equal to N:

$$S(E, N) = -ktr \rho_{E,N} \log \rho_{E,N}$$
(1.16)

Maximization of S under the constraint (1.12) gives at thermal equilibrium

$$\rho_{E,N} = \text{const} \cdot \frac{1}{\underset{E}{\overset{F+6E}{\underset{E}{\int}}}}; g_{N}(E) = \text{density of states}$$
(1.17)

and

$$S(E, N) = k \log \int_{E}^{E+\delta E} g_N(E) dE$$
 (1.18)

Thus, in thermal equilibrium the entropy is essentially equal to the degeneracy of the states of constant energy.

2) Canonical ensemble: All eigenvectors ψ_n belonging to nonvanishing eigenvalues ρ_n lie in the subspace of constant particle number N:

$$F(T, N) = tr \{\rho_N \mathcal{H} + kT \rho_N \log \rho_N\}$$
(1.19)

Minimization under the constraint (1.12) gives at thermal equilibrium

$$\rho_{\rm N} = \frac{\mathrm{e}^{-\beta \mathscr{U}}}{Z_{\rm N}}; \quad Z_{\rm N} = \mathrm{tr}_{\rm N} \; \mathrm{e}^{-\beta \mathscr{U}}; \quad \beta = \frac{1}{\mathrm{kT}}$$
(1.20)

and

$$F(T, N) = kT \log Z_N$$
(1.21)

 $Z_{\rm N}\,$ is the canonical partition function. We shall use most frequently this canonical ensemble.

3) Grand canonical ensemble: No restrictions on ρ .

$$\Omega = \operatorname{tr} \left\{ \rho \mathcal{H} - \rho \mu \mathcal{N} + k \operatorname{T} \rho \log \rho \right\}$$
(1.22)

(\mathscr{N} = particle number operator.) Minimization under the constraint (1.12) gives at thermal equilibrium

$$\rho = \frac{\mathrm{e}^{-\beta(\mathscr{Y} - \mu\mathcal{N})}}{Z}; \quad Z = \mathrm{tr} \, \mathrm{e}^{-\beta(\mathscr{Y} - \mu\mathcal{N})} \tag{1.23}$$

and

$$\Omega(\mathbf{T},\mu) = -\mathbf{k}\mathbf{T}\log \mathbf{Z} \tag{1.24}$$

Z is the grand partition function. It is most convenient to introduce the "grand canonical Hamiltonian" $\mathscr{H}_g = \mathscr{H} - \mu \mathscr{N}$. Then, the grand canonical ensemble becomes formally equivalent to the canonical ensemble.

All these equilibrium statistical operators commute with \mathcal{H} , and are therefore according to Eq.(1.13) constant in time, as is to be required for equilibrium distributions.

For large systems, the thermodynamic properties will be the same in the various ensembles; the fluctuations may, however, be quite different.

Values for thermodynamic quantities can either be obtained as statistical averages of the corresponding observables, or as derivatives of the thermodynamic potentials. Especially,

$$E = tr \rho \mathscr{H} = F - T \frac{\partial F}{\partial T} = \frac{k}{\beta} \frac{\partial (\beta F)}{\partial \beta}$$
(1.25)

$$x = \operatorname{tr} \rho \xi = -\frac{\partial F}{\partial X}$$
(1.26)

where ξ is the observable multiplying the external field X to obtain the interaction term - ξX in the Hamiltonian.

For classical systems, ρ is just the probability density in phase space Γ with the properties

$$\rho \ge 0 \tag{1.27}$$

$$\int_{\Gamma} \rho \, d\Gamma = 1 \tag{1.28}$$

and all the above formulae are transformed into the classical analogues by replacing the trace by an integral over phase space:

$$\operatorname{tr} \rho A \stackrel{\rightarrow}{\xrightarrow{\Gamma}} \rho A d\Gamma$$
(1.29)

2. LINEAR RESPONSE, NORMAL MODES, FLUCTUATIONS

We shall be interested in the response of a system to a small external perturbation, and quote here the fundamental results: Consider a system in thermodynamic equilibrium at time $t = -\infty$. A small external perturbation Y(t) is switched on adiabatically, giving rise to a coupling term

$$\mathcal{H}_{int} = -\eta Y(t) \tag{2.1}$$

in the Hamiltonian. Choose η such that

$$y(t) = \langle \eta(t) \rangle = 0 \quad \text{at} \quad t = -\infty \tag{2.2}$$

The response y(t) at time t is then to first order in Y given by a linear relation

$$y(t) = \int_{-\infty}^{t} \chi(t - t') Y(t') dt'$$
 (2.3)

or in Fourier representation $y(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} y(t) e^{i\omega t} dt$:

$$y(\omega) = \chi(\omega) Y(\omega); \quad \chi(\omega) = \int_{0}^{\infty} \chi(\tau) e^{i\omega\tau} d\tau$$
 (2.4)

The linear response function (generalized susceptibility) $\boldsymbol{\chi}$ is given by the formula

$$\begin{split} \chi(t-t') &= \frac{1}{\hbar} \langle [\eta(t), \eta(t')] \rangle \text{ for } t > t' \\ \chi(t-t') &= 0 \qquad \text{ for } t < t' \end{split}$$
 (2.5)

$$\chi(\omega) = \frac{i}{\hbar} \int_{0}^{\infty} \langle [\eta(\tau), \eta(0)] \rangle e^{i\omega\tau} d\tau \qquad (2.6)$$

where $\eta(t)$ is in the Heisenberg representation of the unperturbed system (interaction representation), and the average is over the unperturbed distribution.

Since y(t) and Y(t) are real, we have

$$\chi^*(\omega) = \chi(-\omega^*) \tag{2.7}$$

The poles of the response function are called the <u>normal mode</u> frequencies. Since the unperturbed system is in thermal equilibrium, none of the normal modes can be growing, i.e. none of the poles can lie in the upper half ω -plane. As a consequence of this analytical property, one obtains the dispersion relation

$$\chi(\omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi(\omega)}{\omega' - \omega} d\omega' \qquad (2.8)$$

relating real and imaginary part of χ to each other. The integration is to be carried out above any singularities which $\chi(\omega')$ may have on the real axis; at $\omega = \omega'$, the principal value must be taken.

There exists a very interesting relation between the imaginary part $\chi''(\omega)$ of the response function and the time correlation function of the fluctuations of the coordinate $\eta(t)$ in the equilibrium ensemble. This fluctuation-dissipation theorem was discovered by H.B. Callen and T.A. Welton and has the form

$$\frac{1}{2} \langle \eta(\tau) \eta(0) + \eta(0) \eta(\tau) \rangle = \frac{\hbar}{2\pi} \int_{-\infty}^{+\infty} \chi^{\prime\prime}(\omega) \coth \frac{\hbar\omega}{2kT} e^{i\omega\tau} d\omega$$
(2.9)

For the mean square fluctuation of the coordinate η one obtains thus

$$\langle \eta^2 \rangle = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \chi^{\prime\prime}(\omega) \coth \frac{\hbar\omega}{2kT} d\omega$$
 (2.10)

If all frequencies for which $\chi^{\prime\prime}(\omega)$ is appreciably different from zero satisfy

 $\hbar\omega \ll kT$ (classical limit) (2.11)

one obtains by the use of the dispersion relation (2.8) the <u>classical</u> fluctuation theorem

$$\langle \eta^2 \rangle = kT\chi(0)$$
 (2.12)

This result can also be obtained directly from calculating $\chi(0)$ as the response to a static field Y: We have in the canonical ensemble from (1.26)

$$y(Y) = -\frac{\partial F}{\partial y} = \langle \eta \rangle_{Y} = \frac{1}{Z} \operatorname{tr} \eta e^{-\beta (\mathcal{H}_{0} - \eta Y)}$$
$$\chi(Y) = \frac{\partial y}{\partial Y} = \frac{1}{kT} (\langle \eta^{2} \rangle_{Y} - \langle \eta \rangle_{Y}^{2})$$
(2.13)

We note here the analogous result for the specific heat:

$$E = \frac{\partial(\beta F)}{\partial \beta} = \langle \mathcal{H} \rangle$$

$$c_{Y} = -k\beta^{2} \left(\frac{\partial E}{\partial \beta} \right)_{Y} = k\beta^{2} \left(\langle \mathcal{H}^{2} \rangle - \langle \mathcal{H} \rangle^{2} \right) \qquad (2.14)$$

The classical approximation consists of the assumption that ηY can be commuted with \mathcal{H}_0 . If one takes the limit $Y \rightarrow 0$, one recovers (2.11).

3. SPECIFIC MICROSCOPIC MODELS

We consider the full Hilbert space \mathscr{S} as the product space of "single particle spaces" \mathscr{S}_i of much lower dimensionality, and write the Hamiltonian in the form

$$\mathcal{H} = \sum_{i} \mathcal{H}_{i} + \mathcal{H}_{int}$$
 (3.1)

where each \mathscr{U}_i operates only in the corresponding component space \mathscr{G}_i . It should be noted that this decomposition is not unique, and it often requires considerable physical (and mathematical) intuition to find that decomposition which brings the essential simplification to the problem to make it tractable. For the same reason, the concept of a "particle" is not unique. One may, for instance, start with a system of interacting atoms, but will then find that a decomposition in which the particles are phonons is more adequate; or one may start with a system of spins and find that a decomposition with spin waves as the particles makes the problem tractable.

In the simplest case, the single particle spaces are only two-dimensional; the full Hilbert space of a system of N particles has then dimension 2^{N} . Since the Pauli matrices together with the unit matrix form a basis for all 2×2 matrices, one can in this case always express the Hamiltonian as a pseudo-spin Hamiltonian:

$$\mathscr{H} = \sum_{i} \mathscr{H}_{i} (\vec{\sigma}_{i}) + \frac{1}{2} \sum_{i,j} \mathscr{H}_{ij} (\vec{\sigma}_{i}; \vec{\sigma}_{j}) + \dots \qquad (3.2)$$

We shall here consider only cases with two-spin interactions (no three and more-spin interactions).

Because of the properties of the Pauli matrices

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1, \quad \sigma_x \sigma_y - \sigma_y \sigma_x = 2i\sigma_z, \text{ etc.}$$

the Hamiltonian can then always be written in the form

$$\mathcal{H} = -\sum_{i} \vec{H}_{i} \cdot \vec{\sigma}_{i} - \frac{1}{2} \sum_{i,j} \vec{\sigma}_{i} v_{ij} \vec{\sigma}_{j}$$
(3.3)

In spite of this severe restriction, the set of problems expressable in this form is remarkably rich. Since most of the spin Hamiltonians will be discussed in the other lectures of this course, we discuss them here only briefly.

The case of non-interacting spins is trivial:

$$Z = 2^{N} \prod_{i} \cosh \beta H_{i}; \quad \langle \vec{\sigma}_{i} \rangle = \frac{\vec{H}_{i}}{H_{i}} \tanh \beta H_{i}$$

Only interactions can give rise to co-operative effects, and a phase transition, in particular, is the result of a competition between interactions favouring an ordered state, and entropy favouring disorder.

<u>Heisenberg magnet</u>: Here, the $\vec{\sigma}_i$ are real spin vectors of electrons at lattice sites i, \vec{H}_i is the external field acting on $\vec{\sigma}_i$, and v_{ij} is the generally anisotropic interaction between $\vec{\sigma}_i$ and $\vec{\sigma}_j$. For isotropic exchange

$$\mathbf{v}_{ij} = \mathbf{v}_{ij} \cdot \mathbf{1} \tag{3.4}$$

For dipolar interaction,

$$\mathbf{v}_{ij} = \frac{p^2}{r_{ij}^5} [3 \vec{r}_{ij} \cdot \vec{r}_{ij} - r_{ij}^2 \cdot \mathbf{1}]$$
(3.5)

where p is the dipole moment.

Ising magnet: This is a Heisenberg magnet with extreme anisotropy:

$$\mathbf{v}_{ij} = \mathbf{v}_{ij} \cdot \vec{\mathbf{e}}_z \vec{\mathbf{e}}_z$$
 (3.6)

In general, one restricts also the field to the z-direction. Then, the model becomes completely classical:

$$\mathcal{H} = -\sum_{i} H_{i} \mu_{i} - \frac{1}{2} \sum_{i,j}' v_{ij} \mu_{i} \mu_{j} ; \quad \mu_{i}^{2} = 1$$
 (3.7)

<u>Lattice gas [1]</u>: This is a particularly simple model of a gas the molecules of which can only occupy lattice sites i, but which still allows one to study the problem of condensation. Two molecules occupying lattice sites i and j interact with an energy w_{ij} , so that the Hamiltonian is

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j}' w_{ij} n_i n_j - \mu \sum_i n_i$$
 (3.8)

We have included the chemical potential term $-\mu \sum n_i$ in the Hamiltonian, since we want to keep only the number of lattice sites constant, but want to use the grand canonical ensemble with respect to the number K of molecules.

Since there are two states per lattice site (it can either be occupied or empty), the Hamiltonian must again be expressable in pseudo-spin form. In fact,

$$n_{i} = \frac{1}{2}(1 + \mu_{i}) \tag{3.9}$$

and therefore with $w_0 = \sum_{i=1}^{n} w_{ij}$:

$$\mathscr{H} = -\frac{1}{8} \sum_{i,j}' w_{ij} \mu_i \mu_j - \left(\frac{\mu}{2} + \frac{w_0}{4}\right) \sum_i \mu_i - \frac{N}{2} \left(\mu + \frac{w_0}{4}\right)$$
(3.10)

Thus, the lattice gas is completely equivalent to the Ising magnet in constant external field. Table I shows the correspondences obtained; the last line follows from the fact that F_{gas} +pN is the identically vanishing potential.

Since the very important hard-core repulsion between atoms is naturally taken into account in the lattice gas model (two atoms cannot get closer than the lattice constant), this model, despite its severe restrictions, is actually superior to models of freely moving atoms which neglect the hard-core repulsion.

TABLE I. COMPARISON OF ISING MAGNET AND LATTICE GAS

Ising magnet	Lattice gas
4v	W
Number of spins N	Volume N (in units of cell volume)
Number of up spins $\frac{1}{2}\left(N+\sum_{i}\mu_{i}\right)$	Number of molecules K
Relative magnetization R = $\frac{1}{N} \sum \mu_i$	2p - 1
$\frac{1}{2}(1+R)$	Density $\rho = K/N$
Н	$\frac{\mu}{2} + \frac{w_0}{4}$
2(H - v ₀)	μ
$F_{Ising} - \frac{1}{2} NH$	$F_{gas} + \frac{1}{4}N\mu$
$H - \frac{v_0}{2} - F_{Ising} / N$	Pressure $p = -F_{gas}/N$

It is a straightforward matter to generalize this model to the case of a binary mixture of two sorts of atoms A and B with interactions w_{AA} , w_{BB} , and w_{AB} .

BCS-Superconductor [2]: The BCS Hamiltonian of a superconductor is

$$\mathscr{H} = \sum_{k} (\epsilon_{k} - \mu)(n_{k\uparrow} + n_{-k\downarrow}) - \sum_{k,k'} v_{kk'} b_{k}^{\dagger} b_{k'}$$
(3.11)

where

$$n_{k\sigma} = c_{k\sigma}^{\dagger} c_{k\sigma}; \quad b_k = c_{k\uparrow} c_{-k\downarrow}; \quad b_k^{\dagger} = c_{-k\downarrow}^{\dagger} c_{k\uparrow}^{\dagger}$$
(3.12)

and the chemical potential term has again been included. To a given set $(k\uparrow, -k\downarrow)$, there belongs a four-dimensional space spanned by the four states $|n_{k\uparrow}, n_{-k\downarrow}\rangle$. This space decomposes again into a product of two two-dimensional subspaces: one spanned by the two pair states

$$\psi_1 = |00\rangle; \psi_2 = |11\rangle$$
 (3.13)

the other spanned by the two single-particle states

$$\varphi_1 = |01\rangle; \quad \varphi_2 = |10\rangle \tag{3.14}$$

If one writes $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$, where

$$\mathscr{H}_{1} = \sum_{k} (\epsilon_{k} - \mu)(n_{k\uparrow} + n_{-k\downarrow} - 1) - \sum_{k,k'} v_{kk'} \mathbf{b}_{k}^{\dagger} \mathbf{b}_{k'} \qquad (3.15)$$

$$\mathcal{H}_2 = \sum_k (\epsilon_k - \mu)$$
 (3.16)

then \mathscr{H}_1 is non-zero only in the pair space, and \mathscr{H}_2 is just a constant. Therefore, \mathscr{H} must again permit a pseudo-spin representation. In fact,

$$\sigma_{k}^{x} = b_{k} + b_{k}^{\dagger}; \quad \sigma_{k}^{y} = \frac{1}{i} (b_{k} - b_{k}^{\dagger}); \quad \sigma_{k}^{z} = 1 - n_{k\uparrow} - n_{-k\downarrow} \quad (3.17)$$

We thus obtain the Anderson spin model of a superconductor

$$\mathscr{H} = -\sum_{k} (\epsilon_{k} - \mu) \sigma_{k}^{z} - \frac{1}{4} \sum_{kk'} v_{kk'} (\sigma_{k}^{x} \sigma_{k'}^{x} + \sigma_{k}^{y} \sigma_{k'}^{y}) + \sum_{k} (\epsilon_{k} - \mu)$$
(3.18)

It is equivalent to a Heisenberg magnet with anisotropic exchange in a non-uniform magnetic field, but the spin operators act on the occupation of pair states in reciprocal space.

Order-disorder ferroelectric [3-5]: Blinc, de Gennes, and Brout, Müller and Thomas have studied a model of a ferroelectric in which each ferroelectric ion sits in a double-well potential in which it can

tunnel back and forth with a tunneling frequency $2\Gamma/\hbar$. Different ions interact with an electrostatic dipole interaction v_{ij} . It is assumed that the properties of the ferroelectric can be adequately described in the subspace which is spanned by the lowest pair of states ψ_i^{symm} and $\psi_i^{antisymm}$ of each ion. With the basis functions

$$\psi_{i}^{r} = \frac{1}{\sqrt{2}} (\psi_{i}^{s} + \psi_{i}^{a}); \qquad \psi_{i}^{\ell} = \frac{1}{\sqrt{2}} (\psi_{i}^{s} - \psi_{i}^{a})$$
(3.19)

one obtains the pseudo-spin Hamiltonian

$$\mathcal{H} = -\Gamma \sum_{i} \sigma_{i}^{\mathbf{x}} - \frac{1}{2} \sum_{i,j} v_{ij} \sigma_{i}^{\mathbf{z}} \sigma_{j}^{\mathbf{z}}$$
(3.20)

It is equivalent to an Ising magnet in a transverse magnetic field. In Fig.1, we have schematically indicated the types of phase transitions found in the various cases.

This pseudo-spin formulation proves to be very convenient. One only has to remember that the directions x, y, z in spin space have nothing to do with directions in real space, and the spin does not have the time reversal behaviour of a real spin.

As an example for a model with higher dimensionality of the singleparticle spaces, we mention only the Heisenberg magnet with $S > \frac{1}{2}$:

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} \vec{\mathbf{S}}_i \mathbf{J}_{ij} \vec{\mathbf{S}}_j - g \sum_i \vec{\mathbf{H}}_i \cdot \vec{\mathbf{S}}_i$$
(3.21)

The single-particle spaces have dimensions 2S+1, the full Hilbert space dimension $(2S+1)^N$.

In the limit of

 $S \rightarrow \infty; \vec{S}/S = \vec{\sigma}$ (3.22)

 $\mathbf{J}_{ii} \mathbf{S}^2 = \mathbf{v}_{ii}$, $g\mathbf{S} = \mathbf{m}$ finite

one obtains the classical Heisenberg magnet

$$\mathscr{H} = -\frac{1}{2} \sum_{i,j} \vec{\sigma}_i \mathbf{v}_{ij} \vec{\sigma}_j - m \sum_i \vec{H}_i \cdot \vec{\sigma}_i; \quad \vec{\sigma}_i^2 = 1$$
(3.23)

the phase space of which consists of the surfaces of N spheres.

4. MOLECULAR FIELD APPROXIMATION

The fundamental difficulty in statistical mechanics is a practical one: Except in very special cases, it is impossible to compute the trace in

I. ISING MAGNET AND LATTICE GAS



Magnetization as function of field at constant temperature.



Magnetization as function of temperature at constant field.

II. SUPER CONDUCTOR



Pair amplitude as function of k at constant temperature $T \leq T_c$.

III. FERROELECTRIC



Density as function of chemical potential at constant temperature.



Density as function of temperature at constant chemical potential.



Pair potential $\Delta_k \approx \sum_{k'} v_{kk'} < \sigma_{k'}^{\perp} >$ as function of temperature.



Polar amplitude $\langle \sigma_z \rangle$ and tunnelling amplitude $\langle \sigma_x \rangle$ as functions of temperature.

FIG.1. Phase transitions in pseudo-spin systems (schematic).

in the limit of a large system. One therefore has to resort to a large extent to approximation methods. We shall discuss in the following the more important ones, and their shortcomings. The simplest approximation scheme available is the molecular field approximation (MFA), which we shall present here for the case of the Ising ferromagnet:

$$\mathscr{H} = -\frac{1}{2} \sum_{i,j}' v_{ij} \mu_i \mu_j - \sum_i H_i \mu_i \quad (\mu_i = \pm 1)$$
(4.1)

The generalization to other cases is straightforward as long as operators acting on different single-particle sub-spaces commute, which is the case for all spin systems.

According to Eq.(4.1), a given ${\rm spin}\,\mu_i$ is under the action of an instantaneous local field

$$H_{i}^{\text{local}} = \sum_{j} v_{ij} \mu_{j} + H_{i}$$
(4.2)

The basic idea of the MFA consists in the following: We know from qualitative arguments that in the ordered state in uniform field H_i = H, there exists a uniform magnetization R:

$$\langle \mu_i \rangle = \mathbb{R}$$
 (4.3)

One assumes that the fluctuations of the magnetization are small, which is possible only if the fluctuations in the local field are small. One therefore approximates the local field by its statistical average, the mean molecular field (Weiss field)

$$H_i^M = \langle H_i^{\text{local}} \rangle = v(0) R + H$$
(4.4)

Here, $v(0) = \sum_{i} v_{ij}$ is the q = 0 component of the Fourier transform of

the interaction

$$\mathbf{v}(\mathbf{q}) = \sum_{j} \mathbf{v}_{ij} \, \mathbf{e}^{-\vec{\mathbf{q}} \cdot \vec{\mathbf{R}}_{ij}} \tag{4.5}$$

But the statistical mechanics of a single spin in a constant field is a trivial problem. One obtains for the average moment of spin μ_i :

$$\langle \mu_i \rangle = R = \tanh \beta [v(0)R + H]$$
 (4.6)

which is a self-consistent condition for determining the magnetization R = R(H, T).

Before discussing the results of the MFA, we shall present two more formal methods to obtain the MFA.

MFA as the best independent particle theory: Another way to express the assumption of negligible fluctuations in the magnetization is to assume

that the μ_i fluctuate independently of each other, i.e. that their correlation is negligible. For completely uncorrelated μ_i 's, the probability $\overline{\rho(\mu_1 \dots \mu_N)}$ splits into a product of single spin probabilities:

$$\rho(\mu_1...\mu_N) = \prod_i \rho_i(\mu_i); \quad tr_i \rho_i = 1$$
(4.7)

We therefore expect to obtain a good approximation to the equilibrium free energy, if we minimize

$$F = tr \{\rho \mathcal{H} - kT \rho \log \rho\}$$
(4.8)

over all product trial functions of the form (4.7). For such product functions,

$$\mathbf{F} = -\frac{1}{2} \sum_{ij} \mathbf{tr}_{ij} \left(\rho_i \rho_j \mathbf{v}_{ij} \mu_i \mu_j \right) - \sum_i \mathbf{tr}_i \left(\rho_i \mu_i \mathbf{H}_i \right) + \mathbf{kT} \sum_i \mathbf{tr}_i \rho_i \log \rho_i$$
(4.9)

It is instructive to find the free energy for given average moments

$$\langle \mu_i \rangle = r_i$$
 (4.10)

which will finally be determined by minimizing F with respect to the r_i . In other words, we perform the minimization of F in two steps: First with respect to all "internal" degrees of freedom, giving a free energy $F(r_1 \ldots r_N, H, T)$ depending on the r_i and H separately; and only finally with respect to the "external" variables r_i , giving the thermodynamic equilibrium values $r_i = r_i$ (H, T).

We then have to find the minimum of (4.9) under the constraints

$$tr_i \rho_i = 1; tr_i (\rho_i \mu_i) = r_i$$
 (4.11)

With the Lagrange multipliers K $_i$ = -kT (log Z_i - 1) and λ_i one obtains for the variations of F

$$\delta \left\{ \mathbf{F} - \sum_{i} \mathbf{K}_{i} \operatorname{tr}_{i} \rho_{i} - \sum \lambda_{i} \operatorname{tr} \rho_{i} \mu_{i} \right\} = \sum_{i} \operatorname{tr}_{i} \left\{ \left[-\Lambda_{i} \mu_{i} + k \operatorname{T} \log \rho_{i} Z_{i} \right] \delta \rho_{i} \right\} = 0$$

whence

$$\rho_i = \frac{1}{Z_i} e^{-\beta \Lambda_i \mu_i}$$
(4.12)

Here,

$$\Lambda_i = H_i^M + \lambda_i$$

H^M_i being the molecular field

$$H_{i}^{M} = \sum_{j} v_{ij} \langle \mu_{j} \rangle + H_{i}$$
 (4.13)

As usual, the Lagrange parameters λ_i are the forces necessary to satisfy the constraints (4.10).

The Lagrange parameters Z_i and λ_i are determined by

$$Z_{i} = \operatorname{tr}_{i} e^{\beta \Lambda_{i} \mu_{i}} = 2 \cosh \beta \Lambda_{i}$$
(4.14)

$$\mathbf{r}_{i} = \frac{1}{Z_{i}} \operatorname{tr}_{i} \mu_{i} e^{\beta \Lambda_{i} \mu_{i}} = \tanh \beta \Lambda_{i}$$
(4.15)

The free energy can be written

$$\mathbf{F} = -\frac{1}{2} \sum_{i,j} \mathbf{v}_{ij} \mathbf{r}_i \mathbf{r}_j - \sum_i \mathbf{H}_i \mathbf{r}_i + \mathbf{kT} \sum_i \mathbf{A}(\mathbf{r}_i) \qquad (4.16)$$

where (see Fig. 2)

$$A(\mathbf{r}_{i}) = \beta \Lambda_{i} \mathbf{r}_{i} - \log Z_{i} = \frac{1 + \mathbf{r}_{i}}{2} \log \frac{1 + \mathbf{r}_{i}}{2} + \frac{1 - \mathbf{r}_{i}}{2} \log \frac{1 - \mathbf{r}_{i}}{2}$$
$$= \mathbf{r}_{i} \operatorname{artanh} \mathbf{r}_{i} + \frac{1}{2} \log(1 - \mathbf{r}_{i}^{2}) - \log 2 \qquad (4.17)$$

has the property

$$\frac{dA(r)}{dr} = \operatorname{artanh} r \tag{4.18}$$

Equation (4.16) has an especially simple form: it expresses the free energy as a sum of two terms, the first of which is just the Hamiltonian $\mathscr{F}(r_1 \ldots r_N)$ taken at the average values, and the second is a universal function of these average values.



Minimizing (4.16) with respect to the \textbf{r}_i gives the self-consistency equations

$$\mathbf{r}_{i} = \tanh\beta\left(\sum_{j}\mathbf{v}_{ij}\mathbf{r}_{j} + \mathbf{H}_{i}\right)$$
(4.19)

In the ferromagnetic case in uniform field, the lowest free energy is obtained for $r_i = R$, where R is determined by (4.6), and

$$F = N\{-\frac{1}{2}v(0) R^{2} - HR + kT A(R)\}$$
(4.20)

This is the most clean-cut derivation of the MFA. It is, however, difficult to see how it could be improved in a systematic fashion. We therefore discuss briefly another method in which the MFA appears as the first term of an expansion.

<u>MFA by an expansion method</u>: Whereas the introduction of prescribed averages r_i was purely optional above, in this method the constraints are vital for its success. We write down the conditions of minimum free energy under the constraints

$$tr \rho = 1 \qquad tr \rho \mu_i = r_i \tag{4.22}$$

permitting arbitrary $\rho(\mu_1 \dots \mu_N)$ as trial functions. We find

$$\rho = \frac{1}{Z} e^{-\beta \mathscr{A}^{(\lambda)}}; \quad Z = \operatorname{tr} e^{-\beta \mathscr{A}^{(\lambda)}}$$
(4.23)

where

$$\mathscr{H}^{(\lambda)} = \mathscr{H} - \sum_{i} \lambda_{i} (\mu_{i} - r_{i})$$
 (4.24)

The free energy is

$$F = -kT \log Z \tag{4.25}$$

We now use a trick to evaluate the partition function. We invent a simpler Hamiltonian \mathscr{H}_0 with a probability distribution

$$\rho_0 = \frac{1}{Z_0} e^{-\beta \mathscr{X}_0} ; \qquad Z_0 = \text{tr } e^{-\beta \mathscr{X}_0}$$
(4.26)

From the identity

$$Z = Z_0 \langle e^{-\beta(\mathscr{Y}^{(\lambda)} - \mathscr{Y}_0)} \rangle_0$$
(4.27)

where the average $\langle \rangle_0$ is taken over ρ_0 , we obtain for the free energy

$$-\beta \mathbf{F} = \log Z_0 + \log \langle e^{-\beta (\mathscr{Y}^{(\lambda)} - \mathscr{Y}_0)} \rangle_0$$
(4.28)

This is still exact. We now assume that \mathscr{H}_0 is sufficiently close to $\mathscr{H}^{(\lambda)}$ that we can expand $\log \langle \exp[-\beta(\mathscr{H}^{(\lambda)} - \mathscr{H}_0)] \rangle$ and keep only the first term. Then,

$$F = -kT \log Z_0 + \langle \mathcal{H}^{(\lambda)} - \mathcal{H}_0 \rangle_0 \qquad (4.29)$$

We now use for \mathscr{H}_0 that particular non-interacting spin Hamiltonian

$$\mathscr{H}_{0} = -\sum_{i} \Lambda_{i} \mu_{i}$$
(4.30)

which gives rise to the same average moments r_i :

$$\langle \mu_i \rangle_0 = \tanh \beta \Lambda_i = r_i$$
 (4.31)

 Λ_i is evidently the molecular field at site i.

Since ρ_0 factors into single-spin probabilities, we have

$$\langle \mathcal{H}^{(\lambda)} - \mathcal{H}_0 \rangle_0 = -\frac{1}{2} \sum_{i,j} \mathbf{v}_{ij} \mathbf{r}_i \mathbf{r}_j - \sum_i \mathbf{H}_i \mathbf{r}_i + \sum_i \Lambda_i \mathbf{r}_i$$

and similar to (4.17)

$$\log Z_0 = \beta \sum_i \Lambda_i \mathbf{r}_i - \sum_i \Lambda(\mathbf{r}_i)$$

Inserting these expressions in (4.29), we recover (4.16).

<u>Results:</u> Let us first find whether the system has a phase transition, and to what type of magnetic order. We start at a high temperature with the system in the disordered state, and gradually reduce the temperature. We obtain a phase transition when at some temperature $T = T_c$ the self-consistency equations (4.19) have a non-trivial solution $r_i \ll 1$ for $H_i = 0$. This leads to a linear eigenvalue problem for T_c :

$$\sum_{j} \mathbf{v}_{ij} \mathbf{r}_{j} - \mathbf{k} \mathbf{T}_{c} \mathbf{r}_{i} = 0$$
(4.32)

The Curie temperature is the largest eigenvalue and the corresponding eigenfunction describes the type of magnetic ordering. We diagonalize (4.32) by Fourier transforms

$$[v(q) - kT_c]r_q = 0 (4.33)$$

The eigenvalues are thus just the Fourier transforms v(q) of the interaction. If v(q) assumes its maximum at q=0, we obtain ferromagnetic ordering with a Curie temperature

$$kT_{c} = v(0)$$
 (4.34)

If v(q) assumes its maximum for q = Q/2, where Q is some reciprocal lattice vector, we obtain simple two-sublattice antiferromagnetic ordering. If v(q) assumes its maximum at a general q-value, we obtain a general antiferromagnetic spin structure with wave number q.

We shall discuss further the case of ferromagnetic ordering. From (4.20) and (4.6),

F = N{
$$-\frac{1}{2}v(0)R^2$$
 - HR + kTA(R)}
R = tanh β [v(0) R + H] (4.35)

we obtain for the energy, specific heat, and susceptibility

$$E = \frac{\partial}{\partial \beta} (\beta F) = N\{-\frac{1}{2}v(0)R^{2} - HR\}$$

$$c_{H} = \left(\frac{\partial E}{\partial T}\right)_{H} = Nk \operatorname{artanh}^{2}R \cdot \frac{1 - R^{2}}{1 - \beta v(0)(1 - R^{2})}$$

$$\chi = \left(\frac{\partial R}{\partial H}\right)_{T} = \beta \frac{1 - R^{2}}{1 - \beta v(0)(1 - R^{2})}$$

$$(4.36)$$

Near T_c , we obtain with $\tau = |T - T_c| / T$

 $R \propto \tau^{\frac{1}{2}}$ $\chi \propto \tau^{-1} \text{ with different coefficient above and below } T_{c}$ $C_{H} \text{ finite discontinuity at } T_{c}$ $R \propto H^{\frac{1}{2}} \text{ at } \tau = 0$ (4.37)

Below T_c , in going from positive to negative fields, we find a first order transition at H=0 without latent heat, but with a finite jump 2R in magnetization. Let us find the stability limits in the metastable regions where R is antiparallel to H. We obtain for small deviations δr_i from the equilibrium state r_i =R

$$\mathbf{F} - \mathbf{F}_{0} = \frac{1}{2} \sum_{ij} \left\{ -\mathbf{v}_{ij} + \mathbf{kT} \frac{\delta ij}{1 - \mathbf{R}^{2}} \right\} \delta \mathbf{r}_{i} \delta \mathbf{r}_{j}$$
(4.38)

or in terms of Fourier transforms

 $\mathbf{F} - \mathbf{F}_{0} = \frac{1}{2} \sum_{q} \left\{ -v(q) + \frac{kT}{1-R^{2}} \right\} \left| \delta \mathbf{r}_{q} \right|^{2}$ (4.39)

Since for the ferromagnet, v(0) > v(q) for all $q \neq 0$, the instability occurs for the q = 0 mode, when

$$1 - R^2 = kT/v(0)$$
 (4.40)

Elimination of R between (4.6) and (4.40) gives the stability limits in the T-H-plane.

With the help of the table given in section 3, it is an easy matter to translate these results to the case of the lattice gas.

We have sketched some of the results in Fig.3. As will be discussed further, they are incorrect in many details, but they do give the correct qualitative behaviour. In order to understand this qualitative success of the MFA, we note that the MFA actually becomes correct in three limiting cases:



Free energy at H=0 and constant temperature as a function of magnetization



Spontaneous magnetization as a function of temperature.



Reciprocal susceptibility at $H \approx 0$ as a function of temperature.



н

 $+1 + 1 + 1 < T_c$ $+1 - T > T_c$ H

Magnetization at constant temperature as a function of field.



Specific heat at H=0 as a function of temperature.



1) At high temperatures, as can be seen from the expansion leading from (4.27) to (4.28).

2) At low temperatures, because then all fluctuations freeze out. This argument is not so good for a Heisenberg ferromagnet, since there the fluctuations freeze out much more slowly because of the low frequency spin waves (see Chapter 8). It does not hold at all for a quantum system with non-vanishing zero point fluctuations, e.g., the Heisenberg antiferromagnet.

3) For long range interactions, since then the local field (4.2) is the sum of contributions of many partners, and we expect its fluctuations to go as 1/z, where z = number of partners interacting with a given spin.

The whole treatment is easily generalized to the other cases mentioned in section 3.

5. ORNSTEIN-ZERNIKE THEORY OF FLUCTUATIONS

We have obtained the MFA under the assumption that the fluctuation of the magnetization is small. We can check the internal consistency by actually calculating the fluctuation from the fluctuation theorem which, for the case of the Ising model, we can use in its classical form (2.13).

When we perturb the system by an incremental field h_i , we obtain a coupling term in the Hamiltonian

$$-\sum_{i} \mu_{i} h_{i} = -\sum_{q} \mu_{q} h_{-q}$$
(5.1)

where μ_{d} and h_{d} are the Fourier components defined by

$$\mathbf{a}_{\mathbf{q}} = \frac{1}{\sqrt{N}} \sum_{i} \mathbf{a}_{i} e^{-i\vec{\mathbf{q}}\cdot\vec{\mathbf{R}}_{i}}$$
(5.2)

According to (2.13), we therefore obtain for the mean square fluctuation of the Fourier component μ_{g} of the magnetization,

$$\langle \mu_q^2 \rangle - \langle \mu_q \rangle^2 = kT \cdot \chi_q$$
 (5.3)

where χ_q is the susceptibility for the linear response to the Fourier component h_q . For uniform magnetization,

$$\langle \mu_{g} \rangle = \sqrt{N} R \delta_{g,0}$$
 (5.4)

By expanding (4.19) around the state of uniform magnetization, we obtain for the susceptibility in MFA

$$\chi_{q} = \frac{\beta(1 - R^{2})}{1 - \beta v(q) (1 - R^{2})}$$
(5.5)

and therefore,

$$\langle \mu_{q}^{2} \rangle - \langle \mu_{q} \rangle^{2} = \frac{(1 - R^{2})}{1 - \beta v(q)(1 - R^{2})}$$
 (5.6)

This result shows the following: At high temperatures in the paramagnetic phase (R = 0), $\beta v(q) < \beta v(0) \ll 1$, and the fluctuations are of order unity and therefore very small compared to \sqrt{N} . As we approach the Curie temperature $\beta v(0) \rightarrow 1$, and the fluctuations of the small q (long wavelength) components of the magnetization become large. At the Curie

temperature itself, the fluctuation diverges for $q \rightarrow 0$. Below the Curie temperature, on the other hand, the factor $1 - R^2$ removes the divergence and very soon enforces again very small fluctuations.

Thus, the MFA appears to be well justified at high and at low temperatures, but becomes drastically inconsistent in the transition region. This difficulty is not accidental, but is inherent in the problem, as can be seen from the following argument: The mean square fluctuation $\langle \mu_q^2 \rangle - \langle \mu_q \rangle^2$ is the Fourier transform of the correlation function

$$g(R_{ij}) = \langle \mu_i \, \mu_j \rangle - \langle \mu_i \rangle \langle \mu_j \rangle$$
(5.7)

As we approach the Curie temperature, the range of the correlation increases and becomes infinite at T_c , indicating the onset of long range order. But an infinite range of $g(R_{ij})$ causes a divergence of the q = 0 Fourier component. In other words: the onset of long range order requires the divergence of the fluctuation.

We can use (5.6) in order to get a first approximation of the correlation function: For small q,

$$v(q) = v(0) \left[1 - \frac{q^2}{\kappa_0^2} \right]$$
 (5.8)

which gives

$$\left\langle \mu_{q}^{2} \right\rangle - \left\langle \mu_{q} \right\rangle^{2} = \frac{\text{const}}{\kappa^{2} + q^{2}}$$
 (5.9)

where

$$\kappa^{2} = \kappa_{0}^{2} \left[\frac{T}{T_{c} (1 - R^{2})} - 1 \right]$$
 (5.10)

The Fourier transform of (5.9) gives for the asymptotic behaviour of the correlation function

$$g(R_{ij}) = \text{const} \frac{e^{-\kappa |R_{ij}|}}{|R_{ij}|}$$
(5.11)

which shows that κ^{-1} is the <u>correlation range</u>. Close to T_c, we obtain

$$\kappa^{-1} \propto \tau^{-\frac{1}{2}}; \qquad \tau = \frac{|\mathbf{T} - \mathbf{T}_c|}{\mathbf{T}_c}$$
 (5.12)

showing clearly the divergence of the correlation range.

6. THE SPHERICAL MODEL [6, 7]:

We insert here a short discussion of the spherical model of Berlin and Kac, mainly because some of our later results will turn out to be identical to those of the spherical model. In the spherical model, the

value of the spin μ_i at a given lattice point i is not restricted to the values ± 1 , but can take on any value between $-\sqrt{N}$ and $+\sqrt{N}$ such that

$$\sum_{i} \mu_{i}^{2} = N \tag{6.1}$$

If one interprets the state $\{\mu_1 \dots \mu_N\}$ as a point in N-dimensional space, (6.1) permits all states corresponding to points on the surface of the N-dimensional sphere, whereas the Ising model permits only states corresponding to the corners of the N-dimensional cube. We assume the same Hamiltonian as in (4.1), but take the magnetic field to be zero:

$$\mathscr{H} = -\frac{1}{2} \sum_{ij} \mathbf{v}_{ij} \boldsymbol{\mu}_i \boldsymbol{\mu}_j \qquad (6.2)$$

This model described by (6.1) and (6.2) has the merit to be rigorously solvable: The partition function can be written

$$Z = \int d\mu_1 \dots \int d\mu_N \, \delta \left(\sum_i \mu_i^2 - N \right) \exp \left(\frac{\beta}{2} \sum_{ij} v_{ij} \mu_i \mu_j \right) \qquad (6.3)$$

Use the integral representation of the δ -function

$$\delta(\mathbf{x}) = \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{s\mathbf{x}} ds$$

make the quadratic form in the exponent positive definite with the aid of (6.1), and perform an orthogonal transformation of the μ_i to their Fourier transforms μ_q in order to diagonalize the quadratic form. Then, the N-fold integral factorizes into a product of N identical single integrals, which are easily evaluated. Performing the remaining integral over s by a saddle-point integration yields the partition function and therefore the free energy, which in turn determines internal energy and specific heat. In order to obtain the susceptibility in the paramagnetic phase, one uses the fluctuation theorem (5.3) with $\langle \mu_q \rangle = 0$ and evaluates $\langle \mu_q^2 \rangle$ by an analogous method as described above. The result is remarkably simple: The susceptibility is

$$\chi_{q} = \frac{1}{1 - \beta[v(q) - \lambda]}$$
(6.4)

it differs from the MFA result only by the appearance of the saddle point parameter λ . This parameter acts as a sort of chemical potential to guarantee the saddle point condition which takes the form of the sum rule

$$\frac{1}{\beta N} \sum_{\mathbf{q}} \mathbf{X}_{\mathbf{q}} \equiv \frac{1}{N} \sum_{\mathbf{q}} \langle \mu_{\mathbf{q}}^2 \rangle = 1$$
(6.5)

The three-dimensional spherical model has a phase transition with a Curie temperature which is somewhat lower than the MFA result (4.32); the two- and one-dimensional spherical models show no phase transition. In the paramagnetic phase, the spherical model turns out to be a much better approximation to the Ising model than the MFA.

Below the phase transition, on the other hand, the spherical model behaves very differently from the Ising model: The specific heat, for example, becomes a constant independent of temperature. This is easily traced to the occurrence of a large fluctuation of the q = 0 Fourier component of the magnetization in the ordered phase which is possible on account of (6.1).

One can try to remedy this deficiency by considering a modified spherical model in which this large fluctuation of the order parameter is avoided: For a given value of the magnetization R, write

$$\mu_i = R + \nu_i \tag{6.6}$$

Assuming negligible fluctuations in the magnetization requires

$$\sum_{i} \nu_{i}^{2} = N(1 - R^{2})$$
 (6.7)

and

$$\mathscr{H} = -\frac{1}{2} \operatorname{N} v(0) \operatorname{R}^{2} - \frac{1}{2} \sum_{i,j} v_{ij} \nu_{i} \nu_{j}$$
(6.8)

We are thus led to consider a spherical model with the ν_i as variables, and (6.8) as the sphericalization condition. The susceptibility in this "modified spherical model" of Brout becomes

$$x_{q} = \frac{1 - R^{2}}{1 - \beta(v_{q} - \lambda)(1 - R^{2})}$$
(6.10)

it differs from the MFA result (5.6) again only by the appearance of a "chemical potential" λ which is determined by

$$\frac{1}{\beta N} \sum_{\mathbf{q}} \chi_{\mathbf{q}} \equiv \frac{1}{N} \sum_{\mathbf{q}} \langle \nu_{\mathbf{q}} \rangle^2 = 1 - \mathbb{R}^2$$
(6.11)

The magnetization R is determined self-consistently by minimizing the free energy with respect to R. The result

$$R = \tanh \left[\beta(v(0) - \lambda)R + H\right]$$
(6.12)

is again the generalization of the MFA formula (4.6).

This modified spherical model has indeed eliminated the large unphysical fluctuations of the magnetization. Unfortunately, it is still not acceptable as a meaningful approximation to the Ising model in the transition region, because in this region it gives an increase of magnetization with increasing temperature (i.e. a first order phase transition somewhat above T_c) and an associated phase transition at finite fields.

This same sphericalization method can, with only slight generalizations, also be applied to the classical Heisenberg magnet (3.23).

7. THE ONSAGER REFINEMENT OF THE MFA [8-11]:

We have seen that the principal failure of the MFA lies in the neglect of correlation. For the particular case of dipolar interaction of classical dipoles, there exists a prescription due to Onsager to modify the molecular field in such a manner that the most important correlations are taken into account. We shall briefly review Onsager's argument, and then turn to a discussion of its generalization to other types of interaction, in particular to the Ising model, and of the justification for the procedure.



FIG.4. a) A dipole oriented by the local Lorentz field \vec{E}^L ; b) Fluctuating dipole carrying a polarization cloud; c) The reaction field \vec{E}^r , parallel to the instantaneous direction of the dipole.

In the case of interacting dipoles, the neglect of correlations leads to a catastrophe: MFA (which is then called Lorentz field theory) predicts a ferroelectric transition of polar liquids with a Curie temperature far above the melting points. In 1936, Onsager [8] pointed out the physical origin of this failure, the principal point being as follows: In MFA, a given dipole is considered to be oriented by the local Lorentz field \vec{E}^L which is the sum of the external field and the <u>average</u> field due to interaction with all other dipoles (Fig. 4a). However, as the dipole fluctuates, it carries a polarization cloud with it (Fig. 4b). The field due to interaction with this polarization cloud - the <u>reaction</u> field \vec{E}^T - is always parallel to the instantaneous direction of the dipole, and has, therefore, no orienting effect on that dipole. Thus, MFA overestimates the orienting field by an amount equal to the average reaction field. The correct orienting field on a given dipole is the cavity field \vec{E}^c

$$\vec{\mathbf{E}}^{\mathbf{c}} = \vec{\mathbf{E}}^{\mathbf{L}} - \langle \vec{\mathbf{E}}^{\mathbf{r}} \rangle \tag{7.1}$$

it is independent of its instantaneous direction, and can be considered as the molecular field at the site of the given dipole, when this dipole is removed from the system (Fig. 40).

The average dipole moment is, in the spirit of effective molecular field theory, given by

$$\langle \vec{p} \rangle = p \mathscr{L} (p E^{c} / kT) \approx p^{2} E^{c} / 3kT$$
 (7.2)

where \mathscr{L} is the Langevin function, and p the dipole moment. For small fields, one obtains the polarizability and hence the dielectric constant ϵ . Onsager uses linear electrostatic theory in continuum approximation to express $\vec{E}^{\,\mathrm{r}}$ and $\vec{E}^{\,\mathrm{c}}$ in terms of ϵ , and thus arrives at a self-consistent equation for ϵ , the solution of which — in contrast to MFA — is found to agree well with the experiment. We wish to emphasize that this good agreement is somewhat surprising at first sight, since one might expect that $\vec{E}^{\,\mathrm{r}}$ and $\vec{E}^{\,\mathrm{c}}$ were strongly influenced by dielectric non-linearities due to local saturation, which have not been taken into account.

Together with R. Brout, the author has extended the Onsager method to other many-particle systems, in particular to the Ising model, and has analysed its physical and formal contents. Our principal finding is:

The Onsager prescription of subtracting the reaction field is the necessary modification of MFA in order to guarantee the fluctuation theorem (2.13), i.e., to remove the inconsistency discussed in chapter 5.

Applying the Onsager concept to the Ising model, we have to determine which part of the instantaneous local field (4.2) changes sign with μ_i , and which part is independent of μ_i . We have

$$H_{i}^{\text{local}}(\mu_{i}=\pm 1) = \sum_{j} v_{ij} \langle \mu_{j} \rangle_{i\uparrow,\downarrow} + H_{i}^{\text{ext}}$$
(7.3)

and obtain for reaction field and cavity field,

$$\mathbf{H}_{i}^{t} = \frac{\mu_{i}}{2} \sum_{j} \mathbf{v}_{ij} \left[\langle \mu_{j} \rangle_{i\uparrow} - \langle \mu_{j} \rangle_{i\downarrow} \right]$$
(7.4)

$$H_{i}^{c} = \frac{1}{2} \sum_{j} v_{ij} \left[\left\langle \mu_{j} \right\rangle_{i\uparrow} + \left\langle \mu_{j} \right\rangle_{i\downarrow} \right] + H_{i}^{ext}$$
(7.5)

Here $\langle \mu_j \rangle_{if,\downarrow}$ is the conditional average of μ_j if μ_i is up or down, respectively.

Following Onsager, we now calculate $\langle \mu_j \rangle_{i\uparrow,\downarrow}$ by using linear response theory. We allow for arbitrary external fields, i.e. for arbitrary unconditional averages $\langle \mu_j \rangle$. We then add a field h_i at lattice site i and obtain in terms of the susceptibilities χ_{ii}

$$\langle \mu_{j} \rangle' - \langle \mu_{j} \rangle = \chi_{ji} h_{i}$$
 (7.6)

where primed quantities are taken at the value h_i , unprimed ones at $h_i = 0$. The field h_i is eliminated by using the same equation for j = i:

$$\langle \mu_{j} \rangle' - \langle \mu_{j} \rangle = \frac{\chi_{ji}}{\chi_{ii}} (\langle \mu_{i} \rangle' - \langle \mu_{i} \rangle)$$
 (7.7)

This equation, which is evidently correct for small h_i , is now used to calculate $\langle \mu_i \rangle_{i\uparrow,\downarrow}$ as the limit $\langle \mu_i \rangle' \rightarrow \pm 1$ (Fig.5).



FIG.5. Calculation of $\langle \mu_j \rangle_{i\uparrow,\downarrow}$ when $\langle \mu_i \rangle^* \rightarrow \pm 1$.

This procedure certainly appears dubious at first sight, since $\langle \mu_i \rangle' \rightarrow \pm 1$ requires $h_i \rightarrow \pm \infty$. In other words, local saturation effects are expected to play an important role. The surprising result is, however, that although Eq.(7.6) becomes invalid for high fields, Eq.(7.7) is actually an exact result. This is a consequence of the fluctuation theorem

$$\chi_{ii} = \beta[\langle \mu_i \mu_i \rangle - \langle \mu_i \rangle \langle \mu_i \rangle]$$
(7.8)

and can be seen as follows: By definition of the conditional averages, one has

$$\mathbf{p}_{i\uparrow} \langle \boldsymbol{\mu}_{j} \rangle_{i\uparrow} + \mathbf{p}_{i\downarrow} \langle \boldsymbol{\mu}_{j} \rangle_{i\downarrow} = \langle \boldsymbol{\mu}_{j} \rangle$$
(7.9)

$$\mathbf{p}_{i\uparrow} \langle \boldsymbol{\mu}_{j} \rangle_{i\uparrow} - \mathbf{p}_{i\downarrow} \langle \boldsymbol{\mu}_{j} \rangle_{i\downarrow} = \langle \boldsymbol{\mu}_{i} \boldsymbol{\mu}_{j} \rangle$$
(7.10)

where $p_{i\uparrow,\downarrow} = \frac{1}{2}(1 \pm \langle \mu_i \rangle)$ is the probability of finding $\mu_i = \pm 1$, respectively. One thus obtains with the help of (7.8)

$$\langle \mu_{j} \rangle_{i\uparrow,\downarrow} - \langle \mu_{j} \rangle = \frac{\langle \mu_{i}\mu_{j} \rangle - \langle \mu_{i} \rangle \langle \mu_{j} \rangle}{\pm 1 + \langle \mu_{i} \rangle}$$

$$= \frac{\chi_{ii}}{\chi_{ii}} (\pm 1 - \langle \mu_{i} \rangle)$$

$$(7.11)$$

This proves that Eq. (7.7) is indeed correct in the limit of complete saturation of spin i, which is all that is needed for the calculation of H_i^r and H_i^c (7.4, 5). But Eq. (7.7) is actually correct for all h_i : since

the H_i^{ext} are completely arbitrary, Eq. (7.11) holds not only for $h_i = 0$, but for any value of h_i :

$$\frac{\chi_{ji}(\mathbf{h}_{i})}{\chi_{ii}(\mathbf{h}_{i})} \equiv \frac{\partial \langle \mu_{j} \rangle'}{\partial \langle \mu_{i} \rangle'} = \frac{\langle \mu_{j} \rangle_{i\uparrow} - \langle \mu_{j} \rangle'}{1 - \langle \mu_{i} \rangle'}$$
(7.12)

This differential equation for $\langle \mu_j \rangle'$ as a function of $\langle \mu_i \rangle'$ has the solution

$$\frac{\langle \mu_{j} \rangle_{i\uparrow} - \langle \mu_{j} \rangle'}{1 - \langle \mu_{i} \rangle'} = \frac{\langle \mu_{j} \rangle_{i\uparrow} - \langle \mu_{j} \rangle}{1 - \langle \mu_{i} \rangle}$$
(7.13)

By again using Eq. (7.11), we obtain (7.7).

From (7.5) and (7.12), we obtain

$$H_{i}^{c} = \sum_{j} v_{ij} \langle \mu_{j} \rangle - \frac{1}{\beta} \frac{\langle \mu_{i} \rangle}{1 - \langle \mu_{i} \rangle^{2}} \sum_{j} v_{ij} \chi_{ji} + H_{i}^{ext}$$
(7.14)

It is this cavity field which is considered as the effective orienting field in the Onsager theory. Therefore,

$$\langle \mu_i \rangle = \tanh \beta \ H_i^c$$
 (7.15)

Since $\chi_{ij} = \partial \langle \mu_i \rangle / \partial H_j^{ext}$, Eqs (7.14) and (7.15) represent a system of N simultaneous first-order differential equations for the functions $\langle \mu_i \rangle = f_i(H_1^{ext}, \ldots, H_N^{ext})$.

In the paramagnetic phase for infinitesimal external fields, we can linearize Eqs (7.14) and (7.15) and obtain

$$\langle \mu_i \rangle = \beta \left\{ \sum_j \mathbf{v}_{ij} \langle \mu_j \rangle - \lambda \langle \mu_i \rangle + \mathbf{H}_i^{\text{ext}} \right\}$$
 (7.16)

or, after taking the Fourier transform,

$$X(\mathbf{q}) = \frac{\langle \mu_{\mathbf{q}} \rangle}{H_{\mathbf{q}}^{\text{ext}}} = \frac{\beta}{1 - \beta [v(\mathbf{q}) - \lambda]}$$
(7.17)

Here,

$$\lambda = \frac{1}{\beta} \sum_{j} \mathbf{v}_{ij} \chi_{ji} = \frac{1}{\beta \mathbf{N}} \sum_{\mathbf{q}} \mathbf{v}(\mathbf{q}) \chi(\mathbf{q})$$

which can be written

$$\frac{1}{\beta_{\rm N}} \sum \chi_{\rm q} = 1 \tag{7.18}$$

We thus find the surprising fact that in the paramagnetic phase the results of the Onsager method are identical to those of the spherical model, Eqs (6.4) and (6.5).

For arbitrary magnetization R, Eqs (7.14) and (7.15) can be somewhat simplified if they are converted into equations for the orienting field $H_i^{cavity} \equiv \xi_i$ by substituting

$$\langle \mu_i \rangle = \tanh \beta \xi_i$$
 (7.19)

One then obtains

$$\boldsymbol{\xi}_{i} = \sum_{j} \mathbf{v}_{ij} \tanh \beta \boldsymbol{\xi}_{j} - \left(\sum_{j} \mathbf{v}_{ij} \boldsymbol{\xi}_{i,j}\right) \tanh \beta \boldsymbol{\xi}_{i} + \mathbf{H}_{i}^{\text{ext}}$$
(7.20)

where we have used the notation

$$\xi_{i,j} = \frac{\partial \xi_i}{\partial \mathbf{H}_j^{\text{ext}}} = \frac{\chi_{ij}}{\beta(1 - \langle \mu_i \rangle^2)}$$
(7.21)

Eqs (7.20) cannot be solved exactly. Therefore we introduce a scheme of successive approximations which may yield physically sensible results after a few iterations. We set

$$H_{i}^{ext} = H + h_{i}$$
(7.22)

and expand around (7.20) the uniformly magnetized state:

$$\xi_i = \frac{1}{\beta} \operatorname{artanh} R + \sum_j \xi_{i,j}^0 h_j + \frac{1}{2} \sum_{ik} \xi_{i,jk}^0 h_j h_k + \dots \qquad (7.23)$$

Equating terms of equal order in the h_i , we obtain a hierarchy of equations for the derivatives of the ξ_i , where the n'th derivative is expressed in terms of all derivatives up to order n+1. We can close this system by neglecting the derivatives of some order n_0 , and thus obtain a hierarchy of approximations.

The leading approximation, in which already the first derivatives $\xi_{i,j}$ are neglected, is the Weiss theory (4.6). In the next approximation, neglecting the second derivatives $\xi_{i,jk}$, one recovers the modified spherical model (Eqs (6.10), (6.11), and (6.12)). We note here that it actually

makes more sense to neglect the field dependence of $\xi_{i,j} = \frac{\chi_{ij}}{\beta(1 - \langle \mu_i \rangle^2)}$ than that of χ_{ij} alone.

As mentioned at the end of chapter 6, this approximation is inadequate. One might expect that a fruitful line of attack is to proceed with one more step of the iteration also including the $\xi_{i,jk}$.

We have thus constructed a molecular field theory which takes the correlations of the magnetization into account. It does not suffer the inconsistency described in chapter 5: The fluctuation theorem has been imposed on the theory and hence is satisfied by the theory. We would, therefore, expect it to be a much better approximation than the usual MFA. This is actually the case: The Curie temperature is within a few percent of the exact value (obtained by numerical methods):

$kT_c/v(0)$ for	s.c.	b.c.c.	f.c.c.
Spherical model:	0.66	0.72	0.74
Exact result:	0.75	0.79	0.81

The nature of the singularities at the phase transition is, however, still different from the exact result:

Spherical model:	$\chi \propto \tau^{-2}$;	$c_H \propto - \tau + const$
Exact result:	$\chi \propto \tau^{-5/4};$	$c_{\rm H} \propto \log \frac{\rm const}{ \tau }$

Further, in two dimensions the spherical model does not have a phase transition at all, whereas the two-dimensional Ising model is the famous exactly solvable model with a phase transition.

In conclusion, we remark that the Onsager method rests on the form (4.2) for $H_i^{local}(\mu_i)$ which is an approximation to the exact expression

$$\mu_{i} H_{i}^{\text{mol}}(\mu_{i}) = kT \log tr' e^{-\beta \mathscr{H}}$$

where tr' means the trace over all spins except μ_i . Further improvement would require an analysis of the nature of this approximation.

8. THE RANDOM PHASE APPROXIMATION [12-17]:

At high temperatures, we expect little difference between the Ising magnet and Heisenberg magnets with less anisotropic interactions. At low temperatures, on the other hand, the magnetization of the Ising magnet approaches saturation much more rapidly than that of the isotropic Heisenberg ferromagnet. The reason for this difference is easy to understand: In the Ising magnet, the lowest excitation consists in turning one spin which costs the finite energy 2v(0), and the number n of reversed spins will be proportional to $exp[-2\beta v(0)]$. Therefore,

R = 1 - 2
$$\frac{n}{N}$$
 = 1 - const $\cdot e^{-2\beta v(0)}$ (8.1)

In the isotropic Heisenberg ferromagnet, on the other hand, there exist transverse excitations of arbitrarily low energies, the long wavelength spin waves, in which the spin direction changes very gradually from one lattice site to the next. Since each spinwave corresponds to one reversed spin, the magnetization will become

$$R = 1 - \frac{2}{N} \sum_{q} \langle n_{q} \rangle = 1 - \frac{2}{N} \sum_{q} \frac{1}{e^{\beta \hbar \omega_{q}}}$$
(8.2)

where $\langle n_q \rangle$ is the average number of spinwave excitations of wave number q, and ω_q their frequency. Since for small q, $\omega_q \propto q^2$, we obtain in three dimensions

R = 1 - const.
$$\int_{0}^{q_{max}} \frac{q^2 dq}{e^{\beta \alpha q^2} - 1} = 1 - const. T^{3/2}$$
(8.3)

The MFA gives the Ising result (8.1). We can interpret its failure for the isotropic Heisenberg magnet again by the same argument as in chapter 5: In order for the MFA to be valid, the fluctuations of the magnetization have to be small. But in the isotropic Heisenberg magnet, in addition to longitudinal fluctuations which are small except in the transition region, there exist transverse fluctuations of the magnetization due to long wavelength spin waves, which are frozen out only very slowly.

Actually, in the two-dimensional case, they cannot be frozen out at any finite temperature: The two-dimensional Heisenberg magnet has no phase transition.

The random phase approximation (RPA) is a method taking the spin wave excitations into account. We shall discuss a method due to Englert which proceeds in the following manner: One calculates the linear response to a small transverse field \vec{h} of frequency ω ; the fluctuation-dissipation theorem then gives the transverse fluctuation of the magnetization. The magnetization is finally determined by a sum rule.

Let us then find the linear response of the isotropic Heisenberg magnet with magnetization along z (constant external field $\vec{H} = \{0, 0, H\}$) to a small transverse field $\{h_i^x(t); h_i^y(t); 0\}$, from the equations of motion for the spin operators $\vec{\sigma}_i$,

$$\dot{\vec{\sigma}}_i = \frac{1}{i\hbar} [\vec{\sigma}_i, \mathcal{H}]$$
 (8.4)

By using the well-known commutation relations for the spin operators, one obtains

$$\dot{\sigma}_{i}^{x} = +\frac{2}{\hbar} \left\{ \sum_{j} \mathbf{v}_{ij} \left(\sigma_{i}^{y} \sigma_{j}^{z} - \sigma_{j}^{y} \sigma_{i}^{z} \right) + \mathbf{H} \sigma_{i}^{y} - \sigma_{i}^{z} \mathbf{h}_{i}^{y} \right\}$$

$$\dot{\sigma}_{i}^{y} = -\frac{2}{\hbar} \left\{ \sum_{i} \mathbf{v}_{ij} \left(\sigma_{i}^{x} \sigma_{j}^{z} - \sigma_{j}^{x} \sigma_{i}^{z} \right) + \mathbf{H} \sigma_{i}^{x} - \sigma_{i}^{z} \mathbf{h}_{i}^{x} \right\}$$

$$(8.5)$$

It is the essence of the RPA to <u>linearize</u> the equations of motion around the equilibrium state, which is equivalent to <u>decoupling</u> the different spin wave modes. This amounts to replacing all σ_j^2 in Eq.(8.5) by their equilibrium values $\langle \sigma_i^z \rangle = R$. Then, by taking Fourier transforms,

$$\hbar \sigma_{q}^{x} = 2 \{ R[v(0) - v(q)] + H \} \sigma_{q}^{y} - 2R h_{q}^{y}$$

$$\hbar \sigma_{q}^{y} = -2 \{ R[v(0) - v(q)] + H \} \sigma_{q}^{x} - 2R h_{q}^{x}$$
(8.6)

We thus obtain for the response

$$\sigma_q^{\pm} = \sigma_q^{x} + i\sigma_q^{y}$$
(8.7)

to a circularly polarized transverse field of frequency ω ,

$$\vec{h}_{q} = \frac{1}{2} h_{q}^{\pm} e^{-i\omega t} \{1; \mp i; 0\}$$
 (8.8)

the transverse susceptibility

$$\chi_{q}^{\pm} = \frac{2R}{\hbar(\omega_{q} \mp \omega)}$$
(8.9)

where ω_q is the frequency of the spinwave with wave number q,

$$\hbar\omega_{\rm q} = 2R[v(0) - v(q)] + 2H \qquad (8.10)$$

The results (8.9) and (8.10) show two things: in RPA, the exchange part of the spin wave frequency is normalized with the magnetization, and the "weight" of the spin wave excitation is also normalized with magnetization. Very recent work seems to show that only the latter result is rigorous; the spin wave frequencies, which become complex in higher approximation, seem to stay finite at the Curie temperature.

In RPA, the imaginary part of the susceptibility is just a δ -function at $\omega=\pm\,\omega_{\,\alpha}$:

$$\operatorname{Im} \chi_{\mathbf{q}}^{\pm} = \pm \frac{2\pi}{\hbar} \operatorname{R} \delta(\omega \pm \omega_{\mathbf{q}})$$
(8.11)

In order to calculate the fluctuation of the magnetization, we have to use a slightly generalized form of the fluctuation-dissipation theorem (2.10). The interaction term with the field h is

$$\mathscr{H}_{int} = -\sum_{i} \vec{h}_{i} \cdot \vec{\sigma}_{i} = -\frac{1}{2} \sum_{q} (h_{q}^{+} \sigma_{q}^{-} + h_{q}^{-} \sigma_{q}^{+})$$
(8.12)

For this case, the fluctuation theorem takes the form

$$\langle \sigma_{q}^{+} \sigma_{-q}^{-} + \sigma_{q}^{-} \sigma_{-q}^{+} \rangle \equiv 2 \langle \sigma_{q}^{x} \sigma_{-q}^{x} + \sigma_{q}^{y} \sigma_{-q}^{y} \rangle$$
$$= 2 \frac{\hbar}{2\pi} \int_{-\infty}^{+\infty} \operatorname{Im} \left[\chi_{q}^{+} (\omega) + \chi_{q}^{-} (\omega) \right] \operatorname{coth} \frac{\beta \hbar \omega}{2} d\omega \qquad (8.13)$$

With Eq. (8.11) we thus obtain for the transverse fluctuation of the magnetization

$$\langle |\sigma_{\mathbf{q}}^{\mathbf{x}}|^{2} \rangle = \langle |\sigma_{\mathbf{q}}^{\mathbf{y}}|^{2} \rangle = \mathrm{R} \operatorname{coth} \frac{\beta \hbar \omega_{\mathbf{q}}}{2}$$
 (8.14)
where we have made use of the symmetry with respect to rotations around the z-axis. Since $\omega_q \propto q^2$ for H = 0, we recognize how very slowly the small q fluctuations are frozen out.

The magnetization is determined from the sum rule

$$(\sigma_{i}^{x})^{2} = \frac{1}{N} \sum_{q} |\sigma_{q}^{x}|^{2} = 1$$
 (8.15)

which gives

$$\frac{R}{N}\sum_{q} \coth \frac{\beta \hbar \omega_{q}}{2} = 1$$
(8.16)

or

$$R = \frac{1}{1 + \frac{2}{N} \sum_{q} \frac{1}{e^{\beta \hbar \omega_{q}} - 1}} = 1 - \frac{2}{N} \sum_{q} \frac{R}{e^{\beta \hbar \omega_{q}} - 1}$$
(8.17)

Since ω_q given by (8.10) depends on the magnetization, this is a self-consistency equation to determine R.

At low temperatures, $R \approx 1$, and we recover conventional spin wave theory. At somewhat higher temperatures, we obtain a T^3 correction which is spurious, because we know from Dyson's theory that the lowest correction to spin wave theory is of the order T^4 . However, the Dyson series breaks down at fairly low temperatures because of the "kinematic" spin wave interactions, which are taken approximately into account in RPA. We therefore expect the RPA to be a better approximation at finite temperatures than the Dyson series, in spite of the spurious T^3 -term. In order to obtain the Curie temperature and the susceptibility in the paramagnetic region, we linearize (8.16) with respect to R and H. We find with $\chi = R/H$:

$$\frac{1}{\beta N} \sum_{q} \frac{1}{[v(0) - v(q)] - \frac{1}{\chi}} = 1$$
(8.18)

which to our great surprise is again the spherical-model result (6.4) and (6.5) for q = 0. This can best be seen by solving Eq.(6.4) for λ , taking q = 0, and substituting this value into Eq.(6.5). Thus, we obtain the same Curie point and the same paramagnetic susceptibility as in the spherical model, and we have already seen that this is an acceptable approximation, except very close to T_c . From (8.16), we obtain for the magnetization immediately below T_c ,

$$R \propto \tau^{1/2} \tag{8.19}$$

Formula (8.14), on the other hand, allows us to calculate the spin wave contribution to the energy, and thus to the specific heat. Close to T_c , we

now obtain a singularity

$$c_{H} \propto \tau^{-1/2}$$
 (8.20)

The exact results are

$$R \propto \tau^{1/3}$$
$$c_{\rm H} \propto \log \frac{1}{|\tau|}$$

For the isotropic Heisenberg ferromagnet, we have thus obtained an approximation which reproduces the Curie point within a few per cent, and which is an acceptable approximation in the whole temperature range with the exception of the immediate vicinity of the transition region. Unfortunately, this satisfactory situation does not extend to the anisotropic Heisenberg magnet; as we reduce the transverse interaction to zero, thus passing from the isotropic Heisenberg magnet to the Ising magnet, the RPA goes over into the MFA, and not into the spherical model.

Let us finally discuss how the RPA goes over into the MFA when the interaction becomes long-range. As the number of partners z interacting with a given spin increases, the Fourier component v(q) of the interaction contains many interfering terms which tend to cancel as soon as $|q|a>1/z^{1/3}$ As a consequence, except in a small volume of order 1/z around the origin, the spin wave frequencies (8.10) become constant:

$$\hbar\omega_{\rm q} = 2[{\rm R}\,{\rm v}(0) + {\rm H}]$$
 (8.21)

With such a spectrum, Eq. (8.16) immediately reduces to the MFA result (4.6).

9. NATURE OF THE PHASE TRANSITION [2, 18]:

With the experience we have gained so far, we shall now try to analyse the physical nature of the phase transition, and to understand the general mechanism of the approximation methods.

If we critically examine the self-consistent field methods (MFA, Onsager method, RPA), we recognize that they must contain a fundamental formal error: the statistical operator we tried to approximate,

$$\rho = \frac{1}{Z} e^{-\vartheta \mathscr{X}}$$
(9.1)

has obviously the full same symmetry of the Hamiltonian \mathscr{H} , and is, therefore, invariant under simultaneous reversal of all spins (in zero external field). But our approximate distributions describe the existence of a spontaneous magnetization below the phase transition, and can, therefore, not be invariant under spin reversal: we have "broken the symmetry" We will now argue that this breaking of symmetry, although formally in error, was the physically correct way to describe the phase transition,

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the principal point being as follows. The exact distribution has zero magnetization, but a macroscopically large fluctuation of the q =0 Fourier component of the magnetization

$$N \langle \mu_0^2 \rangle = \left\langle \left(\sum_i \mu_i \right)^2 \right\rangle \equiv M^2$$
(9.2)

where

$$M = O(N) \tag{9.3}$$

We can think of this distribution as that of an ensemble of macroscopic permanent magnets with magnetic moment $m = \pm M$ with equal probability of pointing up or down. We can suppress these large fluctuations by a magnetic field of order 1/N which does not essentially change the magnetic moment of the dipoles, but which gives rise to an average magnetization

$$\langle m \rangle = M \tanh\beta M H + O(1)$$
 (9.4)

We see that in fact a field H of order $1/{\rm N}$ is sufficient to drive the magnetization to its saturation value M, and at the same time to reduce the fluctuation

$$\langle m^2 \rangle - \langle m \rangle^2 = M^2 (1 - tanh^2 \beta M H) + O(1)$$
 (9.5)

to very small values. We have thus condensed the macroscopic fluctuation of the magnetization into a macroscopic average magnetization by an external field which vanishes in the limit $N \rightarrow \infty$. (For small particles, these macroscopic fluctuations have a very real physical significance, giving rise to the phenomenon of superparamagnetism.)

In the self-consistent field theories, we use the device of the molecular field to condense the macroscopic fluctuation into a non-vanishing order parameter.

This procedure can only be correct for an infinite system. In fact, the partition function of a finite system is the sum of a finite number 2^N of analytic functions of temperature and can, therefore, not have any singularities: the singular behaviour at the phase transition appears only asymptotically as $N \rightarrow \infty$.

The self-consistent field breaks the symmetry of the system. Of course, symmetry can never get lost: whenever a symmetry is broken, a <u>degeneracy</u> must occur which restores the symmetry. This principle of conservation of global symmetry is naturally obeyed by the self-consistent field theories: instead of one state with $\langle m \rangle = 0$ and the full symmetry, we find two degenerate states with $\langle m \rangle = \pm M$, each with broken symmetry, which are transformed into each other by the symmetry operation (spin reversal) which has been broken.

Actually, we see from the above discussion that the degeneracy is larger. For any value of $\langle m \rangle$ between + and - M, there is a probability distribution with the same free energy (in the limit of $N \rightarrow \infty$). We thus discover another formal error of the self-consistent field theories: instead of the two minima of the free energy at $\pm M$ we found in Chapter 4,

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the free energy in zero field ought to be constant between + and - M, thus permitting any value of the order parameter between these limits. As a consequence, the stability limits of the two phases seem to lose their significance. The degeneracy formally removes any hysteresis in going from the + M to the - M state.

We would again argue that the approximate methods, although formally in error, are physically correct; although the system finds a continuous set of degenerate states to go from +M to -M as the field changes sign, it would require an infinite relaxation time for this process. Thus, in an actual physical experiment, we will find a hysteresis which is approximately described by the self-consistent field theories, in spite of the continuous degeneracy of states at H = 0. A deeper understanding of this point would require a discussion of the difficult problem of the dynamics of state changes, which is beyond the scope of this lecture.

We believe that the concepts discussed so far:

- breaking of the symmetry by the self-consistent field;
- condensation of a macroscopic fluctuation into a non-vanishing order parameter;
- degeneracy below the phase transition

although obtained from an analysis of very simple models, represent the correct physical scheme of any phase transition with an order parameter going continuously to zero as $T \rightarrow T_c$. If one adds to these concepts certain analyticity assumptions about the free energy as function of the order parameter (essentially the existence of a Taylor series in the order parameter with finite radius of convergence at all temperatures, including T_c), one obtains the Landau theory of second order phase transitions. This theory leads to the same critical behaviour as the MFA:

$$R \propto \tau^{1/2}; \quad \chi \propto \tau^{-1}$$
 (9.6)

which is in disagreement with the exact results. One has, therefore, to conclude that the analyticity assumptions, however plausible they may appear, become invalid in the critical region.

We finally discuss one other highly interesting feature of phase transitions which is an application of Goldstone's theorem to solid state physics: There exists evidence that the breaking of symmetry always gives rise to the appearance of a zero frequency normal mode. If the spectrum is continuous (which will be the case except for long-range interactions), there will then exist a spectrum of excitations with arbitrarily small excitation energies.

If we break a continuous group (e.g. the group of three-dimensional rotations of spin space in the case of the isotropic Heisenberg ferromagnet, or the three-dimensional translation group in the case of freezing of a liquid), we have a continuous set of degenerate states at all temperatures below the phase transition. This set can be generated by successive applications of an infinitesimal operator (or a set of such) which carries one state into an adjacent one, or, in other words, which "rotates" the state in the space spanned by the set of degenerate states. This "symmetry-restoring operator" is now interpreted as the creation operator of a zero frequency collective mode (q = 0 spin wave in the Heisenberg ferromagnet, q = 0 sound wave in the crystalline solid). We thus see that in the case of the breaking of a continuous group, we obtain a spectrum

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of elementary excitations which extends down to $\omega = 0$ at all temperatures below the phase transition, and the corresponding response function has a pole at $\omega = 0$. This conclusion is obviously well confirmed by experiment: in both examples, we have a spectrum with $\omega \rightarrow 0$ for $q \rightarrow 0$ at all $T < T_c$:

$$ω_q = αq^2$$
 (isotropic-ferromagnet)
 $ω_q = c |q|$ (crystalline solid) (9.7)

However, application of this principle requires some care. Recently, H. Stern has pointed out that the mode created by the symmetry restoring operator is not necessarily the limit of the simple normal mode spectrum. This problem needs still further clarification.

If a discrete group is broken (e.g. spin reversal symmetry in the case of the uniaxial Heisenberg ferromagnet, or space inversion in the case of a uniaxial ferroelectric), the state of our knowledge is still less satisfactory. One will argue in the following way. At temperatures below T_c , the symmetry restoring operator connects states with a finite "distance" and can, therefore, not be interpreted as a creation operator of an elementary excitation. As we approach the phase transition, however, the order parameter goes continuously to zero, and the degenerate states become arbitrarily close. We would therefore conclude that for $T < T_c$ there exists a spectrum with a finite gap, but that the gap goes to zero as $T \xrightarrow{\rightarrow} T_c$. This conclusion is again in good agreement with the behaviour of known systems. The Cochran theory of displacive ferroelectrics [19] is a classical example which shows exactly the described behaviour. For the uniaxial Heisenberg magnet, we obtain in RPA a spin wave spectrum with a finite gap, which goes to zero as $T \rightarrow T_c$ and stays zero above T_c :

$$\omega_{a} = R(T)[\Delta + \alpha q^{2}]$$
(9.8)

and for the pseudospin model of a ferroelectric, the gap given by RPA is finite both above and below T_c , but goes again to zero as $T \rightarrow T_c$:

$$\omega_{\rm q}^2 = A | T - T_{\rm c} | + Bq^2 \quad (T \to T_{\rm c})$$
(9.9)

But we have to emphasize again that the q = 0 mode of this spectrum is not necessarily identical with the zero frequency excitation created by the symmetry restoring operator. This is immediately evident for the case of the uniaxial ferromagnet. The spin waves are transverse excitations, but the symmetry restoring operator creates a longitudinal excitation. We conjecture that it is the spin diffusion mode

$$\hbar\omega_{\rm q} = iDq^2 \tag{9.10}$$

which is connected to the symmetry breaking. The above result for the **spin** wave spectrum appears fortuitous and may not even be right in higher **approximation**.

PHASE TRANSITIONS

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Abstract

1. Introduction. 2. Thermodynamic theory and the role of symmetry in ferroelectric phase transitions. 2.1. Relation between the paraelectric and ferroelectric point groups. 2.2. Symmetry and the thermodynamic "order" of the transition. 2.3. Landau theory and critical phenomena. 2.4. Relations between anomalous quantities near a λ -transition. 3. Lattice dynamics and ferroelectricity. 4. Order-disorder type hydrogen bonded ferroelectrics. 4.1. Elementary excitations of the isolated protonic system. 4.2. Temperature dependence of the protonic "quasi-spin" frequency spectrum. 4.3. Proton-lattice coupling. 4.4. Cluster approximations. 4.5. Exactly soluble models.

. 1. INTRODUCTION

The purpose of these lectures is to present in a reasonably simple form some basic aspects of recent developments in the theory of ferroelectricity. For obvious reasons the presentation has to be brief, and we shall therefore leave out most of the details and concentrate our attention on the basic concepts.

Ferroelectric phase transitions are - as other phase transitions: gas-liquid transition, freezing, ferromagnetism, super-conductivity, Bose-Einstein condensation - marked by a sudden onset of a new phase when external variables (such as temperature) are continuously varied through a critical region. In the critical region itself there is a loss of stability against fluctuations of a certain type, accompanied by anomalies both in thermodynamic and response functions. The onset of the new phase is characterized by the appearance of an order parameter - the spontaneous polarization - and a reduction of the symmetry of the system [1]. In contrast to the case of the isotropic ferromagnets, it is the symmetry of a discrete group which is broken at a ferroelectric phase transition. In the disordered phase the crystal symmetry is described by a space group G. In the new ordered phase the crystal structure is invariant only under those operations of G, which leave the spontaneous polarization invariant.

The sudden onset of the ordered phase is connected with the fact that the symmetry of the system is a property which can appear or disappear only all at once and not gradually. Even an arbitrarily small displacement of the atoms from their initial positions or an arbitrarily small nonequivalence of the "right" and "wrong" lattice sites in a disordered crystal, result in an abrupt change in the symmetry of the crystal lattice.

Though the appearance of the order parameter below the Curie temperature is a spontaneous process, similar changes can always be induced even above this temperature by an external electric field. This statement is very helpful in deriving all possible ferroelectric states for

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a paraelectric crystal with a given space group and, in addition, makes it easier to understand the mechanism responsible for the phase transition. The external electric field is always coupled to that co-ordinate of the system whose non-vanishing expectation value breaks the symmetry below the Curie temperature. The field produces either an ordering of disordered permanent dipoles in the crystal or shifts some of the atoms from their initial symmetrical positions in a given direction thus inducing an electric polarization. The interaction between the dipoles furthers this ordering since parallel allignment is the state of lowest interaction energy. The effect of the external field is thus enhanced through the internal interaction field. Thermal fluctuations tend to upset this ordering. At a sufficiently low temperature, however, the interaction field prevails and the state remains ordered even when the external field is turned off. At the Curie temperature itself, even an infinitesimal external field extablishes a finite polatization. Hence

$$(dP/dE_{ext})_{Eext} = 0$$

$$T = T_{c}$$

$$(1.1)$$

and the zero-field susceptibility is infinite at the Curie point. The polar structure of ferroelectrics is only a slightly distorted non-polar structure. The polarization can thus be reversed by the application of a sufficiently large external field. In a strong alternating electric field the relation between \vec{P} and \vec{E} is therefore given by a hysteresis loop. The reversibility of the spontaneous polarization is such an important characteristic of ferroelectric crystals that Aizu [2] even defined a ferroelectric as a system which has in some direction two stable states at $\vec{E} = 0$, and is capable of alternating between them by means of an electric field \vec{E} .

Whereas the simple local field theories qualitatively explain the occurrence of an ordered phase (because the self-consistent field equation has - below a certain temperature - a non-trivial solution which breaks the symmetry of the problem), the more exact solution of the problem is rather difficult. There have been, however, two important breakthroughs in this field in the last few years. The first is due to Cochran. He showed that at least in "displacive" ferroelectrics the transition from the nonpolar to the ferroelectric phase is a problem in lattice dynamics and the result of an instability of the crystal lattice with respect to long-wavelength transverse optical vibrations. The second one is due to a group of mathematical physicists (Lieb, Wu, Sutherland, C.N. Yang, C.P. Yang) who found an exact solution for a two-dimensional model of hydrogen-bonded ferroelectrics of the order-disorder type. The introduction of the quasispin formalism and the subsequent exploitation of the analogies with the case of ferromagnetism have as well contributed to our enhanced understanding of this field.

2. THERMODYNAMIC THEORY AND THE ROLE OF SYMMETRY IN FERROELECTRIC PHASE TRANSITIONS

The thermodynamic theory of ferroelectricity attempts to relate all macroscopic equilibrium properties of ferroelectrics to each other and to describe them in terms of a few parameters. One of the most important recent developments in this field is the "scaling law" concept, which predicts relations between the "critical indices" describing singularities in various thermodynamic derivatives and correlation functions. Another breakthrough is the generalization of the Pipard equations which provides thermodynamic relations between anomalous quantities in anisotropic dielectrics near a lambda transition, where the Ehrenfest and Clausius-Clapeyron equations become indeterminate. Connections have been established between the symmetry and the coupling of anomalous quantities. Similarly one can now predict all possible ferroelectric space groups and even the possible domain structure if the space group of the paraelectric state is known as well as all possible paraelectric space groups if the space group of the ferroelectric phase and the kind of transition between the two stable states with different polarization is given.

The fundamental concept on which all thermodynamical theories of ferroelectric phase transitions are based is the idea that the transition can be described by an order parameter, whose appearance at the Curie point breaks the symmetry of the paraelectric phase. This parameter measures the amount of long-range ordering of both permanent and induced dipoles in the ordered phase and is identically equal to the spontaneous polarization in case of ferroelectrics (in antiferroelectrics it is equal to the sub-lattice polarization). It vanishes above the critical point and is non-zero below $T_{\rm C}$. It can approach zero continuously as $T \rightarrow T_{\rm C}$ from below or discontinuously in case of first-order transitions. Below $T_{\rm C}$, the order parameter may — in the absence of an external electrical field — assume two or more different values under otherwise identical conditions, i.e., the crystal breaks up into domains.

2.1. Relation between the paraelectric and the ferroelectric point groups

Let the space group of the disordered - paraelectric - phase of the crystal be G. This group contains some symmetry elements which require a zero value for the order parameter. In the ordered ferroelectric phase the crystal structure is invariant only under those operations of G which leave the order parameter unchanged. The first question is whether there is a more stringent relation between G and H and whether any predictions about the possible number of domains can be made.

A simple and physically very clear approach to this problem is the use of the "Curie principle", which has been recently suggested by Janovec [3, 4]. This principle allows the space group of the ferroelectric state H to be determined when both G and the direction of the spontaneous polarization are specified. In addition, it enables us to determine the possible directions of the spontaneous polarization, i.e., the number of possible domains. It is based on the fact that though the appearance of the ordered parameter is a spontaneous change similar changes can always be induced by an external electric field: The change of G to H is the same as the symmetry change under the influence of an external electric field \vec{E} provided that \vec{E} is applied in the direction of \vec{P} . The symmetry of \vec{E} , which is a polar vector (as \vec{P}) is that of the continuous group ∞ mm. The principle can be formulated by saying that H contains all symmetry elements common to G and \vec{E} . By varying the direction of $ec{\mathbf{E}}$ with respect to the symmetry elements of G we can thus find all possible ferroelectric space groups H_1 , H_2 ... H_n for a given paraelectric space group G (Table Ia-Table Ie).

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	Initial state									
Direction of \vec{P}_s (or \vec{E})	m3m	43	43m	m3	23					
·	Possible ferroelectric states									
< 100 >	4 mm (6)	4 (6)	mm (6)	mm (6)	2 (6)					
< 111 >	3m (8)	3 (8)	3m (4)	3 (8)	3 (4)					
< 110 >	mm (12)	2 (12)	m (12)	m (12)	h					
< hko >	h	ו	1 (24)	ſ						
< hkk >	m (24)	1 (24)	m (12)]	> 1 (12)					
< hhk >	IJ		· .	} ^{1 (24)}						
< hkl >	1 (48)	IJ	1 (24)	IJ	þ					

TABLE Ia. POSSIBLE FERROELECTRIC STATES AND DIRECTIONS OF \vec{F}_{4} FOR TRANSITIONS FROM CUBIC POINT GROUPS

TABLE ID. POSSIBLE FERROELECTRIC STATES AND DIRECTIONS OF \vec{P}_s FOR TRANSITIONS FROM HEXAGONAL POINT GROUPS [i = -(h + k)]

	Initial state								
Direction of \vec{P}_{e} (or \vec{E})	6/mm	6mm	6/ m	62	6	62m	6		
3		I	Possible ferr	oelectric s	tates				
<0001>	6 mm(2)	6 mm(1)	6(2)	6(2)	6(1)	3m(2)	3(2)		
<1120>] mm(6)) m(6)	m(6)	2(6)	D	2m(3)	h		
<1010>	J	J	}			h	} m(3)		
<hkio></hkio>	h	1(12)	J		1(6)	- m(6)	J		
<hh2h1></hh2h1>	m(12)	m(6)	h	1(12)		ļ			
<hohl></hohl>	J		1(12)			$\left \right\rangle$ 1(12)			
<hkil></hkil>	1(24)	1(12)	þ	נן]]	h	IJ		
			ľ		<u> </u>		ľ		

It should be stressed that all possible space groups are not necessarily realized in nature. Symmetry only allows but does not say what really occurs. Asher recently proposed that the polar space group H which is indeed realized is the maximum polar subgroup of G. This principle works well for most ferroelectrics but is not fulfilled in NaH₃(SeO₃)₂, as well as in some other ferroelectric crystals. Hence it is safer to reformulate the Asher principle by saying that H is the maximum polar subgroup of G for a given direction of \vec{P} . It can be further shown [3] that the number r of possible domains with different directions of the spontaneous polarization for a given ferroelectric group H is equal to the order of the group G divided by the order of the group H:

$$r = [G : H] = \frac{N_G}{N_H}$$
 (2.1)

			Initial state		
Direction of \vec{P}_{e} (or \vec{E})	3m	3	3m	32	3
- 5 ()		Possi	ble ferroelectric	states	·
<0001>	3m(2)	6(2)	3m(1)	3(2)	3(1)
<1120>	2(6)	1	1(6)	2(3)	
<1010>	J		m(3)		
<hkio></hkio>] 1(12)	1(6)	1(6)		
<hh1></hh1>	J			1(6)	
<hohl></hohl>	m(6)		m(3)		
<hkil></hkil>	1(12)	IJ	1(6)]]	
			1	1	1

TABLE IC. POSSIBLE FERROELECTRIC STATES AND DIRECTIONS OF \vec{F}_{x} FOR TRANSITIONS FROM TRIGONAL POINT GROUPS

TABLE Id. POSSIBLE FERROELECTRIC STATES AND DIRECTIONS OF \vec{P}_{\perp} FOR TRANSITIONS FROM TETRAGONAL POINT GROUPS

Directions of	Initial state								
\vec{P}_{s} (or \vec{E})	4/ mm	4mm	4/m	422	4	42m	4		
		Р	ossible ferr	oelectric	states	J	•		
<001>	4mm(2)	4mm(1)	4(2)	4(2)	4(1)	mm(2)	2(2)		
<100>	mm(4)) m(4)	h	2(4)		2(4)	h		
<110>	μ	ע י	- m(4)	ſ		J Č			
<hko></hko>	h	1(8)	J	Ŋ	1(4)] 1(8)	1(4)		
<hol></hol>	} m(8)	m(4)	ו	1(8)		J			
<hli></hli>	μ	IJ	1(8)			m(4)			
<hkl></hkl>	1(16)	1(8)	J	μ	IJ	1(8)	IJ		

where N stands for the number of symmetry elements in a given group. The paraelectric space group of BaTiO₃, for example, is Pm3m which transforms at 120°C into a tetragonal ferroelectric phase with space group P 4 mm, which is of course a subgroup of Pm 3m. $N_G = 48$, $N_H = 8$, and hence r = 6. For an arbitrary direction of \vec{E} , one could find a ferroelectric point group with no symmetry elements except the identity operation. Hence the point group of H would be H = 1 and $N_H = 1$ resulting in r = 48. Not all possible domains, are, however, realized because of compatibility with the minimum-stress requirement. For triglycine sulphate (TGS), the paraelectric point group is G = 2/m. The possible subgroups are $H_1 = 2$, $H_2 = m$, $H_3 = \overline{1}$, $H_4 = 1$. Below T_C , the crystal belongs to the polar group 2 of the monoclinic system and \vec{P} is parallel to the two-fold axis. Hence the point group of H is H = 2 and the lost symmetry elements of G are m and $\overline{1}$:

$$r = \frac{N_G}{N_H} = \frac{4}{2} = 2.$$

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Direction of	Initial state								
\vec{P}_{s} (or \vec{E})	mmm	mm	222	2/m	m	2	ī	1	
			Possil	ole ferroelee	ctric states	5			
<001>	7	mm(1)	h	2(2)	m(1)	2(1)	1	h	
<010>	- mm(2)) m(2)	2(2)	m(2)	1(2)				
<100>		J	J	[]	m(1)				
<hko></hko>	1	1(4)	h	1(4)	1(2)	1(2)	1(2)	1(1)	
<hol></hol>	(m(4)	() m(2)	11	m(2)	m(1)				
<okl></okl>	J	J	1(4)	1(4)	1(2)				
<hkl></hkl>	1(3)	1(4)	J						
					J	·	Ľ	Ľ	

TABLE Ie. POSSIBLE FERROELECTRIC STATES AND DIRECTIONS OF \vec{P}_s FOR TRANSITIONS FROM ORTHORHOMBIC, MONOCLINIC AND TRICLINIC POINT GROUPS*

* The transitions $m \to m$, $2 \to 2$, $3 \to 3$, $6 \to 6$, etc. are not true ferroelectric transitions, since they are connected with a change in the magnitude of \vec{P}_s and not with a change in direction of \vec{P}_s or a lowering of crystal symmetry. They are included in the table because they are possible under the Curie principle.

In agreement with the theoretical prediction there are, indeed, only two different 180°C domains with antiparallel polarization in this crystal.

The lost symmetry elements evidently determine the possible directions of the polarization and hence the domain structure. The complete domain structure would restore the full symmetry of the paraelectric phase (as is this the case in TGS), but all possible domains cannot co-exist in the general case because of stresses.

2.2. Symmetry and the thermodynamic "order" of the transition:

According to Ehrenfest [5], the thermodynamic "order" of a phase transition is determined by the lowest order of the differential coefficient of the Gibbs function:

$$G_1 = U - TS + pV$$
 (2.2)

which shows a discontinuity on the transition line. In a first-order transition, G_1 is continuous across the line, but its derivatives are discontinuous and hence latent heat is released at the transition point(Fig. 1.). In a second-order transition, the first derivatives of G are continuous, but the second derivatives (such as specific heat) are discontinuous. The classification may be extended indefinitely, but since the discontinuities in the physical properties become less and less significant these higher transitions are not of great interest. There are many transitions, which do not conform to this classification, a well known example being the λ - type transitions, where the specific heat rises to infinity as the transition is approached. For all transitions, however, except those of first order, not only G_1 but also the entropy and the volume are continuous across the transition line.



FIG. 1. Classification of transitions Type 1 is a simple first order transition with latent heat. Types 2 show no latent heat but a discontinuity in C_p , which is infinite in 2c and finite in 2 and 2a. Types 3 represent third order transitions, with a discontinuity in $\partial C_p / \partial T$.

Landau [6, 7] distinguishes two types of phase changes in a crystal: a) An abrupt change by a first-order phase transition accompanied by a discontinuous change in the polarization and the lattice parameters.

At the transition temperature, two different phases are in equilibrium with each other, i.e. their free energies are equal. There are no symmetry requirements for a transition of first order to be possible.

b) A more gradual change by a second-order phase transition, where the polarization goes continuously to zero as one approaches the Curie point from below. At the Curie point itself, there is, of course, still a sudden change in the symmetry. At each temperature, only one phase exists so that this is a transition within one phase. The symmetry of the crystal at the transition point must include all symmetry elements of both states. This type of transition is only possible if the following necessary and sufficient symmetry requirements for a homogeneous body are fulfilled:

1) The symmetry group of one state is a subgroup of that of the other state.

2) The change of the crystal corresponds to a single irreducible representation.

3) Third-order terms in the expansions of the free energy (or G_1) in terms of the order parameter must vanish by symmetry.

Let $\rho_0(x, y, z)$ be the "density function" which determines the distribution of different positions of the atoms above the Curie point and is invariant under all operations of the paraelectric space group. If the crystal changes slightly and continuously so that the symmetry is lowered, the new density function $\rho(x, y, z)$ can be written as:

$$\rho = \rho_0 + \delta \rho \tag{2.3}$$

where $\delta\rho(\mathbf{x}, \mathbf{y}, \mathbf{z})$ is the small change in the density function due to the lowering of the symmetry. The symmetry group of ρ (which is the same as of $\delta\rho$) cannot contain symmetry elements not contained in ρ_0 . Hence the group of ρ is a subgroup of the group of ρ_0 .

Let us now expand $\delta \rho$ in terms of functions $\phi_i^{(n)}$ (\vec{r}), which form the bases of the n irreducible representations of the group of ρ_0 :

$$\delta \rho = \sum_{n}^{t} \sum_{i}^{t} C_{i}^{(n)} \phi_{i}^{(n)}$$
 (2.4)

where the identical representation (which represents no change in symmetry) is omitted. The number of functions i for a given representation n is equal to the dimension of the representation. The actual values of the co-efficients $C_i^{(n)}$ are determined thermodynamically by the equilibrium conditions.

Changes corresponding to two different irreducible representations, are independent and represent two different phase transitions. Hence we can omit the summation over n, assuming that we deal with this irreducible representation, which appears for the transition in question, and we get:

$$\rho = \rho_0 + \sum_i C_i \phi_i$$
 (2.5)

In order that the crystal has the symmetry of ρ_0 at the transition point, all quantities $C_i^{(n)}$ must vanish at this point, i.e.

$$\delta \rho |_{T = T_c} = 0$$
, $\rho |_{T = T_c} = \rho_0$ (2.6)

In view of the second-order nature of the transition, the vanishing of $\delta\rho$ must occur in a continuous manner, i.e. the coefficients C_i must vanish taking arbitrarily small values when we approach the transition from below. As a result of this, we can expand the free energy (or some other thermodynamic potential) in powers of C_i in the vicinity of the transition. Substituting

$$C_{i} = \eta \gamma_{i} , \sum_{i} \gamma_{i}^{2} = 1$$
 (2.7)

so that

$$\eta^2 = \sum_i C_i^2 \tag{2.8}$$

we get for the thermodynamic potential:

$$\mathbf{F} = \mathbf{F}_{0} + \mathbf{A}(\mathbf{p}, \mathbf{T})\eta^{2} + \mathbf{B}(\mathbf{p}, \mathbf{T})\eta^{3} \mathbf{f}^{(3)}(\boldsymbol{\gamma}_{i}) + \mathbf{C}(\mathbf{p}, \mathbf{T})\eta^{4} \mathbf{f}^{(4)}(\boldsymbol{\gamma}_{i}) + \dots$$
(2.9)

Here $f^{l}(\gamma)$ is a homogeneous function of order 1 in the coefficients γ_{i} . The operations of the group of ρ_{0} will transform the γ_{1} into each other. Since the thermodynamic potential must be invariant under all coordinate transformations, it must be invariant under the operations of the group

of ρ_0 . Hence the functions $f^{(1)}(\gamma_i)$ must contain only invariant combinations of γ_i . Because first-order invariants exist only for the identity representation, which is not considered, there is no linear term (proportional to $f^{(1)}(\gamma_i) = 0$) in the expansion (2.9). Further, there is only one quadratic invariant for any representation, which can always be reduced to a sum of squares, so that $f^{(2)}(\gamma_i) = 1$.

The stable state of the crystal is found by minimizing F with respect to η and γ_i . From the stability conditions,

$$\frac{\partial F}{\partial \eta} = 0, \qquad \frac{\partial^2 F}{\partial \eta^2} > 0$$
 (2.10)

we find that the state $\eta = 0$ is stable for A > 0, whereas for A < 0 the stable state corresponds to $\eta \ddagger 0$. Thus, the transition from a state of higher to a state of lower symmetry could occur at A = 0. However if the crystal should in fact be stable at A = 0, $\eta = 0$, F must increase both for positive and negative small changes of η . This can happen only (excluding the isolated case that A and B vanish simultaneously) if $f^{(3)}(\gamma_i)$ is identically zero, i.e. if there are no invariants of third order in γ_i , which transform according to the given irreducible representation of the group of ρ_0 .

Even if conditions 1), 2), and 3) are fulfilled the transition will be of first order if C is not positive but C < 0.

Since second-order terms do not contain the γ_i , these are determined by a minimization of the fourth-order term. The quantities γ_i found in this way determine the symmetry of the crystal in the ferroelectric state:

$$\delta \rho = \eta \sum_{i} \gamma_{i} \phi_{i} \qquad (2.11)$$

Landau [6], Haas [7], and Aizu [2] have shown that in the case of the so called "primitive" transitions where the space group of the ferroelectric state is a subgroup of the space group of the paraelectric state with half the number of symmetry elements, a second-order phase transition is always possible. Examples are the phase transitions in TGS, Rochelle salt, $\rm KH_2PO_4$, and others.

In methylammonium aluminium sulphate dodecahydrate, $(NH_3CH_3)Al(SO_4)_2 \cdot 12H_2O$ the number of symmetry elements is not halved. The transition is thus not "primitive" but "complex" and one must investigate in each case whether conditions 2) and 3) are satisfied [condition 1) is automatically fulfilled]. The paraelectric space group is $T^4 - P2_13$ and the ferroelectric $C_2^2 - P2_1$ with the unit cells being the same for both states. The polarization vector transforms as the three-dimensional representation T, and the transition thus corresponds to this representation. The number of independent invariants of order ℓ is equal to the number of times the identical representation A is contained in the symmetrical direct product T of order ℓ . Since $(T \times T \times T)_{symm}$ is A + 3T, third-order terms (like $P_x P_y P_z$) will occur in the expansion of the thermodynamic potential and a second-order transition is not possible. The transition is indeed found to be of first order.

2.3. Landau theory and critical phenomena

Ginzburg [8], Kadanoff [9] and others have recently applied Landau's theory of phase transitions of the second kind to the study of critical phenomena and fluctuations in ferroelectrics. In this theory, the free energy F near the transition point is expanded in a power series of the order parameters. The theory gives a qualitatively correct view of the phase transition, but - as all theories which neglect fluctuations - breaks down very close to the transition point. Confining ourselves, for the sake of simplicity, to a single parameter - the z component of the spontaneous polarization - we write this expansion as applied to unit volume in the form

$$g = g_0(T) + a(T)P_z^2 + b(T)P_z^4 + c(T)(grad P_z)^2 - EP_z$$
 (2.12)

where

and the first term g_0 represents the free energy per unit volume in the absence of spontaneous polarization. The term $c(\text{grad } P_z)^2$ damps out spatial variations in P_z for c > 0 and is, of course, absent in the spatially homogeneous case. For c < 0, the polarization is never uniform. The last term measures the direct interaction between the applied electric field — which may be varying in space — and the polarization of the sample.

For equilibrium the free energy must be stationary under the infinitesimal change

$$P_{z}(\vec{r}) \rightarrow P_{z}(\vec{r}) + \delta P_{z}(\vec{r})$$
(2.13)

i.e. the first-order change in F due to this transformation must vanish for all values of $\delta \, P_z$:

$$\delta F = \int dV \ \delta P_{z} [2aP_{z} + 4bP_{z}^{3} - 2c \ grad^{2}P_{z} - E] = 0$$
 (2.14)

This is possible only if the bracket is zero. The most probable value of P_{z} is thus obtained from

$$[2a + 4bP_z^2 - 2c \text{ grad}^2]P_z = E$$
 (2.15)

The free energy is obtained by solving Eq. (2.15) for P_z and substituting back into (2.12). From all possible solutions of (2.15) one must choose that which actually minimizes the free energy.

In the spatially homogeneous case Eq. (2.15) reduces to

$$[2a + 4bP_z^2]P_z = E$$
 (2.16)

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which has the following solutions in the absence of an applied field:

$$P_z = 0$$
 (2.17a)

$$P_{z} = \pm (-a/2b)^{\frac{1}{2}}$$
 (2.17b)

In case that b is positive, the first solution (2.17a) minimizes the free energy when a >0. The solutions (2.17b), which correspond to a non-zero spontaneous polarization, minimize the free energy when a < 0. In order that there should be a phase transition, the coefficient a must change sign; at the transition point itself this coefficient must vanish. Thus

$$a > 0$$
 , $T > T_C$ (2.18)
 $a < 0$, $T < T_C$

whereas b > 0 for both phases. Landau further assumes that near the transition point one can write

$$a(T) = a' (T - T_c)$$
 (2.19)

where a' = $\partial a/\partial T \Big|_{T=T_c}$, whereas b(T) and c(T) are equal to constants b(T_c) and c(T_c). This choice results in the fact that at the critical point (T = T_c, E = 0) the system can produce non-zero polarization with an increase in free energy which is of fourth order in P_z. Hence large fluctuations can occur at the critical point with little cost in free energy. Before considering this point in some detail, let us look at some other predictions of the Landau theory. From an inspection of Eqs (2.17b) and (2.19) it can be seen that the Landau theory predicts that the polarization in the vicinity of the Curie point vanishes as $(T - T_c)^{\frac{1}{2}}$. The critical index β which describes the vanishing of the order parameter near T_c at E = 0, is thus obtained as $\beta = 1/2$. For E $\frac{1}{2}$ 0, we similarly obtain from Eq. (2.16):

$$P_z = (E/4b)^{1/\delta}$$
 with $\delta = 3$. (2.20)

The susceptibility below the Curie point is obtained as

$$\chi(-) = \frac{1}{4a' |T-T_C|}$$
(2.21)

whereas above the Curie point we have

$$X(+) = \frac{1}{2a'(T-T_{C})}$$
(2.22)

The susceptibility thus in both cases diverges as $|T-T_c|^{\gamma}$ with $\gamma = \gamma' = 1$.

The entropy of the body near the transition point in the ferroelectric phase is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{P} = \int \left[s_{0} - \left(\frac{\partial a}{\partial T}\right)P^{2}\right] dV = \int \left[s_{0} + \frac{a^{12}}{2b}(T - T_{C})\right] dV \quad (2.23)$$

where $s_0 = -(\partial g_0/\partial T)_p$ so that the entropy remains continuous on going through the transition point. The specific heat, $C_p = T(\partial S/\partial T)_p$, on the other hand, is discontinuous:

$$C_{p} = C_{p \neq 0} - C_{p=0} = \frac{a^{12} T_{C}}{2b}$$
 (2.24)

It should be mentioned that if b < 0, the transition would be of first order with a stepwise change in P_s . At the Curie point, the crystal suddenly loses all the energy associated with the polarization and this causes a latent heat:

$$\Delta Q = T_C \Delta S = \frac{1}{2} a' T_C (\Delta P_s)^2 \qquad (2.25)$$

where ΔP_s is the jump in P_s at T_C . In the following, we shall limit ourselves to transition of the second kind.

So far we have characterized the state of the system under consideration with the mean value of the order parameter and have neglected fluctuations around this mean value due to thermal motion. Since the probability of fluctuations w at constant temperature is proportional to

$$w \propto e^{-\Delta F_t/k_B T}$$
(2.26)

where $\Delta F_t = F - \overline{F}$ is the change in the total free energy due to a given fluctuation, and since at T_c even a large change in the order parameter produces only a small change in the free energy, it is clear that fluctuations will become very large in the immediate vicinity of the transition point and will eventually produce a breakdown of the validity of the Landau theory. To calculate the fluctuations, let us expand the deviation

$$\Delta P_z(\vec{r}) = P_z(\vec{r}) - \overline{P_z}$$
(2.27)

into a Fourier series:

$$\Delta P_{z}(\vec{r}) = \sum_{k} P_{k} e^{i\vec{k}\cdot r}$$
(2.28)

where P_k = P_{-k}^{\ast} . For a non-equilibrium state we get with an accuracy to quadratic terms^1

$$\Delta \mathbf{F}_{t} = \int \left[g(\mathbf{\overline{P}}_{z} + \Delta \mathbf{P}_{z}) - g(\mathbf{P}_{z}) \right] d\mathbf{V} = \mathbf{V} \sum_{k} \left(\frac{g_{0}^{\prime\prime}}{2} + ck^{2} \right) \left| \mathbf{P}_{k} \right|^{2}$$
(2.29)

since the linear term vanishes on integrating over the whole volume. Each of the terms in this sum involves only one of the P_k , so that the fluctuations with different wave vectors are statistically independent. Inserting

¹
$$g(\overline{P} + \Delta P) = g(\overline{P}) + (g'')_{P=\overline{P}} \frac{(\Delta P)^2}{2} + c(grad \Delta P)^2 + \dots$$

the expression in (2, 29) into relation (2, 26) we find the mean-square fluctuation:

$$\overline{\mathbf{P}_{k}}^{2} = A \int_{-\infty}^{+\infty} |\mathbf{P}_{k}|^{2} w(|\mathbf{P}_{k}|) d |\mathbf{P}_{k}| = \frac{k_{B}T}{(g_{0}^{\prime} + 2ck^{2})V}$$
(2.30)

where A is a normalization constant obtained from $\int w(x)dx = 1$. Since $g_0'' \to 0$ as $T \to T_C$, the long wave length fluctuations with $k \to 0$ increase without limit at the transition point and the neglect of fluctuations is no longer justified. It should be noted that this formula applies only for not too large values of k. For larger k values, higher spatial derivatives should be taken into account.

The important quantity is the amount of correlation between fluctuations at different point in space. This is described by the correlation function

$$g(\vec{\mathbf{r}}, \vec{\mathbf{r}}') = \langle [P_z(\vec{\mathbf{r}}) - \overline{P_z(\vec{\mathbf{r}})}] [P_z(\vec{\mathbf{r}}') - \overline{P_z(\vec{\mathbf{r}}')}] \rangle \qquad (2.31)$$

which can be obtained either from the mean square fluctuations by an inverse Fourier transformation, or from the free energy as shown by Kadanoff [9]. In the latter case we write the Hamiltonian as

$$H = H_0 - \int E(\vec{r}) P_z(\vec{r'}) dV' \qquad (2.32)$$

and define

$$\overline{P_{z}(\vec{r})} = \operatorname{Tr} P_{z}(\vec{r}) e^{-\beta H} / \operatorname{Tr} e^{-\beta H}$$
(2.33)

A small variation in $E(\vec{r})$ induces a change in $\overline{P_z(\vec{r})}$, which is obtained from

$$\delta \overline{\mathbf{P}_{\mathbf{z}}(\vec{\mathbf{r}})} = -\beta \operatorname{Tr} \mathbf{P}_{\mathbf{z}}(\vec{\mathbf{r}}) \delta \mathbf{H} e^{-\beta \mathbf{H}} / \operatorname{Tr} e^{-\beta \mathbf{H}} + \beta \operatorname{Tr} \mathbf{P}_{\mathbf{z}}(\vec{\mathbf{r}}) e^{-\beta \mathbf{H}} \operatorname{Tr} \delta \mathbf{H} e^{-\beta \mathbf{H}} / (\operatorname{Tr} e^{-\beta \mathbf{H}})^{2}$$

$$(2.34)$$

using

$$\delta H = - \int dV' P_z(r') \delta E(r') \qquad (2.35)$$

as

$$\delta \overline{P_{z}(\vec{r})} = \beta \int dV' \left[\overline{P_{z}(\vec{r}) P_{z}(\vec{r}')} - \overline{P_{z}(\vec{r})} \overline{P_{z}(\vec{r}')} \right] \delta E_{z}(\vec{r}')$$

$$= \beta \int dV' \left[\overline{P_{z}(\vec{r})} - \overline{\overline{P_{z}(\vec{r})}} \right] \left[P_{z}(\vec{r}') - \overline{P_{z}(\vec{r}')} \right] \delta E_{z}(\vec{r}') \qquad (2.36)$$

$$= (k_{B}T)^{-1} \int dV' g(\vec{r}, \vec{r}') \delta E(\vec{r}')$$

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In Landau's theory we used Eq. (2.16) to determine the average polarization $\overline{P_z}(\vec{r})$. From this equation we get the following relation between the first order changes δP_z and δE

as
$$P_2 \rightarrow P_2 + \delta P_2$$
 and $E \rightarrow E + \delta E$:

$$[2a + 12b \overline{P_z(\vec{r})^2} - 2c \text{ grad}^2] \delta \overline{P_z(\vec{r})} = \delta E(\vec{r}) \qquad (2.37)$$

Inserting expression (2.36) for $\delta \overline{P_z(\vec{r})}$, we get:

$$\int dV' \{ [2a + 12b \overline{P_z(\vec{r})}^2 - 2c \text{ grad}^2] g(\vec{r}, \vec{r}') - k_B T \delta(\vec{r} - \vec{r}') \} \delta E(\vec{r}') = 0$$

Since $\delta E(r')$ is arbitrary, the entire bracket must vanish and we get for the correlation functions the differential equation:

$$[2a + 12b \overline{P_{z}(\vec{r})^{2}} - 2c \text{ grad}^{2}] g(\vec{r}, \vec{r}') = k_{B}T \delta(\vec{r} - \vec{r}') \quad (2.38)$$

For $T > T_C$ and E = 0, $\overline{P}_z = 0$, and we find:

$$[2a'(T-T_{C}) - 2c\nabla^{2}] g(\vec{r}, \vec{r}') = k_{B}T \ \delta(\vec{r} - \vec{r}'), \ T > T_{C} \qquad (2.39)$$

whereas for $T < T_{C}, \ \overline{P}_{z}^{2} = \left(-\frac{a}{2b}\right)$ and

$$[4a' (T_{C} - T) - 2c\nabla^{2}] g(\vec{r}, \vec{r}') = k_{B}T \delta(\vec{r} - \vec{r}'), T < T_{C}$$
(2.40)

The solutions of these differential equations, which can be reduced to $\Delta f - \chi^2 f = -4 \pi \delta(\vec{r} - \vec{r}')$, are well known:

$$f = \frac{e^{-\chi |\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|}$$

Thus we obtained in three dimensions:

$$g(\vec{r}, \vec{r}') = \frac{\exp(-|\vec{r} - \vec{r}'|/\xi)}{|\vec{r} - \vec{r}'|} \frac{k_{B}T}{8\pi c}$$
(2.41)

where

$$\xi = (c/a')^{\frac{1}{2}} (T - T_{C})^{-\frac{1}{2}}, \quad T > T_{C}$$

$$\xi = (c/2a')^{\frac{1}{2}} (T_{C} - T)^{-\frac{1}{2}}, \quad T < T_{C}$$
(2.42)

This solution is again valid only if $|\vec{r} - \vec{r'}|$ is much bigger than a lattice constant. The important point is that the characteristic range ξ of the correlation function becomes very large near T_c , since ξ grows as $(T - T_C)^{-\nu}$ where $\nu = 1/2$ in the Landau theory. At T_C itself, ξ becomes infinite and the correlation of the fluctuations drops off only as 1/R.

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There is a close connection between the anomalies in the correlation functions and the singularities in thermodynamic derivatives near the critical point.

Equation (2.36), for instance, gives the response of the mean polarization to a change in the external field. This, however, is the definition of the susceptibility. Thus one obtains,

$$\chi = \left(\frac{\partial P_z}{\partial E}\right)_{T, E=0} = (k_B T)^{-1} \int dV' g(\vec{r}, \vec{r}') = (2c)^{-1} \xi^2 \qquad (2.43)$$

and

$$X(+) = \frac{1}{2a'(T - T_c)}, \quad T > T_C$$

$$X(-) = \frac{1}{4a'(T_c - T)}, \quad T < T_C$$
(2.44)

i.e. we get the familiar Curie-Weiss law for the dielectric susceptibility as given by Eqs (2.21) and (2.22). This result shows how the divergence in the range of correlation between fluctuations ξ produces a divergence in the thermodynamic derivatives.

Another example of a relation between a thermodynamic derivative and a correlation function is provided by the specific heat at fixed external field and the correlation function for energy density fluctuations. Defining an average energy density

$$\vec{u(\mathbf{r})} = \mathrm{Tr}\,u(\vec{\mathbf{r}})e^{-\beta H}/\mathrm{Tr}\,e^{-\beta H}$$
(2.45)

which is connected with the total mean energy \overline{U} by $\overline{U} = \int u(\vec{r}) dV$ one gets the following relation between the change in temperature, $\delta\beta$, and the response in the mean energy, $\delta\overline{U}$:

$$\overline{\delta U(\vec{r})} = -\int dV' \left[\overline{u(\vec{r})u(\vec{r}')} - \overline{u(\vec{r})u(\vec{r}')} \right] \delta\beta \qquad (2.46)$$

from which one gets the specific heat at constant field:

$$C_{E} = \frac{\partial \overline{U}}{\partial T} |_{E} = (k_{B}T^{2})^{-1} \int dV' g_{uu}(\vec{r}, \vec{r}') \qquad (2.47)$$

where

$$g_{uu}(\vec{\mathbf{r}}, \vec{\mathbf{r}}') = \langle [u(\vec{\mathbf{r}}) - \overline{u(\vec{\mathbf{r}})}][u(\vec{\mathbf{r}}') - \overline{u(\vec{\mathbf{r}}')}] \rangle \qquad (2.48)$$

The parameter, which tells us where fluctuations become important is the normalized difference between the temperature of interest, T, and the Curie temperature, T_C :

$$\epsilon = \frac{\Delta T}{T_{\rm C}} = \frac{T - T_{\rm C}}{T_{\rm C}}$$
(2.49)

TABLE II. PARAMETERS DESCRIBING THE PHASE TRANSITIONS AS $\epsilon \rightarrow 0$ AND VALUES OF CRITICAL INDICES PREDICTED BY THE LANDAU THEORY AND THE TWO DIMENSIONAL ISING MODEL (d = DIMENSIONALITY OF THE PROBLEM)

	,		·		-
Physical quantity	$\epsilon = (T - T_C) / T_C$	E	Behaviour of quantity	Landau	2-d Ising
P	> 0	0	$\overline{\mathbf{P}} = 0$		
	< 0	0	$\overline{P} \sim \pm \epsilon ^{\beta}$	β = 1/2	B = 1/8
	0 .	† 0	$\pm e^{i/\delta}$	δ = 3	δ = 15
$\chi = \left(\frac{\partial P}{\partial E}\right)_{e}$	> 0	0	~ e ^{-y}	$\gamma = 1$	$\gamma = 7/4$
	< 0	0	$\sim \epsilon ^{-\gamma}$	γ' = 1	$\gamma' = 7/4$
$g(\vec{r}, \vec{r'}) = P(\vec{r})P(\vec{r'}) - \vec{P}^2$	0	0	$ \overrightarrow{\mathbf{r}}-\overrightarrow{\mathbf{r}'} ^{-\mathbf{d}+2-\eta}$	$\eta = 0$	$\eta = 1/4$
ξ = range of $g(\vec{r}, \vec{r'})$	> 0	0	$\sim \epsilon^{-\nu}$	v = 1/2	$\nu = 1$
	< 0	0	$\sim \epsilon ^{-\nu}$	v' = 1/2	ν' = 1
CE = specific heat at E = const	> 0	0	$A_{1}\epsilon^{-\alpha'_{+}B_{1}}$	discontinuity in C _E	
	< 0	0	$A_2 \epsilon ^{-\alpha'} + B_2$	_	
or for $\alpha = \alpha' = 0$	> 0	0	$C_1 \log \epsilon^{-1} + D_1$		log ∞ in C _E
	< 0	0	$C_2 \log \epsilon ^{-1} + D_2$		$\alpha = \alpha' = 0$

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For the Landau theory to be valid, $|\epsilon|$ must be larger than a critical value, determined by the condition, that the fluctuations in the order parameter must be small compared to the order parameter itself over distances comparable with the coherence distance ξ :

$$g(\vec{r}, \vec{r}') = \overline{\left[P_{z}(\vec{r}) - \overline{P_{z}}\right]} \left[P_{z}(\vec{r}') - \overline{P_{z}}\right] \Big|_{\vec{r} - \vec{r} \sim \xi} \ll (\overline{P_{z}})^{2}$$
(2.50)

Equations (2.41) and (2.17b) yield:

$$k_B T_c / 4 \pi ec \xi(\epsilon) \ll -a/b$$
 (2.51)

Introducing $\lambda = (c/2a' T_c)^{\frac{1}{2}}$ we get the critical value of ϵ as:

$$\epsilon_{\rm c} = (k_{\rm B}/\Delta C.\lambda^3)^2 (1/16 \ \pi e)^2$$
 (2.52)

where ΔC is the jump in heat capacity per unit volume.

Ginzburg [8] has shown that $\epsilon_{\rm C} \sim 10^{-4}$ in BaTiO₃ and the Landau theory will work for all $|\epsilon| \gg 10^{-4}$. The experimental data support this statement since γ was found to be equal to 1 ± 0.02 for TGS and KH₂PO₄ down to values for $\epsilon = 2.10^{-4}$ and 8.10^{-4} , respectively. The reason for the preservation of this "molecular field" theory and the relatively minor role of fluctuations in ferroelectrics as compared to other critical systems (in the magnetic case $\epsilon_{\rm C} \sim 10^{-2}$) is that the polarization is relatively small as compared to the maximum possible polarization when ions would be displaced by a distance of the order of a lattice distance.

The thermodynamic functions approach a simple behaviour as $\epsilon \rightarrow 0$. The parameters describing the phase transition and the values of the critical indices predicted by the Landau (or any other molecular field) theory and the ones obtained from the exact solution of the two dimensional Ising model are collected in Table II. The experimental data have generally not been collected close enough to the critical point and the accuracy is not such that a comparison between theory and experiment would be fruitful. Using the same set of experimental specific heat data in KH₂PO₄, for instance one group finds a logarithmic singularity $C_E = -A \log \epsilon + B$, whereas another group finds that a law $C_E = K/(T-T_C)^{\alpha} + L$ with $\alpha = 1/2$ is obeyed up to $\epsilon = 10^{-3}$ in agreement with Landau's theory. Only γ has been measured accurately enough and the value – as already mentioned – agrees with the Landau theory ($\gamma = 1$) up to $|\epsilon| \sim 10^{-4}$.

Several authors have recently suggested that the nine critical indices α , α' , β , γ , γ' , δ , ν , ν' and η are not independent but can be expressed in terms of two fundamental quantities. No exact derivation of these results has been given so far, and we shall only list the suggested scaling laws:

$$2-\alpha = 2-\alpha' = d\nu = d\nu' = \gamma + 2\beta = \gamma' + 2\beta = d\gamma/(2-\eta) = \beta(\delta+1)$$
(2.53)

The results of the two-dimensional Ising model completely agree with the scaling law conclusions. Very recently the scaling laws have been generalized to time-dependent correlation functions and yielded some information about the dynamical behaviour in the "critical" region where

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the wavelength is smaller than the coherence distance ξ , so that $k\xi \gg 1$. It should be mentioned that this "critical" region extends down to zero wave number (k=0) as T \rightarrow T_c since the coherence length ξ becomes macroscopic.

2.4. Relations between anomalous quantities near a λ -transition

The Clausius-Clapeyron and the Ehrenfest relations which relate abrupt changes in thermodynamic quantities at a first- or a second-order phase transition become indeterminate at λ -type transitions where some quantities (such as the specific heat) tend to infinity rather than to finite values at the transition point.

To see this let us remember that the entropy and the volume are continuous at a second-order phase transition:

$$S_1 = S_2$$
 (2.54)
 $V_1 = V_2$

Hence

$$\left(\frac{\partial S_1}{\partial T}\right)_p \delta T + \left(\frac{\partial S_1}{\partial p}\right)_T \delta p = \left(\frac{\partial S_2}{\partial T}\right)_p \delta T + \left(\frac{\partial S_2}{\partial p}\right)_T \delta p$$

$$\left(\frac{\partial V_1}{\partial T}\right)_p \delta T + \left(\frac{\partial V_1}{\partial p}\right)_T \delta p = \left(\frac{\partial V_2}{\partial T}\right)_p \delta T + \left(\frac{\partial V_2}{\partial p}\right)_T \delta p$$

$$(2.55)$$

and

$$\frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{\left(\frac{\partial S_2}{\partial T}\right)_p - \left(\frac{\partial S_1}{\partial T}\right)_p}{\left(\frac{\partial S_2}{\partial p}\right)_T - \left(\frac{\partial S_1}{\partial p}\right)_T} = -\frac{\left(\frac{\partial V_2}{\partial T}\right)_p - \left(\frac{\partial V_1}{\partial T}\right)_p}{\left(\frac{\partial V_2}{\partial p}\right)_T - \left(\frac{\partial V_1}{\partial p}\right)_T}$$
(2.56)

whence, taking into account

$$\left(\frac{\partial S}{\partial p}\right)_{T} = -\left(\frac{\partial V}{\partial T}\right)_{p}$$

we obtain

$$\frac{dp}{dT} = \frac{1}{VT} \frac{C_{P_2} - C_{P_1}}{\alpha_2 - \alpha_1} = \frac{\alpha_2 - \alpha_1}{\kappa_2 - \kappa_1}$$
(2.57)

where α is the volume expansion coefficient and κ is the isothermal compressibility. In a λ -type transition, both C_p and α tend to infinity, and Eq (2.57) becomes indeterminate as ∞/∞ .

Janovec [10] has recently generalized the Pipard equations [5] to get relations between anomalous quantities near a λ transition in a dielectric crystal. The quantities which may behave anomalously around a λ transition in a ferroelectric crystal can be arranged in a symmetric compliance matrix, the elements of which are the partial derivatives of the "extensive" variables (entropy per unit volume s, the components of the strain tensor e_{μ} , and polarization P_r) with respect to the "intensive" variables (temperature T, stress σ_{ρ} , electric field E_r):

$$\frac{C}{T}^{\sigma,E} \alpha_{1}^{\sigma,E} \dots \alpha_{6}^{\sigma,E} p_{1}^{\sigma,E} \dots p_{3}^{\sigma,E}
\alpha_{1}^{\sigma,E} S_{11}^{T,E} \dots S_{1}^{T,E} d_{11}^{T,E} \dots d_{13}^{T,E}
\vdots \\
\alpha_{6}^{\sigma,E} S_{61}^{T,E} \dots S_{66}^{T,E} d_{61}^{T,E} \dots d_{63}^{T,E}
p_{1}^{\sigma,E} d_{11}^{T,E} \dots d_{16}^{T,E} \chi_{11}^{T,\sigma} \dots \chi_{13}^{T,\sigma}
\vdots \\
p_{3}^{\sigma,E} d_{31}^{T,E} \dots d_{36}^{T,E} \chi_{31}^{T,\sigma} \dots \chi_{33}^{T,\sigma} \\
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Here

$$C^{\sigma,E} = T(\partial s / \partial T)_{\sigma_{\rho},E_{r}}$$

$$\alpha_{\mu}^{\sigma, E} = \left(\frac{\partial S}{\partial \sigma_{\mu}}\right)_{T, \sigma_{\rho/\mu}, E_{r}} = \left(\frac{\partial Ie_{\mu/\rho}}{\partial T}\right)_{\sigma_{\rho}, E_{r}}$$

$$S_{\mu,\nu}^{T,E} = \left(\frac{\partial e_{\mu}}{\partial E_{\nu}}\right)_{T,\sigma_{\rho}/\mu,E_{r}}$$

$$d_{i,\mu}^{T,E} = \left(\frac{\partial e}{\partial E_j}\right)_{T,\sigma_{\rho},E_{T/j}} = \left(\frac{\partial P_i}{\partial \sigma_{\mu}}\right)_{T,\sigma_{\rho}/\mu,E_T}$$

$$\mathbf{p}_{i}^{\sigma, E} = \left(\frac{\partial S}{\partial E_{j}}\right)_{T, \sigma_{\rho}, E_{r/j}} = \left(\frac{\partial \mathbf{P}_{i}}{\partial T}\right)_{\sigma_{\rho}, E_{r}}$$

and

$$\chi_{ij}^{\mathrm{T},\sigma} = \left(\frac{\partial \mathbf{P}_{i}}{\partial \mathbf{E}_{j}}\right)_{\mathrm{T},\sigma_{\rho}, \mathbf{E}_{r/j}}$$

are the thermal expansion coef-

ficients at constant stress and field

are the isothermal elastic compliances at constant field

are the isothermal piezo-electric coefficients at constant field

are the pyro-electric coefficients at constant stress and field

is the isothermal dielectric susceptibility at constant stress. The symbol ρ / μ means $\rho \neq \mu$.

General relations between the components of this matrix can be found by introducing a new variable

$$t = T - T_C(\sigma_p, E_r)$$

$$(2.59)$$

and expressing derivatives at constant T in terms of derivatives at constant t.

The main results are

$$\alpha_{\mu}^{\sigma,E} = \gamma_{\mu}^{E} \frac{C^{\sigma,E}}{T} + \alpha_{\mu}^{0}$$

$$S_{\mu,\nu}^{T,E} = \gamma_{\nu}^{E} \alpha_{\mu}^{\sigma,E} + S_{\mu,\nu}^{0}$$

$$d_{i,\mu}^{T,E} = \gamma_{\mu}^{E} p_{i}^{\sigma,E} + d_{i,\mu}^{0}$$

$$S_{\mu,\nu}^{T,E} = \gamma_{\mu}^{E} \gamma_{\nu}^{E} \frac{C^{\sigma,E}}{T} + S_{\mu,\nu}^{0} + \alpha_{\mu,\nu}^{0} \gamma_{\nu}^{E}$$
(2.60)

where

$$\gamma_{\mu}^{E} = -\left(\frac{\partial T_{C}}{\partial \sigma_{\mu}}\right)_{E}$$
(2.61)

is a tensor of rank two whose zero components are determined by the point group of the crystal. It measures the negative change of the transition temperature T_c due to mechanical stress and, of course, does not depend on temperature, whereas α^0_{μ} , $S^0_{\mu,\nu}$, $d^0_{i,\mu}$ are slowly varying functions of temperature.

The above equations thus predict the existence of linear relations between the anomalous quantities $\underline{C}^{\sigma,E}$, $\underline{S}_{\mu,\nu}$, $\underline{g}^{\sigma}_{\mu}$ and the pyro- and piezoelectric coefficients $\underline{p}^{\sigma,E}_{i}$ and $\underline{d}^{E}_{i,\mu}$. An anomalous behaviour in the heat capacity, for example, indicates an anomalous temperature dependence in all non-zero components of the thermal expansion coefficient. These predictions have been verified in the case of TGS.

3. LATTICE DYNAMICS AND FERROELECTRICITY

Born and Huang [11] have shown that a crystal will be stable against small deformations if all the normal modes have real frequencies. Cochran [12] and Anderson [13] demonstrated that in some ionic or partly ionic crystals a long-wavelength transverse optical frequency may become imaginary in the harmonic approximation resulting in an instability of the lattice with respect to this normal mode and a ferroelectric phase transition. The theory is based on the argument that in ionic crystals lattice vibrations are accompanied by polarization oscillations which create a local field interacting with the ions through long-range Coulomb forces. If, for a given normal mode, these long-range forces have the same magnitude but are of opposite sign than the short-range forces, the crystal becomes unstable against this mode. Above the Curie temperature anharmonic interactions stabilize the system, making the observable quasi-harmonic frequency real and positive, but temperature dependent.

The anharmonic terms in the potential energy lead to temperature effects connected with thermal expansion or contraction and to constant volume temperature effects, which dominate the temperature dependence

of this "soft" mode. The anharmonic contribution decreases with decreasing temperature and the frequency varies as

$$\omega_{\rm F}^2(0) = \gamma({\rm T} - {\rm T}_{\rm C}) \tag{3.1}$$

and approaches zero as $T\!\!\rightarrow\! T_C$ so that the lattice displacements associated with this mode become unstable and produce a "displacive" ferroelectric phase transition.

The simplest way to understand this behaviour is to go back to the early theory of Slater [14] and to consider the motion of individual ions in the lattice (such as the titanium ion in $BaTiO_3$). The equation of motion of such an ion may be written as:

$$m \ddot{x} + \gamma \dot{x} + (K_s - K_L + BT) x = q E_0 e^{i\omega t}$$
(3.2)

where K_S is the short-range harmonic restoring force constant, $-K_L x$ is the long range electrostatic driving force which tends to drag the ion away from its equilibrium position, and BT is the effective anharmonic restoring force constant, which arises from inclusion of anharmonicity to lowest order. The amplitude of the external electric field of frequency ω is E_0 and q is the effective charge of the ion. Using the relation

$$\mathbf{P} = \mathbf{N}\mathbf{q}\mathbf{x} \tag{3.3}$$

where N is the number of ions per unit volume, and solving Eq. (3.3) with the ansatz $x = x_0 \exp [i(\omega t - \phi)]$, we get the following expression for the susceptibility of the system:

$$\chi = \frac{N q^2/m}{\omega_0^2 - \omega^2 + i\gamma \omega/m}$$
(3.4)

where

$$\omega_0^2 = (BT - K_L + K_S)/m = \frac{B}{m} \left(T - \frac{K_L - K_S}{B}\right)$$
 (3.5)

Expression (3.5) is equivalent to expression (3.1), and expression (3.4) is nothing but the Curie-Weiss law (if $|K_L|$ is slightly larger than $|K_S|$) with

$$T_{\rm C} = (K_{\rm L} - K_{\rm S})/B$$
 (3.6)

as the real part of the low frequency dielectric constant is from expression (3.4) obtained as

$$\epsilon' - 1 = \frac{Nq^2/m}{\omega_0^2} = \frac{C}{T - T_C}$$
 (3.7)

where $C = Nq^2/B$.

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The static (ϵ_0) and high frequency (ϵ_{∞}) dielectric constants of a crystal are related to the long-wavelength lattice vibrations by the Lyddane-Sachs-Teller (LST) relation [15], which for a diagonally cubic crystal with two atoms in the unit cell takes the form

$$\epsilon_0 / \epsilon_\infty = \omega_L^2 / \omega_T^2$$
 (3.8)

Here ω_L and ω_T are the long-wavelength longitudinal and transverse vibrations and - since ϵ_{∞} and ω_L are essentially temperature independent - a vanishing of ω_T leads to a singularity in ϵ_0 . Cochran and Cowley [16] have extended this relation to crystals of other symmetry classes. For crystals having orthorombic symmetry or higher, they obtain

$$\frac{\epsilon_0^{\alpha\alpha}}{\epsilon_{\infty}^{\alpha\alpha}} = \prod_{n=1}^{\infty} \left(\frac{\omega_L(\alpha)}{\omega_T(\alpha)} \right)^2$$
(3.9)

where α is the direction of a crystalographic axis, $\omega_L(\alpha)$ is the frequency of one of the n-1 modes for which the polarization is longitudinal with the wave vector parallel to α and $\omega_T(\alpha)$ is the frequency of one of the n-1 modes for which the polarization is transverse and the wave vector is perpendicular to the α direction. The results have been obtained in the adiabatic, electrostatic and harmonic approximation and are hence not correct in the limit $k \rightarrow 0$.

Cowley [17] has developed a Green's functions approach to study the lattice dynamics of an anharmonic crystal and Wilcox [18] has derived most of these results using a classical diagram technique. His treatment is confined to the study of the relationship between the static dielectric susceptibility tensor and the spectrum of lattice vibrations, and "frequency renormalization" technique is used to obtain a Curie formula for the susceptibility of paraelectric materials.

The potential energy of the crystal in a constant applied field \overline{E} is

$$U(\vec{E}) = U - \vec{E} \cdot \vec{M}$$
 (3.10)

where \vec{M} is the dipole moment of the crystal, whereas the susceptibility is related to the statistical fluctuations of the dipole moment in the absence of the field:

$$\chi^{\alpha\beta} = (\beta/V) \left[\langle M^{\alpha} M^{\beta} \rangle - \langle M^{\alpha} \rangle \langle M^{\beta} \rangle \right]$$
(3.11)

Here $\beta = 1/k_BT$ and the thermal average of the dipole moment is in the classical statistical approximation given by:

$$\langle \vec{M} \rangle = \int \vec{M} e^{-\beta U(E)} dV / \int e^{-\beta U(E)} dV$$
 (3.12)

To evaluate the ensemble averages it is convenient to use complex normal coordinates A_{λ} which contain the square root of the mass of the atoms and where λ stands for (kj) with j standing for a particular branch of the spectrum. The potential energy is expanded as:

$$U = H + V$$
 (3.13a)

where

$$H = \frac{1}{2} \sum \omega_{\lambda}^{2} A_{\lambda}^{*} A_{\lambda} \qquad (3.13b)$$

$$V = V_3 + V_4 + \dots$$

$$V_{3} = \sum_{\lambda \lambda' \lambda_{2}} \Delta (\vec{k} + \vec{k}' + \vec{k}_{2}) V_{3} (\lambda \lambda' \lambda_{2}) A_{\lambda} A_{\lambda'} A_{\lambda_{2}}$$
(3.13c)
$$V_{4} = \sum_{\lambda \lambda' \lambda_{2} \lambda_{3}} \Delta (\vec{k} + \vec{k}' + \vec{k}_{2} + \vec{k}_{3}) V_{4} (\lambda \lambda' \lambda_{2} \lambda_{3}) A_{\lambda} A_{\lambda} A_{\lambda_{2}} A_{\lambda_{3}}$$
(3.13d)

and

$$\vec{M} = \vec{M}_0 + \vec{M}_1 + \vec{M}_2 + \dots$$
 (3.14a)

where

$$\begin{split} \mathbf{M}_{0} &= \text{const} \\ \vec{\mathbf{M}}_{1} &= \sum_{j} \mathbf{M}_{1j} \mathbf{A}_{j} \\ \vec{\mathbf{M}}_{2} &= \sum \Delta(\vec{\mathbf{k}} + \vec{\mathbf{k}}') \mathbf{M}_{2}(\lambda, \lambda') \mathbf{A}_{\lambda} \mathbf{A}_{\lambda'} \quad (3.14b) \end{split}$$

Here ω_{λ} stands for the temperature-independent harmonic frequencies. The summations over λ are over all normal modes in the first Brillouin zone. The Δ functions ensure wave vector conservation since $\Delta(\mathbf{k})$ is zero unless $\mathbf{\vec{k}} = 0$ or a translation vector of the reciprocal lattice, in which case $\Delta(\mathbf{\vec{k}}) = 1$. The quantities V₃ and V₄ are completely symmetric with respect to interchanges of λ 's and the A_{λ} satisfy the relation:

$$A_{-\lambda} = A_{\lambda}^{*} \qquad (3.15)$$

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The evaluation of the susceptibility is thus reduced to the calculation of the quantities

$$\langle \vec{M} \rangle = (e^{-\beta V} M) / (e^{-\beta V})$$

$$\langle M^{\alpha} M^{\beta} \rangle = (e^{-\beta V} M^{\alpha} M^{\beta}) / (e^{-\beta V})$$
(3.16)

where parentheses are used to denote harmonic-ensemble averages for any quantity Q:

$$(Q) = \int Q e^{-\beta H} dV / \int e^{-\beta H} dV \qquad (3.17)$$

By expanding exp $-\beta V$ in its power series, one finds that in lowest order the susceptibility is temperature-independent

$$X_{0}^{\alpha\beta} = \frac{1}{V} \sum_{j} M_{1j}^{\alpha} M_{1j}^{\beta} / \omega_{j}^{2}$$
(3.18)

whereas the first-order term, χ_1 , is proportional to temperature, etc. This expansion in powers of temperature is not very convenient when "soft" low frequency optical modes are present. In particular, it diverges whenever one of the harmonic modes is unstable, $\omega_0^2 < 0$. In this case it is better to take the anharmonic terms into account by a "renormalization" procedure. The new unperturbed Hamiltonian now represents a collection of independent harmonic oscillators with temperature-dependent frequencies $\bar{\omega}_{\lambda}$. The renormalization procedure is as follows:

The potential energy is again divided into an unperturbed part H and a perturbation v:

$$U = \widetilde{H} + \widetilde{v}$$
(3.19)

where

$$H = H + Q$$
 (3.20)

$$v = V - Q$$
 (3.21)

and

$$Q = \frac{1}{2} \sum_{k} A^{+}(\vec{k}) C(\vec{k}) A(\vec{k})$$
 (3.22)

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with C being a positive definite, for the moment unknown, temperaturedependent Hermitian matrix.

Defining new temperature-dependent normal co-ordinates with the unitary transformation

.

$$\mathbf{A} = \mathbf{U}\mathbf{A} \tag{3.23}$$

which also diagonalizes (ω^2 + C), we find that the unperturbed part of the potential energy becomes equal to

$$H = \frac{1}{2} \sum_{\lambda} \overline{\omega}_{\lambda}^{2} \widetilde{A}_{\lambda}^{*} \widetilde{A}_{\lambda}$$
(3.24)

where the matrix of the temperature-dependent "quasi-harmonic" frequencies $\widetilde{\omega}^2$ is given by

$$\overline{\omega}^{2} = U(\omega^{2} + C)U^{\dagger} = U\omega^{2}U^{\dagger} + \hat{C}$$
(3.25)

and

$$Q = \frac{1}{2} \sum_{k} \widetilde{A}^{\dagger}(k) \ \widehat{C}(k) \ \widetilde{A}(k)$$
(3.26)

Equations (3.13c) and (3.13d) are similarly expressed in terms of the \tilde{A}_{λ} replacing the old potential constants $V_3(\lambda\lambda'\lambda_2)$, $V_4(\lambda\lambda'\lambda_2\lambda_3)$ by new temperature-dependent ones $\tilde{v}_3(\lambda\lambda'\lambda_2)$ and $\tilde{v}_4(\lambda\lambda'\lambda_2\lambda_3)$. The harmonic ensemble average of $(\tilde{A}_{\lambda}\tilde{A}_{\lambda'})$ — which is sometimes called a contraction symbol — with respect to H is now

$$\hat{g}_{\lambda\lambda'} = (\tilde{A}_{\lambda}\tilde{A}_{\lambda'}) = \delta_{-\lambda\lambda'}(\beta\overline{\omega}^{2}_{\lambda})^{1} \qquad (3.27)$$

The matrix \hat{C} is now obtained from the requirement that higher-order terms should not contribute to the "propagator"

$$G_{jj'}(\vec{k}) = \langle \tilde{A}_{j}(\vec{k}) \tilde{A}_{j'}(-\vec{k}) \rangle - \langle \tilde{A}_{j}(\vec{k}) \rangle \langle \tilde{A}_{j'}(-\vec{k}) \rangle = \hat{g}_{jj'} + \hat{g}_{j} \tilde{D}_{jj'} \hat{g}_{j'} + \dots$$
(3.28)

Since

$$\widetilde{\mathbf{D}}_{\mathbf{j}\mathbf{j}'} = \mathbf{D}_{\mathbf{j}\mathbf{j}'} + \beta \, \widehat{\mathbf{C}}_{\mathbf{j}\mathbf{j}'} \tag{3.29}$$

the above requirement means that

$$\beta \ddot{\mathbf{C}} = -\mathbf{D} \tag{3.30}$$

which provides an equation for \hat{C} . It should be noted, however, that $D = D(\hat{C})$ so that an iterative procedure must be used.

Introducing

$$\widetilde{M}_{1}^{\alpha} = U M_{1}^{\alpha}$$
(3.31)

the dielectric susceptibility is given in terms of the temperaturedependent optical modes:

$$\chi^{\alpha\beta} = \frac{1}{V} \sum_{j} \tilde{M}_{1j}^{\alpha} \tilde{M}_{1j}^{\beta} / \overline{\omega}_{j}^{2}$$
(3.32)

or, by $using^2$ (3.25)

$$X^{\alpha\beta} = \frac{1}{V} (M_{1}^{\alpha})^{\dagger} (\overline{\omega}^{2} + c)^{-1} . M_{1}^{\beta} \cong \frac{1}{V} \sum_{j} \frac{M_{1j}^{\alpha} M_{1j}^{\beta}}{\omega_{j}^{2} + C_{jj}} + \dots$$
(3.33)

Let us now consider the case with one "soft" mode with renormalized frequency

$$\overline{\omega}_0^2 = (\omega_0^2 + C_0)$$
 (3.34)

In this case,

$$X^{\alpha\beta} = \frac{1}{V} (\omega_0^2 + C_0)^{-1} \sum_{j}' M_{1j}^{\alpha} M_{1j}^{\beta} + \dots \qquad (3.35)$$

where

$$C_0 = -k_B T D_{00}$$
(3.36)

and, for cubic symmetry,

$$D_{00} = -12 \sum_{\lambda} \frac{\vec{v}_4(-\lambda\lambda \ 00)}{\vec{v}_2} + 18 \sum_{\lambda\lambda} \frac{|\vec{v}_3(-\lambda\lambda' \ 0)|}{\vec{\omega}_{\lambda}^2 \ \vec{\omega}_{\lambda}^2}$$
(3.37)
$$_{k=k'}$$

The choice of signs indicates that the unstable harmonic mode, $\omega_0^2 < 0$, is stabilized by the quartic potential to make $\overline{\omega}_0^2 > 0$. If the soft modes do not contribute too strongly to the sums in D_{00} , D_{00} will be approximatively temperature-independent and provided that $\omega_0^2 < 0$, Eq. (3.35) yields a Curie-Weiss law:

$$X = \text{const.} / (T - T_C)$$
 (3.38)

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² Here c is the diagonal part of C.

Silverman [19] proceeded in another way and developed an effective equation of motion for the modes of wave vector k. This equation is obtained by assuming that each mode of wave vector \vec{k} sees the selfconsistent anharmonic potential due to the presence of all other modes. This equation is a lattice-dynamical analogue of the Hartree selfconsistent equations. The temperature dependence of the effective "quasi-harmonic" frequencies arises from averages over the spectrum of temperature independent modes.



FIG.2. Diatomic linear chain with alternating plus and minus charges interacting with nearest (k_1) and next nearest (k_2) neighbour harmonic coupling.

To illustrate this procedure in the simplest possible way let us consider a diatomic linear chain of alternating plus and minus charges with mass m interacting with nearest (k_1) and next nearest-neighbour (k_2) harmonic coupling (Fig. 2). The equations of motion for this system are:

$$m \frac{d^2 X_i}{dt^2} = -2(k_1 + k_2)X_i + k_1(X_{i+1} + X_{i-1}) + k_2(X_{i+2} + X_{i-2})$$
(3.39)

and the frequency spectrum is obtained as:

Acoustic branch: $\omega_{a}^{2}(k) = \frac{4k_{1}}{m} \sin^{2} \frac{kd}{2} + \frac{4k_{2}}{m} \sin^{2} kd$ (3.40)

$$0 \leq k \leq \frac{\pi}{2d}$$

Optical branch: $\omega_0^2(\mathbf{k}) = \frac{4\mathbf{k}_1}{\mathbf{m}} \cos^2 \frac{\mathbf{k}d}{2} + \frac{4\mathbf{k}_2}{\mathbf{m}} \sin^2 \mathbf{k}d$

The frequency of the zero wave vector optical motion is completely determined by the nearest-neighbour coupling k_1 . Choosing k_1 small and negative and k_2 large and positive we build into the system an instability near wave vector zero whereas the system is stable for larger k values (Fig. 3). The Hamiltonian can be written in terms of the harmonically unstable "normal modes":

$$H_{0} = \frac{1}{2} \sum_{k} (p_{k}^{a} p_{-k}^{a} + \omega_{a}^{2}(k) q_{k}^{a} q_{-k}^{a}) + \frac{1}{2} \sum_{k} (p_{k}^{0} p_{-k}^{0} + \omega_{0}^{2}(k) q_{k} q_{-k})$$
(3.41)



FIG.3. Optical and acoustic branch of the frequency spectrum of the above diatomic chain.

Introducing a fourth-order anharmonic interaction between nearest neighbours

H' =
$$\frac{V_4}{4!} \sum_{i} (X_{i+1} - X_i)^4$$
 (3.42)

and expressing it in terms of normal modes, we get

$$H' = \frac{4V_4}{Nm^2} \sum_{k} \left[\sum_{k'} \sin^2 \frac{k' d}{2} \cdot q_{k}^{a} q_{-k'}^{a} \right] \cos^2 \frac{kd}{2} \cdot q_{k}^{0} q_{k}^{0} + \dots$$
(3.43)

An effective "quasi-harmonic" Hamiltonian can be obtained by averaging over the q_k^a , q_{k}^a .

$$H_{eff} = \frac{1}{2} \sum_{k} \left[p_{k}^{a} p_{-k}^{a} + \overline{\omega}_{a}^{2}(k) q_{k}^{a} q_{-k}^{a} \right] + \frac{1}{2} \sum_{k} \left[p_{k}^{0} p_{-k}^{0} + \overline{\omega}_{0}^{2} q_{k}^{0} q_{-k}^{0} \right] \quad (3.44)$$

with

$$\overline{\omega}_0^2 = \left[\frac{8V_4}{Nm^2} \sum_{\mathbf{k'}} \sin^2 \frac{\mathbf{k'} \, \mathbf{d}}{2} \left\langle \mathbf{q}_{\mathbf{k}}^{\mathbf{a}} \, \mathbf{q}_{-\mathbf{k}}^{\mathbf{a}} \right\rangle + \frac{4k_1}{m} \right] \cos^2 \frac{\mathbf{kd}}{2} + \frac{4k_2}{m} \sin^2 \mathbf{kd} \quad (3.45)$$

and an analogous expression for $\overline{\omega}_a^2$, which is however still relatively temperature-independent. Averaging over the acoustic spectrum

$$\langle q_k^a q_{-k}^a \rangle \approx \frac{k_B T}{\omega_a^2(k)} \approx \frac{k_B T}{(4k_2/m) \sin^2 kd}$$
 (3.46)

and restricting ourselves to small wavenumbers, where $\sin\,kd\,\approx kd,$ one obtains

$$\overline{\omega}_{0}^{2}(\mathbf{k}) = \left[\frac{\mathbf{V}_{4}\mathbf{k}_{B}\mathbf{T}}{2\,\mathbf{m}\,\mathbf{k}_{2}} - \frac{4\,|\mathbf{k}_{1}|}{\mathbf{m}}\right]\cos^{2}\frac{\mathbf{k}\mathbf{d}}{2} + \frac{4\mathbf{k}_{2}}{\mathbf{m}}\sin^{2}\mathbf{k}\mathbf{d} \qquad (3.47)$$

The presence of the anharmonic term therefore stabilizes the system above T_C . For $k \rightarrow 0$ the frequency varies with temperature as

$$\omega_0^2(k=0) \propto (T-T_c)$$
 (3.48)

with

$$T_{C} = \frac{8 |k_{1}|k_{2}}{V_{4} |k_{B}}$$
(3.49)

Inelastic neutron scattering results [20] (BaTiO₃), infrared reflectivity measurements [21] (SrTiO₃ and KTaO₃) and Raman scattering data (NaNO₂) have confirmed the predicted variation of \overline{w}_0^2 with temperature (Figs 4 and 5). A very promising technique to study the temperature dependence of the optical modes is also the measurement of the nuclear magnetic resonance spin-lattice relaxation time of nuclei with non-zero quadrupole moments, which is determined by the quadrupole spin-phonon coupling. Near T_C this coupling should be dominated by the "soft" mode so that the spin-lattice relaxation should vary with temperature as

$$T_1 = K (T - T_c)^2 / T^2 + const$$
 (3.50)

FIG.4. Low-lying temperature dependent optical branch from inelastic neutron scattering data compared with optical branch from the above diatomic chain model.

4. ORDER-DISORDER TYPE HYDROGEN-BONDED FERROELECTRICS

In many ferroelectric crystals one of the ions in the unit cell moves in a multiple well potential. In hydrogen (H)-bonded ferroelectrics, in particular, the proton has very often two possible equilibrium sites in




FIG.5. The square of the frequency of the q = 0 mode of the ferroelectric branch versus temperature for SrTiO₃. The broken line represents the temperature dependence of the reciprocal dielectric constant [Cowley (1964)].

the X - H - X bond, thus forming a reversible electric dipole with two equilibrium orientations. Whereas in displacive ferroelectrics (such as in BaTiO₃), the ferroelectric instability is marked by the cancellation of the short-range "restoring" and electrostatic "driving" interactions, which results in ionic displacements and the formation of induced dipoles. it is the ordering of permanent X - H - X dipoles which is responsible for the instability in H-bonded ferroelectrics. The potential field is so anharmonic, that the elementary excitations cannot - even approximately be described as phonons, and the methods developed in the previous chapter are not directly applicable. The problem can sometimes (but not always) be simplified by ascribing to each proton a fictitious spin 1/2(so that $S_z = 1/2$ if the proton occupies the "right" and $S_z = -1/2$ if it occupies the "left" equilibrium site) and writing the Hamiltonian in this pseudo-spin space. The problem of how to determine the elementary excitations is then somewhat similar to the determination of the spinwave spectrum in a ferrimagnet. An additional complication is the presence of a strong proton-lattice coupling which mixes the "quasi-spin" and "phonon" modes. The fact that in some of these crystals the strongest part of the effective interaction between protons is a short-range fourproton or three-proton interaction through intermediate ionic groups is as well a difficulty which is not present in the ferromagnetic case (see Fig. 6).

An excellent review of the state of art in this field till 1962 has been given by Uehling [22]. Since then DeGennes [23] introduced the quasispin formalism, and Matsubara and Tokunaga [24], Novaković [25], Villain and Stamenković [26] as well as Brout, Müller and Thomas [27] used it to investigate the collective excitations in these crystals. Blinc and Ribarić [28] pointed out the importance of the proton-lattice interactions, and Kobayashi [29] recently determined the collective excitations of the coupled proton-lattice system. A cluster approximation method, which allows one to take into account the four-body nature of the protonproton interactions in $\mathrm{KH}_2\mathrm{PO}_4$ and which reduces to the Silsbee-Uehling-Schmidt (SUS) [27] model in the classical limit, has been developed by

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Blinc and Svetina [30]. An exact solution [31] of the two-dimensional Slater [32] model has recently been found by Wu, Lieb, Yang and Yang, and Sutherland, whereas low and high temperature series expansions for the free energy of the classical Slater model were given by Nagle [33].

In the following we shall try to sketch some of the new ideas in this field.



FIG. 6. Crossing of optical phonon and protonic "quasi-spin" branch in H-bonded ferroelectrics.

4.1. Elementary excitations of the isolated protonic system

The total Hamiltonian of the system is of the form:

$$\widetilde{H} = \widetilde{H}_{P} + \widetilde{H}_{L} + \widetilde{H}_{P,L}$$
(4.1)

where \widetilde{H}_{p} stands for the Hamiltonian of the proton system in a rigid lattice, ${}^{\prime}I_{L}$ is the Hamiltonian of the lattice vibrations in the absence of proton motion and $\widetilde{H}_{P,L}$ stands for the proton-lattice interaction.

The proton self-energy Hamiltonian can be written as

$$- \widetilde{H}_{p} = 2 \Gamma \sum_{f=1}^{N} \sum_{\alpha=1}^{n} S_{f\alpha}^{x} + \sum_{f,g}^{N} \sum_{\alpha,\beta}^{n} \{ B_{fg}^{\alpha\beta} S_{f\alpha}^{x} S_{g\beta}^{z} + J_{fg}^{\alpha\beta} S_{f\alpha}^{z} S_{g\beta}^{z} \}$$

$$+ V_{(3)} \{ S^{z} : S^{z} : S^{z} \} + V_{(4)} \{ S^{z} : S^{z} : S^{z} : S^{z} \}$$

$$(4.2)$$

where the first term describes the motion of isolated protons between the two possible sites in a given hydrogen bond with Γ as the tunneling frequency [34], the second term takes account of the effect of the tunneling of one proton on the tunneling frequency of another, and the other three terms describe an interaction between proton sites of two-, three-, and four-body character. $V_{(4)} \{S^{\mathbf{Z}} : S^{\mathbf{Z}} : S^{\mathbf{Z}} : S^{\mathbf{Z}}\}$, for instance, represents in case of KH₂PO₄ the dominant effective short-range interprotonic interaction through the PO₄ groups and can be expressed in the following form:

$$V_{(4)} \{ S^{z} : S^{z} : S^{z} : S^{z} \} = \sum_{f,g,h,j} F_{fghj} S^{z}_{f} S^{z}_{g} S^{z}_{h} S^{z}_{j}$$
(4.3)

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The operators $\mathrm{S}^x_{f\alpha}$ and $\mathrm{S}^z_{f\alpha}$ are represented by the Pauli matrices

$$S^{\mathbf{x}} = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}$$
, $S^{\mathbf{z}} = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}$ (4.4)

and operate on a basis which we label $|\phi_L\rangle$ and $|\phi_R\rangle$. These are the states in which the whole proton is localized either on the right or left hand side of the barrier in the double well potential of a given H-bond.

By definition

$$\begin{aligned} |\phi_{R}^{i}\rangle &= \begin{pmatrix} 1\\0 \end{pmatrix}, \quad S_{i}^{z} |\phi_{R}^{i}\rangle &= \frac{1}{2} |\phi_{R}^{i}\rangle, \\ |\phi_{L}^{i}\rangle &= \begin{pmatrix} 0\\1 \end{pmatrix}, \quad S_{i}^{z} |\phi_{L}^{i}\rangle &= -\frac{1}{2} |\phi_{L}^{i}\rangle \end{aligned}$$

$$(4.5)$$

whereas the eigenfunctions of S^x are the symmetric and anti-symmetric linear combination of $|\phi_R\rangle$ and $|\phi_L\rangle$:

$$|\psi_{I}\rangle = \frac{1}{\sqrt{2}} (|\phi_{R}\rangle + |\phi_{L}\rangle) = \frac{1}{\sqrt{2}} (\frac{1}{1})$$

$$|\psi_{II}\rangle = \frac{1}{\sqrt{2}} (|\phi_{R}\rangle - |\phi_{L}\rangle) = \frac{1}{\sqrt{2}} (\frac{1}{-1})$$
(4.6)

The term associated with the ground state energy doublet is

$$\Gamma \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = 2 \Gamma S^{x}$$
 (4.7)

where 2Γ = $E_{\rm II}$ - $E_{\rm I}$ denotes the splitting of the unperturbed ground state due to proton tunneling.

In the above summations a twofold index labels a unit cell (f or g) and a particular proton in a given unit cell (α or β). The quantities $B_{fg} = B_{gf}$, $J_{fg} = J_{gf}$ depend only on the relative distances $\vec{r}_f - \vec{r}_g$. Of course $B_{ff} = J_{ff} = \dots = 0$.

Let us for the moment forget about the proton-lattice interaction as well as about the three- and four-body coupling terms and let us look for the frequency spectrum of the protonic "quasi-spin" Hamiltonian taking only two-body interactions into account:

$$-\widetilde{H}_{p} = 2\Gamma \sum_{f=1}^{N} \sum_{\alpha=1}^{n} S_{f\alpha}^{x} + \sum_{f,g}^{N} \sum_{\alpha,\beta}^{n} \{B_{fg}^{\alpha\beta} S_{f\alpha}^{x} S_{g\beta}^{x} + J_{fg}^{\alpha\beta} S_{f\alpha}^{z} S_{g\beta}^{z}\}$$
(4.8)

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The important point is that this Hamiltonian is now "harmonic" in the quasi-spin variables and the normal modes can be easily found.

In the simplest, molecular-field approximation, the Hamiltonian (4.8) becomes

$$\tilde{H}_{p} = H_{x} \sum_{f} \sum_{\alpha} S_{f\alpha}^{x} + H_{z} \sum_{f} \sum_{\alpha} S_{f\alpha}^{z}$$
(4.9)

where

$$H_{x} = 2\Gamma + 2B \langle S_{g_{\beta}}^{x} \rangle$$

$$H_{z} = 2 J \langle S_{g_{\beta}}^{x} \rangle$$
(4.10)

and

The molecular field thus forms a vector
$$\tilde{H}_{MF}$$
 = (H_x, 0, H_z) in our pseudo-
spin space which interacts with the spin variables. Here $\langle S^z \rangle$ denotes
the thermal average of S^z:

 $\mathbf{B} = \sum_{\mathbf{f} \alpha} \mathbf{B}_{\mathbf{f}g}^{\alpha \beta}, \quad \mathbf{J} = \sum_{\mathbf{f} \alpha} \mathbf{J}_{\mathbf{f}g}^{\alpha \beta}$

$$S^{z} = \langle S^{z} \rangle + \delta S^{z}$$
 (4.10a)

and terms like δS^z which are dropped in the molecular field approximation , give rise to fluctuation effects and collective motion.

To study the normal "quasi-spin" modes of the system, let us rotate the co-ordinate system in such a way that the molecular field Hamiltonian takes a simple diagonal form:

$$- \widetilde{H}_{p} = H_{MF} \sum_{i,\alpha} S_{i,\alpha}^{\zeta}$$
(4.11)

where

$$H_{MF}^2 = H_x^2 + H_z^2$$
 (4.12)

$$S_{f}^{x} = \cos \phi \ S_{f}^{\xi} + \sin \phi \ S_{f}^{\zeta}$$

$$S_{f}^{z} = -\sin \phi \ S_{f}^{\xi} + \cos \phi \ S_{f}^{\zeta}$$
(4.13)

and

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The rotation angle ϕ is determined by the condition that the term in the Hamiltonian, linear in S[§] vanishes in the new co-ordinate system. The new temperature-dependent axes ξ y ζ are such that at all temperatures $\langle S_{f}^{\xi} \rangle = 0$, whereas $\langle S^{\xi} \rangle$, which is parallel to \dot{H} , is different from zero:

$$\sin \phi = \frac{H_z}{H_{MF}}, \quad \cos \phi = \frac{H_z}{H_{MF}}$$
(4.14)

We are now interested in the collective motion of our system of fictitious spins around the molecular field. For the ground state $\left|G\right>$ of our system – where we assume that in analogy to the case of ferromagnetism all quasi-spins point "up" – we have by definition

$$S_{f}^{\zeta} |G\rangle = S |G\rangle$$
 (4.15a)

whereas

$$S_{f}^{+}|G\rangle = 0 \qquad (4.15b)$$

with

$$S_{f}^{\pm} = S_{f}^{\xi} \pm i S_{f}^{y}$$
 (4.16)

Let us now use the language of second quantization and introduce for S = 1/2 the representation:

$$S_{f\alpha}^{\dagger} = p_{f\alpha}^{\dagger}, \quad S_{f\alpha}^{\dagger} = p_{f\alpha}^{\dagger}$$
 (4.17)

where the creation and annihilation operators $p^{\dagger}_{f\,\alpha}$ and $p^{-}_{f\,\alpha}$ satisfy the commutation relations:

$$p_{f\alpha} p_{g\beta}^{\dagger} - p_{g\beta}^{\dagger} p_{f\alpha} = (1 - 2p_{f\alpha}^{\dagger} p_{f\alpha}) \delta_{fg} \delta_{\alpha\beta}$$

$$p_{f\alpha} p_{g\beta} - p_{g\beta} p_{f\alpha} = 0, p_{f\alpha} p_{f\alpha} + p_{f\alpha} p_{f\alpha} = 0 \qquad (4.18)$$

$$p_{f\alpha}^{2} = 0, p_{f\alpha}^{\dagger} p_{f\alpha} = n_{f\alpha} = 0, 1$$

It should be stressed that the above quasiparticles (called [35] paulions by Agranović and Tosić) behave like bosons at different lattice sites (f \neq g, $\alpha \neq \beta$), whereas at the same lattice site (f = g, $\alpha = \beta$) they behave like fermions. In case that we are interested in such low lying

states that

$$\overline{n} = \langle p_{f\alpha}^{\dagger} p_{f\alpha} \rangle \ll 1$$
(4.19)

one can neglect the term $2p_{f\alpha}^{\dagger}p_{f\alpha}$ in comparison with 1 in the first of the commutation relations (4.18) and the paulions can be treated as bosons. Recently, however, an exact procedure was developed by which one can express paulions in terms of operators satisfying the Bose-Einstein statistics.

Taking

$$p_{f\alpha} = \left[\sum_{\nu=0}^{\infty} \lambda_{\nu} a_{f\alpha}^{+\nu} a_{f\alpha}^{\nu}\right]^{1/2} a_{f\alpha} = \left[\sum_{\nu=0}^{\infty} b_{\nu} a_{f\alpha}^{+\nu} a_{f\alpha}^{\nu}\right] a_{f\alpha}$$

$$p_{f\alpha}^{+} = a_{f\alpha}^{+} \left[\sum_{\nu=0}^{\infty} \lambda_{\nu} a_{f\alpha}^{+\nu} a_{f\alpha}^{\nu}\right]^{1/2} = a_{f\alpha}^{+} \left[\sum_{\nu=0}^{\infty} b_{\nu} a_{f\alpha}^{+\nu} a_{f\alpha}^{\nu}\right]$$

$$(4.20)$$

where the new creation and annihilation operators $a_{\rm f}^{\dagger},~a_{\rm f}$ satisfy the boson commutation relation

$$[a_{f\alpha}, a_{g\beta}^{\dagger}] = \delta_{fg} \delta_{\alpha\beta} \qquad (4.21)$$

we obtain:

$$\lambda_{\nu} = \frac{(-2)^{\nu}}{(1+\nu)!}$$
 (4.22a)

and

$$b_0 = 1, b_1 = -1, b_2 = \frac{1}{2} (1 + \sqrt{3}/3), \text{ etc.}$$
 (4.22b)

so that

$$S_{f\alpha}^{\dagger} = p_{f\alpha} \cong (1 - a_{f\alpha}^{\dagger} a_{f\alpha}) a_{f\alpha}$$

$$S_{f\alpha}^{-} = p_{f\alpha}^{\dagger} \cong a_{f\alpha}^{\dagger} (1 - a_{f\alpha}^{\dagger} a_{f\alpha}) \qquad (4.23)$$

$$S_{f\alpha}^{\xi} \cong 1/2 - a_{f\alpha}^{\dagger} a_{f\alpha}$$

The above expressions differ from the approximate expansion formulas of Holstein and Primakoff as here the third-order terms in the $a_{f\alpha}^{\dagger}$ and $a_{f\alpha}$ are larger by a factor of two, which was lost in their approximate treatment.

At very low temperatures the third-order terms in expressions (4.23) can be dropped. Doing this and expressing the Hamiltionian (4.8) in terms of Fourier-transformed coupling constants and operators:

$J_{\alpha\beta}(\vec{q}) = \sum_{g,f} J_{fg}^{\alpha\beta} e^{i\vec{q}\cdot(\vec{R}_{f}-\vec{R}_{g})}$	(4.24)
$B_{\alpha\beta}(\vec{q}) = \sum_{g,f} B_{fg}^{\alpha\beta} e^{i\vec{q}\cdot(\vec{R}_{f}-\vec{R}_{g})}$	
$a_{\vec{q}\alpha} = \frac{1}{\sqrt{N}} \sum_{f} e^{i\vec{q}\cdot\vec{r}_{f}} a_{f\alpha}$	(4.25)
$a_{\vec{q}\alpha}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{f} e^{-i\vec{q}\cdot\vec{r}_{f}} a_{f\alpha}^{\dagger}$	
$[a_{\vec{q}}, a_{\vec{q}}^{\dagger}] = \delta_{\vec{q}} \delta_{\vec{q}}$	(4.26)

and

where

the Hamiltonian (4.8) takes the form:

$$H_{p} = \sum_{\vec{q}} \left\{ \sum_{\alpha=1}^{n} (\mathbf{J} + \Delta \mathbf{H}) \mathbf{a}_{\vec{q}\alpha}^{\dagger} \mathbf{a}_{\vec{q}\alpha}^{\dagger} - \sum_{\alpha,\beta=1}^{n} V_{\alpha\beta}(\vec{q}) \mathbf{a}_{\vec{q}\alpha}^{\dagger} \mathbf{a}_{\vec{q}\beta} \right.$$

$$\left. - \frac{1}{2} \sum_{\alpha,\beta=1} V_{\alpha\beta}(\vec{q}) (\mathbf{a}_{-\vec{q}\alpha}^{\dagger} \mathbf{a}_{\vec{q}\beta}^{\dagger} + \mathbf{a}_{\vec{q}\alpha}^{\dagger} \mathbf{a}_{-\vec{q}\beta}) \right\}$$

$$(4.27)$$

Here

,

$$V_{\alpha\beta}(\vec{q}) = V_{\beta\alpha}(\vec{q}) = \frac{1}{2} (B_{\alpha\beta}(\vec{q}) \cos^2 \phi + J_{\alpha\beta}(\vec{q}) \sin^2 \phi)$$

$$(4.28)$$

$$\Delta H = (2B \sin^2 \phi + 2 J \cos^2 \phi) \langle a_{f\alpha}^{\dagger} a_{f\alpha} \rangle$$

The Hamiltonian (4.27) can be brought to a diagonal form by a linear Bogolyubov transformation

$$A_{\vec{q}\alpha}^{\ddagger} = \sum_{\beta} \left[u_{\alpha\beta}(\vec{q}) a_{\vec{q}\beta}^{\ddagger} - v_{\alpha\beta}(\vec{q}) a_{-\vec{q}\beta} \right]$$

$$A_{\vec{q}\alpha}^{\ddagger} = \sum_{\beta} \left[u_{\alpha\beta}(\vec{q}) a_{\vec{q}\beta}^{\ddagger} - v_{\alpha\beta}(\vec{q}) a_{-\vec{q}\beta}^{\ddagger} \right]$$

$$(4.29)$$

where $u_{\alpha\beta}(\vec{q})$ and $v_{\alpha\beta}(\vec{q})$ are even and real functions of \vec{q} .

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In terms of these operators the Hamiltonian becomes

$$H = \sum_{\alpha} \sum_{\vec{q}} \omega_{\alpha}(\vec{q}) A^{\dagger}_{\vec{q}\alpha} A_{\vec{q}\alpha} \qquad (4.30)$$

and the collective "quasi-spin" proton modes $\omega_{\alpha}(\vec{q})$ are obtained from

det
$$\begin{vmatrix} J + \Delta H - \omega_{\alpha}(\vec{q}) - V(\vec{q}) & - V(\vec{q}) \\ - V(\vec{q}) & J + \Delta H + \omega_{\alpha}(\vec{q}) - V(\vec{q}) \end{vmatrix} = 0 \quad (4.31)$$

Here $V(\vec{q})$ is a n \times n matrix with elements $V_{\alpha\beta}(\vec{q})$.

In $\rm KH_2PO_4$ the primitive cell contains four non-equivalent protons (which surround a given PO₄ group) so that $\alpha = 1, 2, 3, 4$, but because of the symmetry axis perpendicular to the XY plane (V₁₂ = V₁₄) we get only 3 different "quasi-spin" modes:

$$\omega_1^2(\vec{q}) = H^2 - 2 H[V_{11}(\vec{q}) + 2 V_{12}(\vec{q}) + V_{13}(\vec{q})] \qquad (4.32)$$

$$\omega_{3}^{2}(\vec{q}) = \omega_{3}^{2}(\vec{q}) = H^{2} - 2 H[V_{11}(\vec{q}) - V_{13}(\vec{q})]$$
(4.33)

$$\omega_{4}^{2}(\vec{q}) = H^{2} - 2 H[V_{11}(\vec{q}) - 2 V_{12}(\vec{q}) + V_{13}(\vec{q})]$$
(4.34)

where $H = J + \Delta H$.

 ω_1 has the lowest frequency and belongs to the irreducible representation Γ_4 of D_{2d}, whereas $\omega_2 = \omega_3$ below to Γ_5 and ω_4 to Γ_2 .

It should be noted that at low temperatures ΔH will be small and $H \sim J$, whereas $V_{\alpha \beta} \Rightarrow B_{\alpha \beta}(\vec{q})$. An elementary excitation $\omega_{\alpha}(\vec{q})$ in the region of small \vec{q} values in a direction \vec{s} has the energy

$$\omega_{\alpha}(\vec{q}, \vec{s}) = \omega_{\alpha}(0, \vec{s}) + \frac{\hbar^2 q^2}{2 m_{\alpha}^{*}(\vec{s})} + \dots$$
 (4.35)

and propagates through the crystal with a group velocity

$$\left|\vec{v}_{\alpha}(\vec{q},\vec{s})\right| = \left|\frac{1}{\hbar} \frac{d\omega_{\alpha}(\vec{q},\vec{s})}{d\vec{q}}\right| = \left|\frac{\hbar \vec{q}}{m_{\alpha}^{\chi}(\vec{s})}\right| \qquad (4.36)$$

Here one has, following Novaković [36]:

$$\omega_1(0, \vec{s}) = \sqrt{J^2 - JB}; \frac{\hbar^2}{2 m_1^x(\vec{s})} = \frac{J Ba^2}{12(J^2 - JB)^{1/2}}$$
 (4.37)

with a² being the square of a lattice distance.

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The group velocity is hence proportional to B and should therefore be strongly mass-dependent. In particular, it should be much larger in KH₂PO₄ than KD₂PO₄. In this respect, it is interesting that Bjorkstam indeed found a great difference in the tip velocity of ferroelectric domains of KH₂PO₄ and KD₂PO₄, the ratio $v_{KH_2PO_4}/v_{KD_2PO_4}$ being of the order of 10⁵.

4.2. Temperature dependence of the protonic "quasi-spin" frequency spectrum

The temperature dependence of the "quasi-spin" modes can be obtained in the random phase approximation (RPA) by a linearization of the transformation (4.23) which consists in replacing $S_f^t = (1 - a_f^t a_f) a_f$ by $S_f^t \simeq (1 - \langle a_f^t a_f \rangle) a_f$ and $S_f^r = a_f^t (1 - a_f^t a_f) by S_f^r \approx a_f^t (1 - \langle a_f^t a_f \rangle)$. After this has been done the Hamiltonian is diagonalized by two further successive transformations as in Eq.(4.1).

The results are:

$$\omega_{1}^{2}(\vec{q}) = H^{2} - 2H[V_{11}(\vec{q}) + 2V_{12}(\vec{q}) + V_{13}(\vec{q})]$$

$$\omega_{2}^{2}(\vec{q}) = \omega_{3}^{2}(\vec{q}) = H^{2} - 2H[V_{11}(\vec{q}) - V_{13}(\vec{q})] \qquad (4.38)$$

$$\omega_{4}^{2}(\vec{q}) = H^{2} - 2H[V_{11}(\vec{q}) - 2V_{12}(\vec{q}) + V_{13}(\vec{q})]$$

where H is the molecular field and

$$V_{\alpha\beta}(\vec{q}) = \langle \langle S_{f\alpha}^{\zeta} \rangle + \frac{\delta^2}{2} \rangle [B_{\alpha\beta}(\vec{q}) \cos^2 \phi + J_{\alpha\beta}(\vec{q}) \sin^2 \phi] \qquad (4.39)$$

with

$$\delta = 1/2 - \langle S_{f\alpha}^{\xi} \rangle \tag{4.40}$$

measuring the deviation of $\langle S^{\xi} \rangle$ from the ideal one-half value at low temperatures. Neglecting the small correction, quadratic in δ , one obtains³ for ω_1 in the vicinity of T_C :

$$\omega_1^2(q) = \gamma (T - T_c) + Q q^2 \qquad (4.41)$$

whereas the other three "quasi-spin" modes do not reveal any anomaly on going through the Curie point. We see that for $q \rightarrow 0$, $\omega_1 \rightarrow 0$ as $T \rightarrow T_C$. The "quasi-spin" mode ω_1 thus exibits the same behaviour as the "soft" phonon modes in displacive ferroelectrics.

The same result is obtained if the Heisenberg equations of motion are linearized for the spin variables instead of Eq. (4.23).

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³ Note that for $T = T_{C}$: $[V_{11}(0) + 2V_{12}(0) + V_{13}(0)] = H/2$

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To illustrate this procedure and to demonstrate the T-dependence of the molecular field H let'us consider the Hamiltonian

-
$$H_p = 2 \Gamma \sum_{f} S_f^{x} + \sum_{fg} \{ B_{fg} S_f^{x} S_g^{x} + J_{fg} J_f^{z} J_g^{z} \}$$
 (4.42)

where we now, for the sake of simplicity, assume that there is just one proton per unit cell. Again we first transform the molecular-field Hamiltonian

$$- H_{p} = H_{x} \sum_{f} S_{f}^{x} + H_{z} \sum_{f} S_{f}^{z}$$

$$H_{x} = 2\Gamma + 2 B \langle S_{f}^{x} \rangle \qquad (4.43)$$

$$H_{z} = 2 J \langle S^{z} \rangle$$

to diagonal form

-
$$H_p = H \sum_{i} S_f^{\zeta}$$
, $H^2 = H_x^2 + H_z^2$ (4.44)

by the transformation from xyz to $\xi y \zeta$ where $\cos \phi = H_z/H$, $\sin \phi = H_x/H$, and evaluates

$$\langle S_{f}^{\zeta} \rangle = \frac{\operatorname{Tr} S_{f}^{\zeta} e^{-\beta H_{p}}}{\operatorname{Tr} e^{-\beta H_{p}}} = \frac{d}{d(\beta H_{p})} \ln \operatorname{Tr} e^{-\beta H S_{f}^{\zeta}} = 1/2 \operatorname{tgh}(\beta H/2)$$
(4.45)

Using this result one easily gets:

$$\langle S^{\mathbf{z}} \rangle = \cos \phi \langle S^{\zeta} \rangle = \frac{2 J \langle S^{\mathbf{z}} \rangle}{H} \frac{1}{2} \operatorname{tgh} (\beta H/2)$$
 (4.46)

$$\langle S^{\mathbf{x}} \rangle = \sin \phi \langle S^{\zeta} \rangle = \frac{2\Gamma + 2B \langle S^{\mathbf{z}} \rangle}{H} \frac{1}{2} \operatorname{tgh} (\beta H/2)$$
 (4.47)

Since $\langle S^z \rangle$ is proportional to the spontaneous polarization, Eq.(4.46) represents a self-consistent field equation for P_s.

The transition temperature is obtained as the boundary of the region beyond which there is no non-zero solution for $\langle S^z \rangle$. It is given by:

$$\frac{H}{J} = tgh \ (\beta H/2) \text{ or for } T \rightarrow T_C: \ \frac{2\Gamma}{J-B} = tgh \left(\frac{\Gamma}{kT_C} \ \frac{1}{1-B/J}\right) \approx tgh \left(\frac{\Gamma}{kT_C}\right)$$
(4.48)

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The condition for the existence of a ferroelectric transition temperature T_C is thus: (J - B) $> 2 \, \Gamma$. Above $T_C \langle S^z \rangle$ and H_z are zero so that cos $\phi = 0$, sin $\phi = 1$. Below T_C , on the other hand, $\langle S^z \rangle \ddagger 0, \langle S^x \rangle = \Gamma/(J-B)$, and sin $\phi = 2\Gamma/(J-B)$.

Having the molecular field results we can investigate oscillations about the mean state by linearizing the Heisenberg equations of motion

$$i \hat{n} : \vec{S}_{\vec{q}} = \hat{n} \omega : \vec{S}_{\vec{q}} = [\vec{S}_{\vec{q}}, H_{\vec{p}}]$$
(4.49)

for the Fourier components of \vec{s}

$$\vec{S}_{\vec{q}} = \sum_{f} \vec{S}_{f} e^{i\vec{q}\cdot\vec{R}_{f}}$$
(4.50)

in the RPA approximation. An exp^(-iwt) time dependence for S is as well assumed. These Fourier-transformed "quasi-spin" operators are now collective variables in the sense that S^{α}_q is related to all sites i, j, etc. in the sample. RPA assumes that each Fourier component S^{α}_q fluctuates independently. It isolates terms proportional to S^{α}_q and replaces other operators occurring in such terms by their expectation values.

The solution of Eq. (4.49) is then reduced to the problem of solving a set of homogeneous linear equations for S_q^x , S_q^y , S_q^z :

$$\hbar \omega_{\vec{q}} \vec{S}_{\vec{q}} = \underline{M} \vec{S}_{\vec{q}}$$
(4.51)

where

$$\underline{\mathbf{M}} = \begin{pmatrix} \mathbf{0} & \mathbf{J} \langle \mathbf{S}^{\mathbf{z}} \rangle & \mathbf{0} \\ - [\mathbf{J} - \mathbf{B}(\mathbf{\dot{q}}) \langle \mathbf{S}^{\mathbf{z}} \rangle & \mathbf{0} & \Gamma - [\mathbf{J}(\mathbf{\dot{q}}) - \mathbf{B} \langle \mathbf{S}^{\mathbf{x}} \rangle \\ \mathbf{0} & - \Gamma - \mathbf{B} \langle \mathbf{S}^{\mathbf{x}} \rangle & \mathbf{0} \end{pmatrix}$$
(4.52)

The non-zero eigenfrequencies are:

$$(\hbar \omega_{\vec{q}})^2 = 4[\Gamma + B \langle S^x \rangle] [\Gamma - (J(\vec{q}) - B) \langle S^x \rangle] + 4J(J - B(\vec{q})) \langle S^z \rangle \qquad (4.53)$$

In the limit $q \rightarrow 0$, this expression reduces to:

$$T > T_{C}: (h \omega_{0})^{2} = 4 (J - B) (\Gamma + B \langle S^{x} \rangle \left[\frac{\Gamma}{J - B} - \langle S^{x} \rangle \right]$$

$$T < T_{C}: (h \omega_{0}) = 2 \sqrt{J (J - B)} \langle S^{z} \rangle$$
(4.54)

Below T_C , ω_0 is proportional to the spontaneous polarization and goes to zero as $\langle S^2 \rangle$ when $T \rightarrow T_C$. If $\langle S_z \rangle$ is proportional to $(T_C - T)^{1/2}$,

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the "soft"-mode temperature dependence is exhibited. Above T_C , however, where $\langle S^X\rangle$ = $\langle S^{\zeta}\rangle$ = 1/2 tgh ($\beta \rm H/2$), ω_0 goes to zero as

$$\omega_0^2 = \gamma (T - T_C)$$
 (4.55)

and thus again exhibits the Cochran "soft"-mode-type behaviour. This mode, however, is so strongly damped in the paraelectric phase, that it should be very difficult to observe it directly, even if the coupling with the lattice vibrations were absent.

It is interesting to note that this tunnelling "quasi-spin" wave model predicts not only an isotope effect in the Curie temperatures on replacing H by D, but also an isotope effect in the pressure dependence of the Curie temperatures, dT_C/dp , since dT/dp > 0 and strongly mass-dependent. Both effects have been observed.

4.3. Proton-lattice coupling

In view of the strong proton-lattice coupling, the "adiabatic" rigidlattice approximation is not appropriate and the complete Hamiltonian has to be diagonalized:

$$H = H_{p} + H_{L} + H_{P,L}$$
 (4.57)

and not just H_p . Dropping the small $BS_f^x S_g^x$ term in (4.42), we have

$$\mathcal{H}_{p} = -2\Gamma\sum_{f} S_{f}^{x} - \sum_{f,g} J_{fg} S_{f}^{z} S_{g}^{z}$$
 (4.58)

$$\mathscr{H}_{L} = \frac{1}{2} \sum_{q} \left(\mathbf{P}_{q} \mathbf{P}_{-q} + \Omega_{q}^{2} \mathbf{Q}_{q} \mathbf{Q}_{-q} \right)$$
(4.59)

and

$$\mathcal{H}_{P,L} = -\sum_{q} V_{q} Q_{q} S_{-q}^{z}$$
(4.60)

where S_{-q}^{z} is a Fourier component of S_{f}^{z}

$$S_{q}^{\alpha} = \sum_{j} S_{j}^{\alpha} e^{i \vec{q} \cdot \vec{R}_{j}}$$
(4.61)

and $H_{P,L}$ stands for the interaction of the proton with "inert" polar lattice vibrations via the electrostatic Coulomb field. The interaction of the proton with the high-frequency non-inert component can be included

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in the H-bond potential and leads to a renormalization of the parameters occurring in H_{P}

Rewriting $H_P\, and \, H_{P,\,L}$ in the ξ y ζ system, introducing S^{\pm} = $S^{\xi}\pm\, i\, S^{y},$ so that

$$H_{P,L} = \sin \varphi \sum_{\vec{q}} (V_{\vec{q}} (S_{\vec{q}}^{\dagger} + S_{\vec{q}})Q_{q} - \cos \varphi \sum_{\vec{q}} V_{\vec{q}} S_{\vec{q}}^{E} Q_{\vec{q}}$$

and finally expressing H_p in terms of the Fourier components (4.61), as well as using the commutation relations:

$$[Q_{K}, P_{K'}] = i\hbar \delta_{KK'}$$

$$[S_{q}^{\pm}, S_{q'}^{\pm}] = \pm 2S_{q+q'}^{\sharp}$$

$$[S_{q}^{\xi}, S_{q'}^{\pm}] = \pm S_{q+q'}^{\pm}$$
(4.61a)

we obtain the coupled equations of motion

$$i\hbar \frac{dO_q}{dt} = \hbar \omega O_q = [O_q, \mathcal{H}]$$
 (4.62)

with

$$O_q = S_q^+, S_q^-, Q_q, P_{-q}$$

Linearizing these equations in the RPA approximation, and solving the resulting biquadratic equation for ω , one gets:

$$\omega_{\pm}^{2} = \frac{1}{2} \left\{ \left(\omega_{p}^{2}(q) + \Omega_{q}^{2} \right) \pm \sqrt{\left(\omega_{p}^{2}(q) - \Omega_{q}^{2} \right)^{2} + \frac{16NV_{q}^{2}\Gamma^{2}\langle S^{\ell} \rangle}{H} \right\}$$

$$(4.63)$$

where $\omega_p(\mathbf{q})$ stands for the protonic "quasi-spin" collective mode, Ω_q is the polar lattice vibration to which the proton motion is coupled, and H is the molecular field.

It has been shown in the previous chapter, that $\omega_p(0) \to 0$ as $T \to T_0$ whereas Ω is temperature-independent. An inspection of Eq. (4.63) shows that the frequency of the coupled "quasi-spin"-phonon mode, ω_{-} , tends to zero even above T_0 . At T_0 , where $\omega_p(0)$ is zero, ω_{-} is imaginary as the second term in Eq. (4.63) is larger than the first one.

The ferroelectric transition temperature is within this model determined as the temperature where $\omega_{-}(0) = 0$ and obtained as:

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$$T_{c} = T_{0} + \frac{N V_{0}^{2}}{k_{B} \Omega_{0}^{2}}, \quad \omega_{-}^{2} = K (T - T_{c})$$
 (4.64)

where K depends on the mass of the hydrogen isotope. The slope of the ω^2 versus temperature curve should thus be different for KH₂PO₄ or KD₂PO₄.

This remarkable formula is now, in principle, able to explain qualitatively the shifts of the Curie temperatures in the $\rm KH_2PO_4$ family. Equation (4.48) shows that T_0 is strongly mass-dependent (due to the dependence of the tunneling matrix element Γ on the mass of the hydrogen isotope), explaining the shifts in the Curie temperatures on deuteration. Ω_0 , on the other hand, which is essentially a translational vibration of K⁺ against the PO₄ group, changes when the K ion is replaced by Rb or Cs and the P ion by As, thus explaining the isotope effects in this series of isomorphous ferroelectrics. According to this model, these shifts come from the second term in Eq. (4.64) the contribution of which to T_c is small.

It should be stressed that whereas in displacive ferroelectrics the lattice instability arises from the cancellation of the short-range restoring and electrostatic driving interactions, it is the ordering of the protons $(\omega_p(0) \rightarrow 0)$ which produces the ferroelectric instability in KH₂PO₄-type hydrogen-bonded crystals.

While ω_{-} (which is always smaller than Ω) goes to zero at the Curie temperature, ω_{+} does not significantly change at the ferroelectric transition and is always larger than Ω_{-}

An inspection of the eigenvectors of the system (4.62) further shows that

$$\frac{(Q_0/S_0^{\sharp})_{\omega_{-}}}{(Q_0/S_0^{\sharp})_{\omega_{+}}} = \frac{\omega_{+}^2 - \Omega_0^2}{\omega_{-}^2 - \Omega_0^2}$$
(4.65)

Since $\omega_{+}^{2} > \Omega_{0}^{2}$, $\omega_{-}^{2} < \Omega_{0}^{2}$, in one of the coupled modes (ω_{-}), the proton system and the lattice oscillate in phase, whereas in the other coupled mode (ω_{+}) they oscillate 180°C out of phase.

The above treatment is still oversimplified though it accounts for many characteristic features. A more satisfactory treatment should include:

- (i) Non-linear terms to account for damping effects;
- (ii) Higher excited states to account for phonon-assisted tunnelling which dominates the deuteron and, to some extent, also the proton dynamics in the paraelectric state;
- (iii) The change of the "quasi-spin" modes at low temperatures to the "diffusion" mode at higher temperatures.

4.4. Cluster approximations

While the above "quasi-spin" wave treatment elucidates the dynamical aspects of the phase transition, it is not very appropriate for a calculation

of the partition function and other thermodynamical quantities in the vicinity of the transition temperature where the interactions between the "quasi-spin" waves cannot be neglected.

For this high temperature region, where the long-range correlations start to disappear, a cluster approximation method was developed [30] which takes the four-body nature of the interactions between the protons surrounding a given PO₄ group explicitly into account. The aim of the cluster expansion is to obtain a rapidly convergent series for the free energy of a N-body system with the successive treatment of one-, twoand more-particle problems. The procedure developed in Ref. [30] consists in the separation of the Hamiltonian into an unperturbed singleparticle part and a perturbed many-particle part, introducing a, for the moment, unknown ordering parameter Δ :

$$H(E) = H_0(E, \Delta) + H'(E, \Delta)$$
 (4.66)

with E being the external electric field. The free energy of the system can consequently be written as

$$F(E,T) = F_0(E, T, \Delta) + F'(E, T, \Delta)$$
 (4.67)

Expanding F' in terms of the number of particles in a cluster, we get a series of approximations for the free energy: $F_{(1)}$, $F_{(2)}$ $F_{(n)}$ where n is determined by the size of the cluster.

Each approximate free energy is a function of the external field, temperature, and an, up to now, arbitrary ordering parameter Δ . This is to be determined in such a way that the approximation is thermodynamically consistent. Differentiating the approximate free energy we get

$$dF_{(n)} = \frac{\partial F_{(n)}}{\partial T} dT + \frac{\partial F_{(n)}}{\partial E} dE + \frac{\partial F_{(n)}}{\partial \Delta} d\Delta$$
(4.68)

The entropy and the polarization of the system are defined as

$$S_{(n)} = -\left(\frac{\partial F_{(n)}}{\partial T}\right)_{E}$$
, $P_n = -\left(\frac{\partial F_{(n)}}{\partial E}\right)_{T}$ (4.69)

respectively. The thermodynamic relation dF = -SdT - PdE is then satisfied by the approximate free energy for the value of Δ for which

$$\frac{\partial \mathbf{F}(\mathbf{n})}{\partial \Delta} = 0 \tag{4.70}$$

i.e. our approximate free energy must be stable for small variations of Δ .

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The successive approximations to the free energy of the KH_2PO_4 and KD_2PO_4 model Hamiltonian are an example of the above procedure. The model Hamiltonian of KH_2PO_4 reads in the notation of Ref. [30] as:

$$H = \sum_{i=1}^{N} \left\{ -\frac{1}{2} \Gamma \sum_{j=1}^{4} (S_{ij}^{+} + S_{ij}^{-}) + [\omega _{1}(N_{i0} + N_{i4}) + \omega _{1}(N_{i1} + N_{i3}) + \epsilon N_{i2}] + \frac{1}{2} \sum_{j=1}^{4} [-\gamma \langle p \rangle (n_{ij1}^{-} - n_{ij1}^{-}) + \frac{1}{2} \gamma \langle p \rangle^{2}] \right\}$$

$$(4.71)$$

where S_{ij}^+ and S_{ij}^- are proton "jump" operators

$$S_{ij}^{+} = b_{ij\uparrow}^{+} b_{ij\downarrow}$$
, $S^{-} = b_{ij\downarrow}^{+} b_{ij\uparrow}$ (4.72)

whereas the n_{ij} are the proton "number" operators. The $N_{i\sigma}$ ($\sigma = 0, 1...4$) are four-particle operators, describing the arrangement of the protons around a given PO_4 group and $\langle p \rangle$ is the mean value of the reduced hydrogen-bond dipole-moment operator:

$$\langle \mathbf{p} \rangle = \langle \mathbf{n}_{ij\uparrow} - \mathbf{n}_{ij\downarrow} \rangle$$
 (4.72)

The unperturbed part, H_0 , and the perturbation term, H' are:

$$H_{0} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{4} \left[-\Gamma(S_{ij}^{+} + S_{ij}^{-}) - (\gamma \langle p \rangle + \Delta) (n_{ij\uparrow} - n_{ij\downarrow}) \right] + N\gamma \langle p \rangle^{2}$$

with $H' = H - H_0$.

The first approximation to the free energy is to include into the cluster four protons (thus taking the short-range interactions around one PO_4 ion exactly into account), and the second is to include the seven protons around two neighbouring PO_4 groups. The free energies are:

$$F_{(4)} = -kTN [\ln Tr e^{-\beta H}(4) - 2 \ln Tr e^{-\beta H}(1)] + N \gamma \langle p \rangle^{2}$$

$$(4.73)$$

$$F_{(7)} = -kTN [2 \ln Tr e^{-\beta H}(7) - 3 \ln Tr e^{-\beta H}(4)] + N \gamma \langle p \rangle^{2}$$

with

$$H_{(1)} = -\Gamma (S_{ij}^{+} + S_{ij}^{-}) - (\gamma \langle p \rangle + \Delta) (n_{ij\uparrow} - n_{ij\downarrow})$$

$$H_{(4)} = \sum_{i=1}^{4} \left\{ -\Gamma (S_{ij}^{+} + S_{ij}^{-}) - (\gamma \langle p \rangle + \frac{1}{2} \Delta) (n_{ij\uparrow} - n_{ij\downarrow}) \right\} + \left[\varkappa_{1} (N_{i0} + N_{i4}) + \varkappa_{1} (N_{i1} + N_{i3}) + \epsilon N_{i2}^{+} \right]$$

$$H_{(7)} = \sum_{i=1}^{7} \left\{ -\Gamma (S_{ij}^{+} + S_{ij}^{-}) - \gamma \langle p \rangle (n_{ij\uparrow} - n_{ij\downarrow}) \right\} + \sum_{i=\alpha,\beta} \left[\varkappa_{1} (N_{i0} + N_{i4}) + \varkappa_{1} (N_{i1} + N_{i3}) + \epsilon N_{i2}^{+} \right] - \sum_{i=1}^{6} \frac{\Delta}{2} (n_{ij\uparrow} - n_{ij\downarrow})$$

The ordering parameter is determined from the equations $\partial\,F_{(n)}\,/\partial\Delta$ = 0, which yield for both approximations

$$\operatorname{Tr} (\mathbf{n}_{ij\uparrow} - \mathbf{n}_{ij\downarrow}) \rho_{(1)} = \frac{1}{4} \operatorname{Tr} \sum_{j=1}^{4} (\mathbf{n}_{ij\uparrow} - \mathbf{n}_{ij\downarrow}) \rho_{(4)}$$
(4.75a)

$$\operatorname{Tr} \sum_{j=1}^{4} (n_{ij\uparrow} - n_{ij\downarrow}) \rho_{(4)} = \frac{2}{3} \operatorname{Tr} \sum_{j=1}^{7} (n_{ij\uparrow} - n_{ij\downarrow}) \rho_{(7)}$$
(4.75b)

respectively, and where

$$\rho_{(1)} = \frac{e^{-\beta H_{(1)}}}{\operatorname{Tr} e^{-\beta H_{(1)}}}, \quad \rho_{(4)} = \frac{e^{-\beta H_{(4)}}}{\operatorname{Tr} e^{-\beta H_{(4)}}}, \quad \rho_{(7)} = \frac{e^{-\beta H_{(7)}}}{\operatorname{Tr} e^{-\beta H_{(7)}}}$$
(4.76)

The convergence of the series is very good in predicting both the temperature of the phase transition and the shape of the polarization curve. In the classical limit ($\Gamma \rightarrow 0$) the results of the four-particle cluster approximation reduce to the SUS model of $\mathrm{KD}_{2}\mathrm{PO}_{4}$.

4.5. Exactly soluble models

It has been recently shown [31] that the two-dimensional classical ($\Gamma = 0$) Slater KH₂PO₄ model can be solved exactly. The model is based on the original suggestion of Slater that each of the four hydrogens surrounding a given PO₄ group has a choice of two off-center equilibrium sites in the O-H--O bond subject to the condition that there are always only two hydrogens close to the PO₄ group. This condition limits the number of possible configurations to six.

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The above simplified picture permits a well defined mathematical model to be constructed by associating arrows to lattice bonds and energies to lattice sites. We consider a hydrogen bonded N \times N square lattice with periodic boundary conditions. The rule is that there are always two arrows pointing toward and two arrows away from a given lattice site, so that a hydrogen atom near a site is represented by an arrow directed towards the site. Then there are altogether six possible arrow configurations that can be associated to a site. A zero site energy is associated with two of the six configurations and an energy $\epsilon > 0$ with the remaining four.



Each distinct way of associating arrows to the lattice as a whole is a state of the lattice. The energy of a given state is simply $n(\epsilon)\epsilon$, where $n(\epsilon)$ is the number of sites with energy ϵ ,

$$Z = \sum_{\text{all states}} e^{-\pi(\epsilon)\epsilon/kT}$$
 (4.77)

and has been evaluated [31] by the transfer-matrix method: The results are as follows:

(a) A phase change occurs at $kT_C = \epsilon \ln 2$ in agreement with Slater's mean field result;

(b) Below T_C , the specific heat is zero, C = 0;

(c) The transition is of first order with a latent heat.

(d) Near and above T_C the specific heat goes as C \sim (T - T_C)^{-1/2}

in contrast with Slater's result that C is finite at T_c.

(e) Near and above T_c the susceptibility goes as $X \propto (T - T_c)^{-1}$.

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METHODS OF NEUTRON SPECTROSCOPY

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Abstract

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 4.3. Structure analysis peetrometer methods. 5.2.1. Triple axes spectrometer (TAS). 5.2.2. The neutron crystal spectrometer methods. 5.3.2. The roof-methods. 5.3.1. The TOF methods using a monochromatic incident beam. 5.3.2. The TOF methods. 6. Outlook for the future.

1. INTRODUCTION

The aim of these three lectures is to give an overall, general and up-to-date account of the principles of the methods of neutron spectroscopy. They are meant, in principle, for those experimental and theoretical physicists who are not specialists either in X-ray or in neutron diffraction. For this reason, the lectures (particularly the first one) present the subject in a very elementary and simplified way and stress only the main features of the methods.

The first lecture - which is of an introductory character - is devoted to a brief review of the basic experimental methods of neutron spectroscopy and illustrates the usefulness of the reciprocal lattice concept for the description of neutron diffraction phenomena. The second lecture deals with methods of neutron spectroscopy for structure analysis of solids, and the third shows how neutrons can be used in studies of lattice dynamics.

Although these lectures are supposed to deal with methods of neutron spectroscopy only, for didactic reasons the X-ray spectroscopy methods are also occasionally discussed.

Those who are or will become interested in a certain problem will find at the end of this text a list of references to textbooks, monographs, proceedings of scientific conferences and papers published in scientific journals, where they can find a more detailed description and discussion of that particular problem.

In the textbooks for elementary physics the word "spectroscopy" is usually found for the first time in connection with the description of the

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famous experiment of Newton concerning the study of the composition of light by means of a glass prism. Using more modern expressions, one would say that Newton studied the wave-length distribution or the spectral distribution of light. In this sense the word "spectroscopy" was in the course of time applied to measurements of wave-length distribution of other types of radiation, e.g., infra-red, ultra-violet, X-rays, neutrons.

However, very soon it was discovered that spectroscopy of radiation scattered by or transmitted through matter can supply useful information on the matter itself. In this connection special methods using the interaction of radiation with matter as a means of studying the properties of matter have been developed. As a general rule, they include not only wave-length distribution measurements (i.e., spectroscopy in the original sense), but also angular distribution measurements. In some cases (as, for example, in X-ray structure analysis using a monochromatic beam) only the angular distribution is measured. It is common, however, to call these methods also methods of spectroscopy, e.g., methods of X-ray or neutron spectroscopy.

We shall first treat the methods of neutron spectroscopy in the original sense of the word, and afterwards we shall learn how they are used for studies of structure and lattice dynamics of solids.

2. METHODS OF SPECTRAL DISTRIBUTION MEASUREMENTS

2.1. General remarks

There are two main methods of spectral distribution measurements of electromagnetic radiation and neutrons. One uses the wave properties, the other one the corpuscular properties of radiation. The two methods are briefly described in this section. It will be shown afterwards (in sections 4 and 5) that both methods can be applied to studies of structure of solids and lattice dynamics.

There are also other methods of spectral distribution measurements of radiation (e.g., resonance methods); however, they will not be discussed in these lectures.

2.2. Methods using the wave properties of radiation

2.2.1. Electromagnetic radiation

2.2.1.1. Light (visible, infra-red, ultra-violet)

Figure 1 shows schematically the principle of a spectrophotometer for studies of wave-length distribution of visible light, infra-red and ultra-violet radiation. By moving the arm of the detector we can measure the angular distribution of the refracted or diffracted beams and by using the equations for prisms or gratings it is possible to calculate the wavelength distribution of the radiation to be studied. (As is well known, in such measurements several corrections must be introduced). It is also possible to keep the arm of the detector fixed and to rotate the prism or the grating. In both cases the angular distribution leads to the wave length distribution.





2.2.1.2. X-rays and gammas (see Refs [1, 2])

Figure 2 shows schematically the principle of an X-ray or "soft" gamma spectrometer. It is analogous to that in Fig. 1 with one important exception. Because in this case the Bragg reflection is used, the angle of incidence must always be equal to the angle of reflection. To ensure this, both the analysing single crystal and the arm of the detector must be rotated (with an angular velocity ratio of 1:2). By measuring the angular distribution it is possible, using the Bragg equation,

$$2 d_0 \sin\theta = \lambda \tag{1}$$

(where do is the known interplanar spacing) to obtain the wave-length distribution. As in the previous case, several corrections are needed (e.g. wave-length-dependent reflectivity of the single crystal, efficiency of the detector, absorption, extinction, geometrical factors). Some difficulties also exist with the so-called higher-order reflections (this point will be discussed in section 3.5). However, regardless of some technical details, also in this case, the angular distribution leads to the wave-length distribution.

2.2.2. Neutrons [3-5]

In order to use the wave properties of the neutron, in this case it is necessary to ascribe to it a wave-length

$$\lambda = \frac{h}{mv}$$
(2)

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FIG. 2. The principle of an X-ray spectrometer for wave-length distribution measurements.

v	1000	4000	. m/s
E	5	80	meV
λ	4	1	Å

TABLE I. NEUTRON VELOCITIES, ENERGIES AND WAVE-LENGTHS

where h is Planck's constant, m the mass of the neutron, and v its velocity. For studies of structure and lattice dynamics of solids the wave-lengths of the most useful neutrons are between 1Å and 4Å. Table I shows the corresponding velocities and energies.

The arrangement for wave length distribution measurements of a neutron beam is similar to that for X-rays (Fig. 2). The dimensions of the spectrometer are, however, larger because of the low intensity of neutron sources compared to X-ray sources. Of course, a neutron counter (e.g. a gas BF_3 counter) must be used instead of an X-ray detector. The corrections to be applied are similar to those listed in sub-section 2.1.1.2. Figure 3 shows a typical wave-length distribution of neutrons from a thermal nuclear reactor. It is nearly Maxwellian, at least in the middle part.

As can be seen from what was said above, the angular distribution here again leads to the wave-length distribution. This is usually the case when the measurement of the spectral distribution of the radiation under investigation is based on its wave properties.



FIG. 3. A typical wave-length distribution of neutrons from a thermal nuclear reactor.

2.3. Methods using the corpuscular properties of radiation

2.3.1. Electromagnetic radiation

For electromagnetic radiation we have

$$\lambda = \frac{c}{\nu} = \frac{hc}{E_f}$$
(3)

where c is the velocity of light, ν the frequency, and E_f the energy of the photon.

Equation (3) shows that by measuring the energy distribution of photons it is possible to obtain the wave length distribution of the electromagnetic radiation to be studied. Nowadays it is especially easy to measure the energy distribution of X-ray and gamma photons in the energy range from about 10 keV to several MeV by means of semiconductor detectors. Figure 4 shows schematically the arrangement to be used. It can be shown that the height of the electric pulse obtained from a semiconductor detector (e.g. Ge or Si Li-drifted) is proportional to the energy E_f of the photon absorbed by the detector. The electric pulses from the detector are registered in appropriate channels of a multichannel pulse height analyser (according to their height), and in this way the energy of the photon is proportional to the number of the channel in which this photon was registered. Figure 5 shows an example of an energy distribution measured by means of a semiconductor detector and a multichannel pulse height analyser. Of course, in this case also, several corrections must be introduced in order to obtain the correct spectral distribution.

2.3.2. Neutrons [3]

To run through a distance 1 a neutron of velocity v needs the time

$$t = \frac{1}{v}$$
(4)

By combining Eqs (4) and (2) we obtain

$$\lambda = \frac{h}{ml}t$$
 (5)

Semiconductor detector









which shows that the wave-length of the neutron is proportional to the time needed by this neutron to run through a certain distance l. This feature can be used for wave-length distribution measurements and the method using it is called the time-of-flight method (TOF). Figure 6a shows schematically the principle of a TOF arrangement. A collimated neutron beam is chopped by means of a rotating disc (chopper) with one opening (slit). The disc is made of a material not transparent¹ to neutrons, and the neutron beam will be let through the disc in small intervals of time only when the slit is opposite to the collimator. In this way neutron pulses with frequency ω and half-time width $\Delta t = \Omega/\omega$ (see Fig. 6a) will be obtained². For the kind of neutron studies which will be discussed later, Δt is usually about 10-15 μ s and ω about 300-600 s⁻¹. Every time the neutron pulse leaves the chopper, the multichannel time analyser starts to count.

If the detector is located at point A (Fig. 6a) very close to the slit and if the channel width δt is greater than Δt , then all neutrons would be recorded in the first channel (Fig. 6b, diagram A)³. If, however, the

¹ In practice, no ideally non-transparent material exists, and therefore a part of the neutrons always runs through and contributes to the background.

 $^{^{2}\,}$ Providing that the cross-section of the collimator has the same size and shape as the slit.

³ Because all neutrons would be recorded in the first channel, the number of counts per channel for the first channel would be very large.



FIG. 6. a) The principle of a time-of-flight arrangement for wave-length distribution measurements of neutrons emitted from a neutron source. b) Number of neutrons per channel versus channel number for various positions of the detector shown in Fig. 6a.

detector is located at point C, the neutrons will be recorded in different channels according to the time of their arrival at the detector. In general, neutrons arriving within the time interval $(t, t+\delta t)$, where t is counted from the moment when the neutron pulse leaves the chopper, will be recorded in channel number $N = t/\delta t$. These neutrons have a wave-length within the interval $(\lambda, \lambda + \Delta \lambda)$, where

$$\lambda = \frac{h}{ml} \delta t N \tag{6}$$

and

$$\Delta \lambda = \frac{h}{ml} \,\delta t \tag{7}$$

All these facts show that the distribution of neutrons recorded in various channels of the time analyser leads to the wave-length distribution of neutrons of the analysed beam. An example of the result of this kind of measurement performed with the detector at point C can be seen at Fig. 6b, diagram C. From Eq. (7) one also sees that the wave length interval $\Delta\lambda$ increases with the decrease of l. For example, at point B (Fig. 6a) $\Delta\lambda$ is twice as big as at point C and, consequently, the wavelength distribution measured at B will be squeezed compared to that at C (Fig. 6b, diagram B).

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To obtain the correct wave-length distribution from the distribution recorded by the multichannel time analyser, several corrections must be introduced. The most important is the transmission of the chopper. A disc chopper like that shown in Fig. 6a has a transmission practically independent of wave-length; however, other kinds of choppers have transmission functions which, in general, depend on both λ and ω .

In these lectures the term "chopper" will be used for a chopping device which (although it may change the spectrum of the transmitted beam) produces polychromatic neutron pulses. In section 5.3.1. chopping devices producing a monochromatic pulsed neutron beam will be described; they will be called "mechanical monochromators" in order to distinguish them from choppers as defined above.

3. CRYSTAL LATTICE; MOMENTUM SPACE, CRYSTAL MONOCHROMATORS [2, 6]

3.1. Crystal lattice in real spaces

As is well known, a crystal lattice can be built up from unit cells, one of which is shown in Fig. 7. The vectors $\{\vec{a}_i\}$, where i = 1, 2, 3, are called basic vectors. For reasons of simplicity all further considerations will be limited to lattices with basic vectors \vec{a}_i perpendicular to each other (cubicoidal lattices), although most of the discussion is valid also for other types of lattices.

Let us consider first a two-dimensional lattice, as shown in Fig. 8 with the basic vectors \vec{a}_1 and \vec{a}_2 . The lattice points are marked by dots. Any plane crossing lattice points is called a crystallographic plane. In a two-dimensional lattice, crystallographic planes reduce to straight lines. To a set of parallel crystallographic planes in a three-dimensional lattice (a set of parallel crystallographic straight lines in a two-dimensional lattice) the Miller indices (hkl) can be ascribed. This can be done in several equivalent ways. For simplicity, we shall define them as

$$h = \frac{a_1}{x_0}; k = \frac{a_2}{y_0}; l = \frac{a_3}{z_0}$$

where $(x_0, 0, 0)$, $(0, y_0, 0)$ and $(0, 0, z_0)$ are the co-ordinates of the crossing points of the crystallographic plane nearest to the origin point and the axes 0x, 0y, 0z respectively. Two remarks should be made in this connection. First, that the Miller indices are ascribed to a set of parallel crystallographic planes and not to one crystallographic plane, in particular. Second, that the Miller indices are integers with no common factor. If the parallel set of crystallographic lines in the two-dimensional lattice shown in Fig. 8 would represent a set of parallel crystallographic planes in a three-dimensional lattice parallel to the z axis $(z_0 = \infty)$ the indices of this set would be

and one would write (210).



FIG. 7. Unit cell of a crystal lattice $(\vec{a}_1, \vec{a}_2, \vec{a}_3^-)$ basic vectors, A_j -position of the j atom, μ_j - its magnetic moment).



FIG. 8. A two-dimensional lattice with (hkl) crystallographic planes.

The interplanar distance $d_{hkl}\,$ between subsequent crystallographic planes (hkl) is equal to the distance from the origin to the nearest crystallographic plane. For a cubicoidal lattice, it is easy to calculate that

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a_1}\right)^2 + \left(\frac{k}{a_2}\right)^2 + \left(\frac{1}{a_3}\right)^2}}$$
(8)





3.2. Reciprocal lattice [2,6]

The reciprocal lattice is a lattice with basic vectors $\vec{a}_j * (j=1,2,3)$ satisfying the equation

$$\vec{a}_{i} \vec{a}_{j}^{*} = \delta_{ij}$$
 (i, j = 1, 2, 3) (9)

For a cubicoidal lattice

$$a_{i}^{*} = \frac{1}{a_{i}}$$
 (i = 1, 2, 3) (10)

and vectors \vec{a}_i and \vec{a}_i^* are parallel to each other. Figure 9 illustrates how to construct a reciprocal lattice for a two-dimensional lattice. In this case, according to Eq. (10)

$$a^{*=}\frac{1}{a_{1}}$$

and

$$a_2^{*}=\frac{1}{a_2}$$

It can be shown that the vector $\vec{\tau}_{11}$ (Fig. 9) in the reciprocal lattice is perpendicular to the crystallographic straight line (11) in the real space and that $\tau_{11} = 1/d_{11}$. For the three-dimensional lattice we find that $\vec{\tau}_{hkl}$ is perpendicular to the (hkl) plane and that

$$\tau_{\rm hkl} = \frac{1}{d_{\rm hkl}} \tag{11}$$

where, as was said before, hkl have no common factor (this restriction will be discussed below).

We see that a straight crystallographic line in the real two-dimensional space corresponds to a point in the reciprocal lattice. In a threedimensional case each crystallographic plane (hkl) in the real space is represented by a point (hkl) in the reciprocal lattice and a vector $\vec{\tau}_{hkl}$, called reciprocal lattice vector. It should be stressed, however, that points (hkl) in the reciprocal lattice in the case when hkl have a common integer do not correspond to any crystallographic plane in the real space. For example, to the reciprocal lattice point (20) on Fig. 9 there would correspond a straight crystallographic line in real space labelled with a question mark in order to stress that this is not a crystallographic line because it does not cross any lattice point. Therefore, as has been said above, $-1/\tau_{hkl}$ equals the interplanar spacing of a set of crystallographic planes only in the case when hkl have no common factor. The physical meaning of τ_{hkl} in the other cases will be discussed in the next section.

3.3. Bragg's equation [2,4]

As is well known, the Bragg equation can be derived from Laue's equations which take into account interference phenomena and the wave properties of X-rays and neutrons. In textbooks the Bragg equation is often written in the form

$$2 d \sin \theta_n = n \lambda_0 \quad (n = 1, 2, 3, ...)$$
 (12)

and illustrated by a figure like Fig. 10 where d is the interplanar spacing, λ_0 the wave-length of the monochromatic X-ray or neutron beam, and n the order of reflection. The physical meaning of n is evident from Fig. 10:

$$AB + AC = n\lambda_0$$

As can be seen from Eq. (12), for each λ_0 several reflections can be obtained corresponding to different θ_n . These reflections can be studied by using a crystal spectrometer shown schematically in Fig. 11. Since $\sin\theta \leq 1$, the number of reflections cannot be greater than $2d/\lambda_0$.

Equation (12) can be rewritten in the following way:

$$2\left(\frac{\mathrm{d}}{\mathrm{n}}\right)\sin\theta_{\mathrm{n}}=1\lambda_{0},\tag{13}$$

which can be formally interpreted as a first-order reflection from a set of crystallographic planes with an interplanar spacing d/n.



FIG. 11. The principle of an X-ray or neutron crystal spectrometer.



FIG. 12. Real and "formal" interplanar spacings.

Let us now suppose that d is the interplanar spacing of a set of crystallographic planes (hkl). Remember that hkl do not have a common factor. Then using Eq. (8) we obtain

$$\frac{d_{hkl}}{n} = \frac{1}{\sqrt{\left(\frac{nh}{a_1}\right)^2 + \left(\frac{nk}{a_2}\right)^2 + \left(\frac{nl}{a_3}\right)^2}}$$
(14)

and we could write formally

$$\frac{d_{hkl}}{n} = d_{nh, nk, nl}$$
(15)

remembering, however, that $d_{nh, nk, nl}$ does not mean a <u>real</u> interplanar spacing, but one of the kind shown in Fig.12. However, taking into account Eq.(11), we obtain

$$\frac{d_{\mathbf{hkl}}}{n} = \frac{1}{\tau_{\mathbf{n}\mathbf{h},\mathbf{n}\mathbf{k}\mathbf{l},\mathbf{n}\mathbf{l}}}$$
(16)

where, as shown in section 3.2, $\overrightarrow{\tau}_{nh, nk, nl}$ corresponds to a reciprocal lattice point (nh, nk, nl). This means that a reciprocal lattice point (nh, nk, nl) represents the nth order reflection ("higher-order reflection"⁴) from the (hkl) crystallographic plane. The term "(nh, nk, nl) reflection" will from now on be used in this sense, e.g., reflection (3915) will mean the third-order reflection from the (1 3 5) crystallographic plane.

3.4. Ewald's construction [2,4]

Let us now look at the Bragg equation, taking into account the corpuscular properties of the X-ray photon or the neutron. Both the photon and the neutron have a momentum $\hbar \vec{k}$ where \vec{k} is the wave vector of the photon $(2\pi/\lambda)$ or the neutron $(2\pi/\lambda = mv/\hbar)$. Figure 13 shows how the direction of the momentum of the photon or neutron changes in the process of a Bragg reflection. The Bragg reflection takes place without change of wave-length such that

$$k_0 = k_i$$

which means that the energy of the photon or neutron has not changed in this process and the crystal lattice has neither gained nor lost any energy.

The law of momentum conservation leads, however, to the conclusion that the crystal has transferred to the photon or neutron the momentum

$$\hbar \vec{Q} = \hbar \vec{k} - \hbar \vec{k}_0$$
(17)



FIG. 13. The momentum change of neutron or the X-ray photon in a Bragg reflection,

⁴ See end of section 3.5.

With the help of Fig. 13 and the Bragg equation

 $2d_{bkl}\sin\theta_{B} = n\lambda_{0}$

where $\lambda_0 = 2\pi/k_0$, we obtain

$$Q = \frac{2\pi n}{d_{hkl}}$$

or, using Eq. (16),

 $Q = 2\pi \tau_{nh nk nl}$

Remembering that the vector $\vec{\tau}_{nhnknl}$ is perpendicular to the crystallographic plane (hkl), we see immediately from Fig. 13 that the vectors \vec{Q} and $\vec{\tau}$ have the same direction and, therefore,

$$\vec{Q} = 2\pi \vec{\tau}_{nh nk n!}$$

or

 $\hbar \vec{Q} = 2\pi \hbar \vec{\tau}_{nh nk nl}$ (18)

Equation (18) leads to the physical meaning of the reciprocal lattice vector $\vec{\tau}_{hkl}$ (where hkl may have a common factor): the reciprocal lattice vector multiplied by $2\pi\hbar$ represents the momentum which is, must and can be transferred by the lattice to the photon or neutron whenever a Bragg reflection occurs. In this sense the reciprocal lattice vectors (multiplied by $2\pi\hbar$) form a discrete set of momenta which can be supplied by the lattice without change of its energy. For this reason, the reciprocal lattice represents a momentum space. Whenever this will not lead to confusion it will be assumed $\hbar = 1$ and \vec{k}_0 , \vec{k} , \vec{Q} , $2\pi\vec{\tau}$ will be simply called momentum. The symbols d_{hkl} and (hkl) will also be used with regard to the restriction that they have no common factor. However, d_{hkl} will mean $1/\tau_{hkl}$ (and not necessarily the real interplanar spacing) and hkl will mean a reflection only (and not the Miller indices of a crystallographic plane). To avoid confusion we shall use the symbol (hkl) to denote a crystallographic plane and the symbol hkl (without parentheses) for a reflection.

The above considerations lead to the Ewald construction, enabling one to find in an easy way the directions in which a Bragg reflection should occur. Figure 14, with a momentum diagram in the two-dimensional reciprocal lattice, is closely related to Fig. 13 in real space. $\vec{k_0}$ pointed to the origin of the reciprocal lattice (point 000) represents the direction and momentum of the incident photon or neutron. The circle has a radius $k_0 = k$. Whenever the circle crosses a reciprocal lattice point the law of momentum conservation is fulfilled and one gets a reflection. On Fig. 14 it takes place for one reciprocal lattice point marked hkl. The circle is called an Ewald circle. In the case of a three-dimensional lattice we have an Ewald sphere instead of a circle. If several reciprocal lattice points are lying at the sphere several reflections will occur.

Using the Ewald construction (Fig. 15 - the Ewald circles are not shown explicitly) it is possible to explain the existence of higher-order

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FIG. 14. The Ewald construction in the two-dimensional reciprocal lattice.



FIG. 15. The Ewald construction explaining higher-order reflections of a monochromatic neutron (or X-ray) beam.

reflections of a monochromatic beam under different Bragg angles discussed previously in section 3.3. We see that in the case presented in Fig.15 the reflections 111, 222 and 333 are possible; however, higher-order reflections will not occur because $2k_0 < 2\pi\tau_{444}$.



FIG. 16. The available part of the Maxwellian spectrum of neutrons and wave-length of higher-order reflections $\left(\frac{\lambda_1}{2}, \frac{\lambda_1}{3}, \frac{\lambda_1}{4}\right)$ of a polychromatic neutron beam diffracted under a fixed angle.



FIG. 17. The Ewald construction explaining higher-order reflections (222, 333, 444) of a polychromatic neutron beam diffracted under a fixed angle.

3.5. Single crystal monochromators [3, 4, 5]

When a "white" (polychromatic) beam of neutrons (X-rays) is reflected from a single crystal under a fixed angle of incidence θ_0 then the reflected beam will contain neutrons (X-rays) of wave lengths λ_{hkl} fulfilling the Bragg equation

$$2d_{hkl} \sin\theta_0 = \lambda_{hkl} \tag{19a}$$

Let us suppose that the polychromatic beam contains wave lengths between λ_{min} and λ_{max} (Fig. 16) of a Maxwellian spectrum of neutrons.

 λ_{\min} corresponds to k_0^{\max} and λ_{\max} to k_0^{\min} . Let us make the Ewald construction (Fig. 17) for k_0^{\min} (the smallest circle). The circle does not cross any reciprocal lattice point – no reflection occurs. Let us now continuously increase the radius of the circle up to k_0^{\max} . For k_1 , k_2 , k_3 and k_4 it will happen that the Ewald radius crosses the reciprocal lattice points 111, 222, 333 and 444. This means that in the direction shown by $\vec{k_1}$ (it is the same as for $\vec{k_2}$, $\vec{k_3}$ and $\vec{k_4}$) one will observe reflections 111, 222, 333 and 444. They correspond to wave lengths λ_1 , $\lambda_1/2$, $\lambda_1/3$, $\lambda_1/4$ on Fig. 16. They are also called higher order reflections, but they are not of the same nature as those discussed in para.3.3. There we had a monochromatic beam and we were changing the angle of incidence; here we deal with a polychromatic beam and the angle of incidence is fixed.

The discussion above shows that by Bragg reflection from a single crystal one does not obtain a truly monochromatic beam. It is always contaminated by higher-order reflections. However, methods exist of decreasing or removing the higher-order reflections.

4. STRUCTURE ANALYSIS

4.1. Introductory remarks

To know the crystal structure means in general terms to know:

- a) The unit cell (the basic vectors \vec{a}_i);
- b) The kinds and positions (x_j, y_j, z_j) of all atoms A_j in the unit cell (Fig. 7);

c) The mean square displacements of all atoms $A_{\rm j}$ in the unit cell. Knowing a) and b) we can ascribe an appropriate space group to each structure to be studied.

For the knowledge of the magnetic structure it is necessary to know in addition the direction and values of the magnetic moments $\vec{\mu_j}$ of all paramagnetic atoms (ions). It may happen that the crystal unit cell is different from the magnetic unit cell.

Crystal and magnetic structure analysis can be performed using single crystals or powered crystal. As a general rule, the single-crystal methods are more precise than the powder methods, however, it is often difficult to obtain the sample in the form of a single crystal.

We shall first discuss single-crystal methods and afterwards powder methods. No detailed description of the methods or techniques applied will be given. Only the principles will be outlined and the general "philosophy" mentioned.

4.2. Structure analysis using single crystals

4.2.1. Crystal spectrometer method (rotating crystal method)

4.2.1.1. X-rays [1,2]

Figure 18 shows schematically the principles of an X-ray spectrometer applied to single crystal structure analysis using the rotating crystal method. A monochromatic X-ray beam of wave length λ_0 is scattered on a single crystal which is slowly (or stepwise) rotating around


FIG. 18. The principle of an X-ray spectrometer for single crystal structure analysis.



FIG. 19. Reflections (a) and their intensities (b) along the $2\theta_{hkl}$ "axis" obtained using the X-ray spectrometer shown in Fig. 18.

the axis perpendicular to the plane of the figure. Whenever the Bragg equation

$$2d_{hkl} \sin\theta_{hkl} = \lambda_0 \tag{19b}$$

for a certain set of hkl planes is fulfilled (and the structure factor is not equal to zero - see sub-section 4.2.1.2) the incident X-ray beam is reflected and its intensity recorded by the X-ray film. Figure 19 shows schematically the recorded reflections (dark lines) and their intensities measured along the $2\theta_{hkl}$ "axis" by means of a photometer. Measuring θ_{hkl} one can - with the help of Eq.(19) - obtain a set of d_{hkl} values. By rotating the crystal round another zone⁵ axis it is possible to obtain another set of dhkl values. Elaborate techniques already exist for calculations of the basic vectors \vec{a}_i of the unit cell and the indices of the observed reflections from the measured sets of d_{hkl} values (also taking into account the presence or absence of some reflections). From X-ray diffraction patterns, as shown in Fig. 20, one can also (after subtracting the background) measure the areas under the peaks (e.g. the shadowed part of the peak 010). As will be briefly explained later (sub-section 4.2.1.2), the knowledge of the areas under the peaks enables one to calculate the positions of atoms in the unit cell.

The formation of reflections in the rotating crystal method can be better understood with the help of the reciprocal lattice and the Ewald

⁵ Crystallographic planes of different (hkl) parallel to a straight line form a crystallographic zone; this straight line is called zone axis.



FIG. 20. The Ewald construction explaining the rotating crystal method.

construction. The Ewald circle in Fig. 20 has the radius k_0 and is fixed in the laboratory system. The reciprocal lattice is, however, rotating in this system about the axis perpendicular to the plane of the figure and crossing this plane at point 000 Each point of the reciprocal lattice moves round a circle as shown in Fig. 20. The crossing point of this circle and the Ewald circle represents a reciprocal lattice point (at a certain position of the rotating crystal) for which a Bragg reflection occurs. As can be seen in Fig. 20 (for the particular lattice represented there), the following reflections will be observed: 010, 100, 110, 020, $\frac{1}{120}$, etc. They can be seen in the directions of $\vec{k_1}$, $\vec{k_2}$, $\vec{k_3}$ etc., and $\vec{k_1}$, $\vec{k_2}'$, $\vec{k_3}'$ etc. If, starting from point 000, which is the centre of rotation, straight lines parallel to $\vec{k_1}$, $\vec{k_2}$, $\vec{k_3}$... and $\vec{k_1}'$, $\vec{k_2}'$... are drawn, then the points of interception of these lines with the X-ray film will indicate the position of reflections on the film (compare Figs. 19 and 20).

4.2.1.2. Neutrons [4,7,8]

The rotating crystal method using neutrons was developed about twenty years ago and was based on the already known method for X-rays as outlined above. Figure 21 shows schematically the principles of a neutron crystal spectrometer (we shall call it double crystal spectrometer or,



FIG. 21. The principle of a neutron crystal spectrometer for single crystal studies.

for short, DAS) for single crystal studies by means of the rotating crystal method. Since the reflected neutrons are recorded, not by a film covering the whole range of angles 2θ , but by a neutron counter located on the spectrometer's arm (not shown on the figure) both the crystal and the arm must be rotated. Only when both the counter and the crystal are in a position fulfilling the Bragg equation the diffracted beam can be both produced and reflected. Thus, if the counter arm is set for automatic rotation with the crystal synchronized to follow with half the angular velocity, the record will include only successive orders of reflection from a <u>single</u> set of parallel planes, for example the reflections 310, 620, 930, etc. To record other reflections in the same zone, such as 220, 440, 660, etc. it is necessary to make a different adjustment of the azimuthal

setting of the crystal in relation to the counter. Methods exist nowadays for doing this completely automatically. Figure 22 shows an example of a single crystal diffraction pattern of potassium bromide.

It can be shown that in the rotating crystal method the areas I_{hkl} under the peaks (see Fig. 19) fulfil the following equation:

$$I_{hkl} = const \left[\frac{|F|^2}{sin2\theta} \right]_{hkl}$$
(20)

where F_{hkl} is the structure factor for the hkl reflection and $2\theta_{hkl}$ the scattering angle for this reflection. As is well known, the structure



FIG. 22. An example of a single-crystal diffraction pattern of potassium bromide (G. Bacon, Ref. [4], p. 83).

factor F_{bk1} is equal to

$$F_{hkl} = \sum_{\substack{\text{unit} \\ \text{cell}}} f_j e^{2\pi i \left(\frac{hx_j}{a_1} + \frac{ky_j}{a_2} + \frac{1z_j}{a_3}\right)}$$
(21)

where f_j is the scattering amplitude for the jth nucleus (magnetic scattering will not be discussed - see Refs [4, 7, 8]).

For a particular symmetry of the crystal, F_{hkl} can be equal to zero for certain values of hkl and if this happens no reflection hkl appears. Thus the presence or absence of certain reflections is one of the clues which helps to solve the problem of crystal structure. Another important piece of information is supplied by the measured areas under the peaks. As can be seen from Eq. (20), by measuring I_{hkl} and θ_{hkl} one obtains

$$|F_{hkl}|_{o}^{2} = const. I_{hkl} sin2\theta_{hkl}$$
 (22)

where subscript "o" means observed or measured. Many practical techniques exist to deduce the structure of the crystal from the measured positions of the peaks and their intensities [7]. However, they cannot be described in this kind of brief review; here only the general "philosphy", which leads to the values x_j , y_j and z_j of the atoms in the unit cell will be briefly outlined.

We assume a model of the unit cell and calculate - using formula (21) - the structure factors for that model and afterwards the reliability factor R defined as

$$\cdot \sum_{hkl} \left| |\mathbf{F}_{c}|^{2} - |\mathbf{F}_{o}|^{2} \right|$$

$$\mathbf{R} = \frac{hkl}{\sum_{hkl} |\mathbf{F}_{0}|^{2}}$$

$$(23)$$

where subscript "c" means calculated. Finally, the factor R is minimized by appropriate changes of x_j , y_j and z_j ; that means by changing the model of the unit cell. The values of x_j , y_j and z_j which give R_{min} (usually

 $R_{min} \simeq 1-5\%$) are supposed to describe the correct positions of the atoms in the unit cell. In this way, the structure is assumed to be solved.

Formula (20) is not exact in the sense that the "constant" appearing there usually depends also on θ_{hkl} . Therefore several corrections should be introduced (extinction, absorption, etc.). For details see Refs [4, 7]. The "constant" also contains the Debye-Waller factor, which depends on θ_{hkl} , too, and takes into account the mean square displacements of the atoms due to thermal motion. The procedure of minimizing R should include also the Debye-Waller factor and in that way mean square displacements of all atoms are becoming known.

For complicated structures with many atoms in the unit cell, many reflections (sometimes of the order of 10000) are needed in order to solve the structure. They are taken from a number of zones. As mentioned before, the process of collecting data is nowadays fully automatic and the handling of data is done by modern computers.



FIG. 23. The principle of the TOF method for structure studies of single crystals.

4.2.2. Time-of-flight method [9]

This method has been developed recently and is an application of the TOF method described in section 2.3.2 to structure analysis of single crystals. Figure 23 illustrates the principle of the method. A pulsed⁶ collimated polychromatic neutron beam is scattered on a single crystal sample with its zone axis perpendicular to the plane of the figure. Their intensities are measured by a circular type detector connected to a multichannel time analyser, which - as is known from section 2.3.2 - segregates the reflections (peaks) according to the reflected wave-lengths. Figure 24 shows an example of a neutron pattern of an aluminium single crystal with its zone axis [110] perpendicular to the plane of the experiment. Because the angle $\Delta \theta$ (Fig. 23) was only about 50°, only several peaks are visible. Using the reciprocal lattice and the Ewald construction it is easy to find what reflections would be recorded for $\Delta \theta = 2\pi$. This is shown in Fig. 25. If BO represents the length of the smallest k_{min}^0 vector represented in the pulsed polychromatic beam (corresponding to the largest wave-length) and AO is the largest k_{max}^0 vector represented in the beam (corresponding to the smallest wave-length) then the reciprocal lattice points in the

⁶ A pulsed polychromatic neutron beam can be obtained at steady state reactors by means of a chopper as shown in Fig. 23 (see section 2.3.2). A pulsed reactor is another (very intense) source of polychromatic neutron pulses [9].



FIG. 24. An example of a neutron pattern of an aluminium single crystal with its zone axis [110] perpendicular to the plane of the experiment obtained using the TOF method.



FIG. 25. The Ewald construction explaining the TOF method for single-crystal structure analysis for $\Delta \theta = 2\pi$ (see Fig. 23).

shadowed area correspond to the reflections to be recorded. For a $\Delta \theta$ angle as shown in Fig. 23, the picture in the reciprocal lattice will be like that in Fig. 26.

There is a technique of indexing the peaks recorded by this method and of calculating the respective d_{hkl} values. Computation of the observed structure factors can be carried out by means of Laue's formula

$$I_{hkl} = \text{const.} [i(\lambda) \lambda^2 d^2 | F|^2]_{hkl}$$
(24)

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FIG. 26. The Ewald construction explaining the TOF method for single crystal structure analysis for $\Delta \theta = 2(\theta_{max} - \theta_{min})$.

where $I_{hkl}\,$ is the area under the peak (after subtraction of background), $i(\lambda)$ the neutron flux per unit interval of wave length, λ is the neutron wave length, d is the interplanar spacing, F the structure factor and the subscript hkl indicates that the quantities are connected to the hkl reflection.

The further procedure of solving the structure is similar to that described in section 4.2.1 and similar corrections must be taken into account. It should be clear, however, that, in the TOF method, in order to solve the structure it is necessary, as can be seen from formula (24), to know the spectral distribution $i(\lambda)$ of the incident neutron beam.

The main advantages and disadvantages of the TOF as compared with the rotating crystal method will be discussed briefly in section 4.4. At that point it should be said only that the TOF method is especially suitable for searching for reflections in a certain direction in the reciprocal space. In that case $\Delta\theta$ (see Fig. 23) must be very small and the picture in the reciprocal lattice is, in principle, the same as shown in Fig. 17. Figure 27 shows the diffraction pattern for the [010] direction in chromium. We see the reflections 020, 040, 060, 080 and, in addition, on both sides of the forbidden reflection (structure factor equals zero) 010 two reflections S₁ and S₂ called "satellites". They are of a magnetic nature and disappear at temperatures higher than the Néel temperature of chromium.

4.3. Structure analysis using powdered crystals

4.3.1. Crystal spectrometer method (DAS)

The experimental set-up for this method is very similar to that shown schematically in Fig. 21; however, instead of a single crystal



FIG. 27. Neutron diffraction pattern for the [010] direction in chromium obtained using the TOF method (B. Buras et al., Phys. Stat. Sol. 11 (1965)567).



FIG. 28. An example of a powder $(MgFe_2O_4)$ neutron diffraction pattern obtained by the DAS method (L. M. Corliss et al., Phys. Rev. <u>90</u> (1953)1013).

sample a powdered crystal sample is put on the table of the spectrometer, and the arm of the neutron detector is not coupled with the table of the sample, as it is in the case of the rotating-crystal method. The arm of the spectrometer, with the neutron detector, are rotated stepwise and the neutrons scattered by the polycrystalline sample are recorded. Figure 28 shows an example of a powder neutron diffraction pattern.

The formation of reflections in this case can be easily understood with the help of the reciprocal lattice. Let us look at Fig. 20 and imagine that the reciprocal lattice is rotating not only about the axis perpendicular to the plane of the figure, but also about other axes going through point

000 This means, however, that the position of the reciprocal lattice in the laboratory system is random. And this is, of course, the case when a polycrystalline (powdered) sample is studied. This will mean that all reciprocal lattice points are distributed at radom on spheres.

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The interception of each of these spheres with the Ewald circle represents a reciprocal lattice point for which a Bragg reflection occurs. In this sense the picture will be very similar to that shown in Fig. 20 with one important difference. In the rotating-crystal methods only reflections from one zone and in the powder method reflections from all zones can be recorded. This may look, at first glance, like an advantage; however, this is really a disadvantage because most of the peaks overlap and finally only a limited number of reflections can be used for structure analysis. Consequently the information obtained by means of the powder method is not so accurate as that for single crystals.

The procedure for indexing the peaks is similar to that for the single crystal method. In this case, the Bragg equation

$$2d_{hkl} \sin \theta_{hkl} = \lambda_0 \tag{25}$$

is used. The intensities of the peaks (areas under the peaks) lead to the measured values of structure factors; however, the formula is different in this case from that for single crystals and reads as follows:

$$I_{hkl} = const. \left[\frac{j |F|^2}{\sin\theta \sin 2\theta} \right]_{hkl}$$
(26)

where F and θ have the same meaning as before, and j is the multiplicity factor which gives the number of equivalent (hkl) planes. The procedure for solving the structure is, in general, similar to that outlines in section 4.2.

4.3.2. Time-of-flight method (TOF) [9]

Figure 29 illustrates the principle of the method. A pulsed polychromatic neutron beam is scattered on a powdered crystal sample and the intensity of the scattered neutrons at a fixed angle $2\theta_0$ is measured by means of a neutron counter connected to a multichannel time analyser. Whenever the Bragg equation

$$2d_{hkl} \sin\theta_0 = \lambda_{hkl} \tag{27}$$

is satisfied for a certain neutron wave-length contained in the polychromatic beam, neutrons with that wave-length are scattered in the direction of the counter and recorded by the multichannel time analyser. Therefore to each d_{hkl} a corresponding λ_{hkl} , in accordance with Eq. (27), can be ascribed. But, as is known from section 2.3.2,

$$\lambda_{hkl} = \frac{h}{mv_{hkl}} = \frac{h}{ml} t_{hkl}$$
(28)

where 1 is the distance between the neutron source and the sample counter. Finally Eqs (27) and (28) lead to

$$d_{hkl} = \frac{h}{2ml \sin\theta_0} t_{hkl}$$
(29)



FIG. 29. The principle of the TOF method for powdered samples.



FIG. 30. An "early" neutron diffraction pattern of powdered silicon obtained using the TOF method with a chopped neutron beam from a steady-state reactor.

which shows that a very simple relation exists between d_{hkl} and the time t_{hkl} at which the time analyser records the intensity of the hkl reflection. Figure 30 shows a neutron pattern obtained in the early days of the TOF method using a chopped neutron beam from a steady state reactor.

Figure 31 shows the arrangement for this method used at the IBR pulsed reactor at the Joint Institute of Nuclear Research at Dubna (see Ref.[10]). Scattering angles of 52° and 90° were used, the flight path was about 18m, and the average power of the reactor several kW (peak power about 20 MW). Figure 32 shows a typical neutron pattern obtained with this arrangement.

As in other methods, the structure factors can be calculated with the help of the formula for integrated intensity. For this method the following formula must be used:

$$I_{hkl} = const [i(\lambda) \lambda^3 j] F^{2}_{hkl}$$
(30)



FIG. 31. The arrangement at the IBR reactor at Dubna used for neutron structure studies of powdered samples by means of the TOF method (A.C. Dariewski et al., Report No. 2411, JINR Dubna (1965). 1) Reactor core; 2) moderator; 3) collimators; 4) scintillation counters; 5) neutron (vacuum) guide tube; 6) sample; 7) concrete shielding; 8) water shielding.



FIG. 32. A typical neutron pattern obtained at the IBR reactor using the TOF method (powdered silicon).

Here also, as for the TOF method for single crystals, the incident neutron spectrum $i(\lambda)$ must be known.

This method was developed several years ago and several laboratories are already using it for structure analysis.

4.4. Crystal spectrometer methods (DAS) vs. TOF methods for structure analysis

Crystal spectrometer methods have almost half a century's tradition in X-ray crystal structure analysis and have been used for about twenty years for neutron structure determination. The TOF is very young (it started for powders in 1963 and for single crystals in 1965); therefore

		DAS .	TOF
Neutron beam		Monochromatic	Polychromatic
Necessary to measure		λο	i(X)
High-order contaminations arising from monochromatization		Present (can be removed by special measures)	Absent
Neutron flux of the incident beam		Constant	Pulsed
Sample seen by the neutrons		The whole time of the measurement	During short periods of time (stroboscopic method)
The measured distribution of scattered neutrons		Angular	Spectral
Geometry of the experiment		Changes in the course of measurements	Fixed
Reflection measured		One after another	Simultaneously
Resolution high for		Small interplanar spacings	Large interplanar spacings
intensity	Steady state reactor	Comparable	
	Pulsed reactor		High

TABLE II. MAIN FEATURES OF THE DAS AND TOF METHODS

it is not so highly developed as the DAS method. Table II presents the main features of both types of methods, and Fig. 33 shows how the resolution in the DAS and TOF methods depends on the interplanar spacing. Note the very good resolution obtained with the TOF method used at the IBR reactor. Which method should be used will always depend on the problem to be studied. Those interested in a more detailed comparison BURAS



FIG. 33. Resolution versus interplanar spacing for the DAS and TOF methods (L. H. Schwartz, Nucl. Instrum. Meth. 42 (1966)82; the curve D^{TOFX} for the BR reactor added by the author of this contribution.

of the methods and in some special applications of the TOF method will find some additional information in Refs [11] and [12].

5. LATTICE DYNAMICS STUDIES [3, 5, 13-15]

5.1. Introductory remarks

In this brief review only the main methods for phonon frequency distribution measurements and dispersion relation measurements will be discussed. Other methods as, for example, for magnon dispersion relation measurements or critical scattering studies, will be omitted; however, some of the methods discussed here can be applied to those studies.

Let us, using the reciprocal lattice, look first at energy and momentum relations for inelastic scattering of neutrons. In Fig. 37 \vec{k}_0 is the wave vector of the incident neutron, \vec{k} the wave vector of the inelastically scattered neutron, \vec{q} the wave vector of the phonon which takes part in this process (only single-phonon processes will be discussed) and $2\pi\vec{\tau}$, as usual, is the reciprocal lattice vector. The law of conservation of momentum gives the following equation:

$$\vec{k}_0 - \vec{k} = 2\pi \vec{\tau} + \vec{q}$$
 (31)

and the law of conservation of energy leads to

$$\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 k_0^2}{2m} = \epsilon \hbar \omega, \qquad (32)$$

where $\hbar\omega$ is the energy of the phonon and ϵ equals +1 or -1 for phonon annihilation or phonon creation processes, respectively.

The frequency ω of the phonon and its wave vector \vec{q} are related by the dispersion relation

$$\omega = \omega_i \left(\vec{q} \right) \tag{33}$$

which specifies the frequency ω in terms of its polarization <u>i</u> and wave vector \vec{q} .

Knowing the values of $\vec{k_0}$ and \vec{k} and their directions with respect to one another and to the crystal lattice, we can easily - with the help of Eq. (31) and the reciprocal lattice diagram (Fig. 34) - find both the



FIG. 34. Conservation of a momentum for the phonon creation process in the reciprocal lattice.



FIG. 35. Principle of a triple axis spectrometer (TAS).

direction and the value of the momentum \vec{q} of the phonon. From Eq. (32) it is possible to find the frequency of the phonon and in this way to know both the momentum and frequency of the phonon. If this is done for a number of phonons propagating in a certain direction we obtain the dispersion curve for phonons travelling in that direction. This shows that neutron measurement can supply direct information on dispersion relations.

- For this type of measurements it is in general necessary
- a) to produce neutrons with a known wave vector \vec{k}_0 ;
- b) to measure \overline{k} (both value and direction);
- c) to have the possibility of changing the angles between \vec{k}_0 and \vec{k} and also between \vec{k}_0 (or \vec{k}) and the single crystal.

There are a number of methods by which these requirements can be met. They can be divided into two categories:

i) utilizing neutron crystal spectrometers at steady-state reactors;

ii) utilizing the TOF method and a pulse source (a steady-state reactor with a chopping device or a pulse reactor).

Dispersion relation measurements can be made for single crystals scattering coherently (at least partly). For frequency distribution $\omega(q)$ measurements, pure incoherent scatterers are ideal; however, an admixture of coherent scattering is tolerable. In general, for such measurements only polycrystalline samples are needed.

In the following sections the main methods will be briefly discussed.

5.2. The neutron crystal spectrometer method [3]

5.2.1. The triple-axes spectrometer (TAS)

Figure 35 shows schematically a triple-axes crystal spectrometer. By changing the angle $\theta_{\rm M}$ it is possible to change k₀; by a proper setting of the table of the sample (angle ψ) one obtains the desired angle between \vec{k}_0 and a certain (hkl) plane of the single crystal to be studied; by rotating the second arm the angle Φ between \vec{k}_0 and \vec{k} can be changed and by rotating the third arm (with single crystal analyser synchronized to follow with half the angular velocity) the scattered neutron beam in the direction \vec{k} can be analysed. This shows a very great flexibility of the triple-axes spectrometer; however, because the neutron beam is scattered by three crystals, the final intensity measured by the counter is usually not very high and therefore much effort is needed to keep the background low. Because all quantities needed to solve Eqs (31) and (32) can be measured by means of the described triple axes spectrometer, one can obtain the frequencies ω and corresponding momenta \vec{q} of phonons. However, the directions of the phonons will be, in general distributed at random in the reciprocal lattice and, in addition, their energies may not cover the range necessary to draw dispersion curves. For this reason, several techniques already exist to ensure a quick and automatic collection of data of phonons enabling dispersion curves to be obtained both for acoustical and optical phonons. Those interested in these techniques will find more detailed information in Refs [3, 13-15]. Figure 36 shows a typical picture of phonon dispersion relations obtained by this method.

5.2.2. The neutron crystal spectrometer with a polycrystalline filter in front of the detector

Figure 37 shows schematically this type of apparatus. A collimated polychromatic neutron beam from the reactor is monochromatised by the single crystal M and is scattered by the sample. The scattered beam is passing a polycrystalline filter (e.g., Be filter) and is recorded by a counter (or set of counters).

As is known, a polycrystalline filter lets through all neutrons with wave lengths larger than $2d_{max}$ (where d_{max} is the maximum interplanar spacing of the crystal used as a filter) because those neutrons cannot be reflected by any plane of the crystal. Neutrons with wave length smaller. than $2d_{max}$ will be reflected by the polycrystalline sample in all directions



FIG. 36. A typical picture of phonon dispersion relations (for a single crystal of silicon) (G. Dolling, Ref. [14] 2 41).



FIG. 37. Principle of a crystal spectrometer with a polycrystalline filter in front of the detector.

and finally absorbed by the walls of the filter. For beryllium d_{max} equals approximately 4 Å which corresponds to 5 meV. Figure 38 shows the neutron spectrum before and after passing a beryllium filter. The spectrum obtained is called "edge spectrum". The mean energy of neutrons obtained in this way is about 3 meV.

Taking this into account, it is reasonable to assume that in the set-up presented in Fig. 38 the neutrons which reach the counter have a fixed energy of about 3 meV. In this sense, k is also fixed. k_0 can be changed continuously by changing θ_M , the angle Φ and the orientation of the crystal could also be changed. Thus, in principle, this arrangement could be used for measurements of phonon dispersion relations. However, the resolution would be very poor and therefore it is used only for frequency distribution g(ω) measurements.

As mentioned before, pure incoherent scatters are ideal for such measurements. This will be illustrated in a simple example. The double differential cross-section for inelastic incoherent scatters for a monatomic substance with a cubic structure has a very simple form:

$$\frac{\mathrm{d}^2 \sigma^{\mathrm{inc}}}{\mathrm{d}\Omega \mathrm{dE}} \sim \frac{\mathrm{k}}{\mathrm{k}_0} \frac{\mathrm{Q}^2}{\omega} \frac{\mathrm{e}^{-2\mathrm{W}}}{\mathrm{e}^{\hbar\omega/\kappa\,\mathrm{T}} - 1} g(\omega) \tag{34}$$



FIG. 38 The neutron spectrum before and after passing a beryllium filter.



FIG. 39. An example of energy distribution of neutrons scattered by NH_4I at -150°C measured using the arrangement shown in Fig. 37. (K. Mikke, A. Kroh, Ref. [14], 2 243).

where

$$\vec{Q} = \vec{k} - \vec{k}_0$$

and $\exp(-2W)$ is the Debye-Waller factor. From Eq. (33) it is evident that by measuring the differential cross-section as a function of k_0 (k is fixed in this experiment) we can - with the help of Eqs (32) and (34) calculate the frequency distribution $g(\omega)$. Figure 39 shows an example of energy distribution of neutrons scattered by NH₄I (-150°C) measured by the method described above. From this energy distribution the frequency distribution could be calculated.

5.3. The TOF methods [3]

5.3.1. The TOF methods using a monochromatic incident beam

5.3.1.1. Filter method

Figure 40 shows schematically the arrangement using a semimonochromatic incident neutron beam obtained by means of a filter



FIG. 40. Principle of an arrangement for neutron inelastic scattering studies using "cool" neutrons and the TOF technique.

(see section 5.2.2). This beam is chopped by means of a chopper (usually with curved slits in order to secure a good transmission of long wavelength neutrons) and scattered at the sample. The scattered neutron beam is analysed by the time-of-flight method (see section 2.3.2.). k_0 in this method is fixed, but the orientation of the crystal (angle ψ) and the angle φ between \vec{k}_0 and \vec{k} can be changed. This enables us to measure both phonon dispersion relations and frequency distributions. Since the energy of the incident neutrons is very small ("cold neutrons") only processes involving phonon annihilation can be measured. Not all techniques which enable a quick and automatic collection of data needed for phonon dispersion relations can be applied to this method. Nevertheless, it is often used, especially on medium neutron flux reactors.

This method can also be used at a pulsed reactor and in that case, of course, the chopper is not needed. However, at pulse reactors other methods are more powerful (see sub-sections 5.3.2.1. and 5.3.2.2.).

5.3.1.2. Mechanical monochromator method [3.13-15]

Figure 41 gives a general idea of this method. A polychromatic collimated neutron beam from a steady-state reactor is chopped by means of a rotating disc. As can be seen from Figures 6a and 6b and the discussion in section 2.3.2., the spectral distribution of neutrons in the beam at point C (very close to the rotating disc II) will have the shape as shown in the lower left corner of Fig. 41. Because the rotating disc II lets the neutrons through only in a short interval of time, $\delta_2 t$, the spectrum of the neutrons at point D will be as shown in Fig. 41. That means the neutrons will be monochromatic with a certain spread of wave-length depending on $\delta_2 t$ and the distance between the two rotating discs. By a proper choice of the time interval between the moments when the beam is passing disc I and disc II, the desired wave-length of the monochromatic beam can be obtained. Such an arrangement, as described above, is called a mechanical monochromator. The technical details of mechanical monochromator can be quite different from what is shown on Fig. 41; however, the main idea is always the same.



FIG. 41. Principle of mechanical monochromator method for neutron inelastic scattering studies.

The monochromatic beam is scattered on a sample and the scattered neutrons are analysed by the time-of-flight method. Several detectors and several multichannel analysers can be used (this applies also to the arrangement described in sub-section 5.3.1.1.). Similar comments can be made as in sub-section 5.3.1.1.; however, using this arrangement, a better resolution is usually obtained on account of the lower intensity.

A mechanical monochromator can also be applied to a pulsed reactor. In this case the monochromator should be synchronized with the pulsing device of the reactor.

5.3.1.3. Rotating crystal [3, 13-15]

This method of obtaining monochromatic neutron pulses is illustrated in Fig. 42. A polychromatic collimated neutron beam is reflected under the scattering angle $2\theta_B$ from a rotating single crystal. Reflection takes place only when the Bragg equation is fulfilled.

$$2d_{hkl} \sin\theta_B = \lambda_{hkl}$$
 (35)

which happens (the crystal rotates!) only for short periods of time. In that way a pulsed monochromatic (with some higher-order contaminations – see section 3.5) neutron beam is obtained. The remaining part of the apparatus is similar to that described in sub-sections 5.3.1.1. and 5.3.1.2.

The rotating crystal can be - at least in principle - used at a pulsed reactor in order to obtain monochromatic neutrons and to shorten the



FIG. 42. Principle of the rotating crystal method for neutron inelastic scattering studies.

neutron pulse. In this case the rotation of the crystal should be synchronized with the pulsing device of the reactor.

5.3.2. The TOF methods using a polychromatic incident beam [11, 12]

5.3.2.1. TOF spectrometer with a beryllium filter and crystal monochromator in front of the counter [11, 12, 16]

Figure 43 shows the principle of this arrangement. A pulsed polychromatic neutron beam (from a pulsed reactor or a steady state reactor equipped with a chopper) is scattered on a sample. The scattered beam goes through a beryllium filter, is reflected by a single crystal (set for a Bragg reflection of neutrons of about 4 Å wave-length in order to increase the resolution) and recorded by a neutron counter connected to a multichannel time analyser. This arrangement is similar to that shown in Fig. 37 and described in section 5.2.2. The principal difference is the following. In the set-up presented in Fig. 37 the wave-length of the incident neutron beam is performed by changing the angle θ_M and therefore for a certain value of k_0 the whole arrangement must be put in a certain position (by rotating the arm of the spectrometer on which both the sample and the filter, together with the counter, are located). This means that measurements are performed step-wise, point by point. In the set-up shown in Fig. 43 the value of the wave vector \vec{k}_0 at point A (that means when the neutron is scattered) is a function of time. Thus, the multichannel time analyser records the intensity distribution of the scattered neutrons for continuously changing wave vectors of the incident neutron beam. The full spectral distribution of the scattered neutrons is in this way measured in one run. Such an arrangement is working very satisfactorily at the IBR reactor at Dubna (see Ref. [16]); it is used for frequency-distribution measurements.

5.3.2.2. TOF spectrometer for dispersion relation measurements [17]

The principle of an arrangement similar to that described in subsection 5.3.2.1. - but meant for dispersion relation measurements - is shown in Fig. 44. The direction of $\vec{k_0}$ is fixed, but its value is a function of time. The orientation of the crystal (angle ψ) and the direction of \vec{k} (angle Φ) can be changed by rotating the crystal and the arm of the spectrometer. The value of \vec{k} is determined by the Bragg angle θ_A .



FIG. 43. Principle of the TOF spectrometer with a beryllium filter and crystal monochromator in front of the counter used at the IBR reactor at Dubna. (K. Parlifski et al., Ref. [11] 179.)



FIG. 44. Principle of a TOF spectrometer for dispersion relation measurements.

This allows, for one fixed position of the spectrometer, simultaneous measurement of phonons for the same preset \vec{k} value. By changing ψ , Φ and θ_A it is, in principle, possible to follow a prescribed programme of measurement. A preliminary check of this type of arrangement has been made at the IBR reactor and the results for resolution and intensity are promising.

5.4. Crystal spectrometer methods vs. TOF methods [12]

Both the crystal spectrometer methods and the TOF methods briefly outlined above have been applied very successfully to a variety of problems. A comparison of both methods should take into consideration the particular problem in which one is interested. As it stands now it seems that for dispersion relation measurements the triple-axes spectrometer is more favourable, and for frequency distribution measurements the TOF methods seem to be more appropriate. A more detailed comparison of both kinds of methods can be found in Ref. [12].

6. OUTLOOK FOR THE FUTURE [11, 12]

The general overall picture presented in these three lectures on methods of neutron spectroscopy, although very elementary and simplified, shows that a variety of methods exist both for structure analysis of solids and lattice dynamics studies. However, for studies of tiny and subtle effects, still better resolution and higher intensities are required. This needs reactors with very high fluxes. Until recently, only steady-state reactors were available (with neutron fluxes up to 10¹⁵ neutrons per cm and second). The only existing pulsed reactor, IBR in the Joint Institute for Nuclear Research in Dubna, has been working only since 1960. Experience with the IBR reactor and the expectation of very high cost, together with the technolgical difficulties connected with steady-state reactors with fluxes of the order 10^{16} and higher, led in recent years to a comparison of the merits of steady-state and pulse systems. Several mettings have been devoted to this problem and those interested in the future of neutron spectroscopy can find in Refs [11] and [12] a number of papers dealing with new concepts of reactors and their applications to solid-state physics.

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Note: The references are mainly to textbooks, monographs and proceedings of scientific conferences. References to particular papers are made only in very few cases in connection with methods developed very recently. Thus, the list of references does not pretend to present any balanced picture of contributions to the vast field of neutron spectroscopy methods. No special references have been made to other lecture notes of this course of the theory of condensed matter.

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NEUTRONS AND CRITICAL PHENOMENA

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Abstract

Introduction. 1. Phase transition and critical phenomena. 2. Neutron scattering. 3. Experimental results: 3.1. Critical scattering by magnetic materials; 3.2. Critical scattering by non-magnetic materials. 4. Conclusions.

INTRODUCTION

In preceding lectures we have reviewed critical phenomena as well as neutron scattering in solid state physics. A special development of this application of neutron scattering to critical phenomena may, at first view, look somewhat surprising. We can give two reasons for this development. The first reason is the fact that critical phenomena, which are very generally associated with second-order phase transitions, must be the object of systematic studies to find out if there are any general laws or rules in such transitions. The large amount of literature, both in theory and experiment, which appeared in this field during the last two years, is just a consequence of this necessity. Thus, three more lectures on this subject may be useful. The second reason, as we shall see in more detail later on, is that neutrons are among the best tools for performing such studies. This can be seen from the expression for the scattering crosssection in the Born approximation, in which the leading term is

$$\int_{0}^{\infty} e^{i\vec{q}\cdot\vec{r}} g(r) dr$$

where $g(\mathbf{r})$ is the pair-distribution function and \vec{q} the scattering vector. So the cross-section is sensitive to $g(\mathbf{r})$ mostly for

$$\mathbf{r} \simeq \frac{1}{q} = \frac{\lambda}{4\pi \sin \frac{\theta}{2}}$$

where λ is the wavelength of the radiation used for the experiment and θ is the scattering angle. For visible light of $\lambda \approx 6000$ Å the situation is rather insensitive to what happens at a scale of, say, 100 Å. For X-rays, with a wavelength of 1 Å, even if small angles are used, one sees the material at an atomic scale or, at most, at a few hundred Å. In the case of neutrons incident wavelengths between 1 and 20 Å are available. Thus, one can adjust this tool of observation which is at its best anywhere between the atomic scale and 1000 Å.

We shall see also that the neutron magnetic moment, and the low energy of neutrons which allow dynamic study are of great importance. Before explaining this in detail, we shall briefly review phase transition, and the theory of neutron scattering as it applies to this special case, in order to see the characteristics of this radiation. Then we shall review the results obtained up to now.

1. PHASE TRANSITION AND CRITICAL PHENOMENA

Since this question has already been treated in much detail, we shall only review the important facts to be used as a guide in experiments with neutrons. Good review of these problems can be found in the proceedings of a conference on critical phenomena held in Washington in 1965 and in a paper by Kadanoff et al. [2].

In what follows we shall only consider second-order phase transitions [3], which are characterized by continuous first derivative of the thermodynamical potential Φ (e.g., the entropy), but a discontinuity in the second derivatives of this potential (specific heat at constant volume C_v , etc...). There is a great variety of such transitions: magnetic transitions, orderdisorder transitions in alloys, λ point in liquid helium, ferroelectric transitions, etc... This behaviour of the potential shows up also at the critical points of fluids (liquid-gas critical point), or liquid mixtures. It is of very great importance to find a general theory of these transitions, independent of the nature of the interactions, which are completely different for, e.g., ferromagnets and liquid helium. The fact indicating the possible existence of such a general theory is the similarity in the behaviour of some physical quantities, as, e.g., the specific heat, at these points.

The first theoretical approach to this problem was the introduction of an order parameter η done by Landau [4]. In all phase transitions mentioned above (critical points must be considered separately), the transition is between an ordered phase (ferromagnet, He II, etc.) and a less ordered or disordered phase (paramagnet, He I, etc.) of higher symmetry. The parameter η is a measure of the order in the less symmetric phase. η is zero in the disordered phase. The fact that the transition is of second order is expressed by the fact that η vanishes continuously at the temperature of transition T_c . The exact physical meaning of η is not always simple. For a ferromagnet, it will simply be the spontaneous magnetization M, and for an antiferromagnet, the sub-lattice magnetization. But in the case of a superconductor it will be the wave function ψ which is related to the gap.

The next step in the Landau theory is an expansion of the potential ϕ in powers of η near T_c. Landau shows that, if such an expansion exists, it should be of the form

$$\phi = \phi_0(\mathbf{p}, \mathbf{T}, \ldots) + \mathbf{A}(\mathbf{p}, \mathbf{T}, \ldots) \eta^2 + \mathbf{c}(\mathbf{p}, \mathbf{T}, \ldots) \eta^4 + \ldots$$
(1)

with

$$A(p_c, T_c) = 0 \tag{2}$$

Starting from these assumptions one is able to derive the behaviour of all physical quantities near T_c . Before going further, we must now

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give a classification of these quantities and of the related parameter which will be derived from the Landau theory (or from other theories) and eventually checked by experiments.

For reasons of simplicity, we shall list these quantities for the case of magnetic transitions, which is the most important for neutron scattering. Close to T_c we have the following relations:

below T_c:

$$M \sim (T_c - T)^{\beta}$$
(3)

where M is the spontaneous magnetization (for ferromagnets) or the sub-lattice magnetization (for antiferromagnets)

$$\chi \sim (T_c - T)^{\gamma}$$
(4)

where χ is the susceptibility of the lattice (ferromagnets) or of the sublattice (antiferromagnets)

$$C_v = A + B(T_c - T)^{-\alpha'}$$
(5)

at T_c :

$$M \sim H^{\frac{1}{\delta}}$$
(6)

where H is the applied magnetic field

above T_c :

$$\chi \sim (T - T_c)^{\gamma}$$
(7)

$$C_v = A' + B' (T - T_c)^{-\alpha}$$
(8)

The last quantity to be introduced is the correlation function g(r, r'), defined in this case as

$$g(\mathbf{r},\mathbf{r'}) = (\widetilde{\mathbf{M}}(\mathbf{r}) - \langle \vec{\mathbf{M}}(\mathbf{r}) \rangle)(\vec{\mathbf{M}}(\mathbf{r'}) - \langle \vec{\mathbf{M}}(\mathbf{r'}) \rangle)$$
(9)

As a consequence of the form of ϕ near T_c , large fluctuations of η (in this case \vec{M}) can take place. These fluctuations, which are neglected in (1) since they give only a very small contribution to the free energy, can be calculated by a general theorem of statistical mechanics [4]; one finds that for large distances

$$g(\mathbf{r},\mathbf{r'}) \sim \frac{1}{(\mathbf{r}-\mathbf{r'})} e^{-K_1(\mathbf{r}-\mathbf{r'})}$$
 (10)

with

$$K_1 \sim (T_c - T)^{\nu}$$
 below T_c (11)

$$K_1 \sim (T - T_c)^{\nu}$$
 above T_c (12)

and

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In fact, the existence of these long-range fluctuations (when $T \rightarrow T_c$, K^{-1} becomes infinite) play a fundamental role in critical phenomena. Now we come back to the Landau theory, in which it is further assumed that

$$A(T) = a(T - T_c)$$
 (13)

From this, all the parameters listed above can be derived. It is found from the Landau theory that:

$$\beta = 3$$

$$\gamma = \gamma' = 1$$

$$\nu = \nu' = \frac{1}{2}$$

For the specific heat, Landau theory predicts a finite jump. This last point is rather strongly contradicted by experiments, which, instead of a finite jump, indicate a specific heat which seems to become infinite at T_c . Also the values of the other parameters do not seem to be confirmed by experimental data. Nevertheless, this theory gives a useful frame for the interpretation of neutron scattering and other data. We must note that molecular field theory is just the same as Landau theory as far as phase transitions are concerned. The fundamental reason for this failure seems to be the fact that the expression for the thermodynamical potential does not include the fluctuations which appear to be very large at T_c . Thus, this theory is not completely self-consistent.

The case of critical points, such as fluid critical points, should be treated differently as was pointed out by Landau. In this case, the critical point is isolated and it is possible to turn around it. So this point is not a separation between two phases. In this case the Landau theory is slightly different. The fourth-order term of (1) is zero at T_c and the specific heat is expected to become infinite. Nevertheless, the physical quantities show a behaviour which is rather similar to that given above. The correspondence between the magnetic and the one-fluid case is given by

$$M \to \rho_1 - \rho_g$$

where ρ_1 is the liquid density, ρ_g the gas density and κ the compressibility; $\beta, \alpha, \alpha', \gamma, \gamma', \nu, \nu'$ can also be defined in this case. But $(\rho_1 - \rho_g)$ cannot really be regarded as an order parameter since liquid and gas phases have the same symmetry.

The next step in the theory was to calculate numerically the critical quantities in specific models such as the Ising models. Reference to the literature on this problem may be found in Refs [1] and [2]. A more ambitious approach has been made by Kadanoff [2]. The physical foundation of this theory consists of considering cells which are much larger than the atomic distances, but much smaller than the correlation range K^{-1} . This is possible since K^{-1} goes to infinity at T_c . Kadanoff assumes that the interactions between the cells play a fundamental role in critical

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phenomena. He assumes the details of the interaction to be of no importance and that the cell assembly has a critical behaviour which can be scaled on the critical behaviour of the atomic assembly. From dimensional arguments he then derives relations between the critical parameters. The relations obtained by this theory are called the "scaling laws" for a three-dimensional system

$$2 - \alpha = 2 - \alpha' = 3\nu' = 3\nu = \frac{3\gamma}{2 - \eta} = \gamma + 2\beta$$
(14)

The parameter $\eta,$ often named the "Fisher" parameter, gives the correlation function at $T_{\rm c}$ as

$$g(\mathbf{r})\Big|_{T_{c}} = \frac{1}{r^{1+\eta}}$$
(15)

The above-mentioned calculations with specific models are a good check of this theory. To see if the relations [14] are correct is one of the purposes for which the experiments are made. Up to now, we have considered the substance near the phase transition to be a static assembly. More precisely, we have not introduced the time of evolution of the fluctuation. As neutrons are going slowly through matter, we cannot make the simplification called "static approximation". Thus, as we shall see later on from the cross-section, neutron scattering will give information on this dynamical aspect of the fluctuations. Some macroscopic quantities like the self-diffusion coefficient and transport properties are related to this dynamical behaviour.

The theoretical aspect of this behaviour is still much more intricate than the static aspect as it makes use of the concept of an irreversible thermodynamic process; an introduction of these theories is not the scope of these lectures. We shall give here just a few qualitative statements which are useful in the interpretation of the neutron data. First, we must give a generalization of the pair-correlation function and make it time-dependent, i.e., g(r, t). Now, if we consider a configuration with some local order at t = 0, this configuration will develop with a certain relaxation time. Two forces are active in producing this evolution: under effect of heat, the disorder in the system increases, but the interactions between elements (e.g., Heisenberg forces in a magnet) are acting towards more order. T_c is just the temperature at which these two effects cancel so that there is no active force to relax the system. This effect is the "thermodynamic slowing-down". It has the consequence that the time of evolution of a system near T_c is very long.

To analyse this relaxation, one makes a Fourier analysis of the correlation function and looks for the time of relaxation of each of these components. As pointed out explicitly by several authors [5], [6], the process of relaxation will be of different nature according to the value of the ratio q/K (where K⁻¹ is the range of correlation). For q/K \ll 1 one assumes the relaxation of a fluctuation of the extent 1/q much larger than the range of correlation 1/K and one is in the field of hydrodynamics, where phenomena are analysed by a diffusion process. For q/K \gg 1, however, relaxation within the range of correlation is considered. This case, which is perhaps of more fundamental importance, is very difficult

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from the theoretical point of view, as in this case the interaction has to be considered in detail. We shall come back to this point when analysing the neutron data in ferromagnets and anti-ferromagnets.

2. NEUTRON SCATTERING

The theory of neutron scattering has already been set forth in preceding lectures and will not be repeated here. Only the results will be given. The general formalism of neutron scattering introduced by Van Hove [7] is the most suitable, as it expresses the neutron cross-section in terms of the generalized pair-distribution function g(r, t) which we have just introduced. In the case of nuclear scattering the cross-section has two parts:

a) The coherent cross-section

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\epsilon} = \frac{\langle \mathbf{a} \rangle^2 \mathbf{N}}{2\pi\,\hbar} \,\frac{\mathbf{k}_1}{\mathbf{k}_0} \int \,\mathrm{e}^{\mathrm{i}(\vec{q}\cdot\vec{r}-\omega t)} \,\mathrm{g}(\vec{r},t) \,\mathrm{d}\vec{r} \,\mathrm{d}t \tag{16}$$

where a is the scattering amplitude, k_0 and k_1 are wave vectors of incident and scattered neutrons respectively, and q is the momentum transfer in the scattering.

b) The incoherent cross-section

$$\frac{d^2\sigma}{d\Omega \ d\epsilon} = \frac{\langle a^2 \rangle - \langle a \rangle^2}{2\pi \hbar} \frac{k_1}{k_0} \int e^{i(\vec{q} \cdot \vec{r} - \omega t)} g_s(\vec{r}, t) d\vec{r} \ dt$$
(17)

In this case, the general correlation function g(r, t) is replaced by the "self-correlation function" $g_s(r, t)$ which gives the space distribution at time t of a given scatterer, which was at the origin at time t = 0. The coherent part of the cross-section gives information of the same nature as X-ray scattering, but, in addition, measures the time dependence of the correlation function. The incoherent part of the cross-section describes the space behaviour of a scatterer as a function of time. In the limit of very long times it will yield the self-diffusion coefficient.

In the case of magnetic scattering, the cross-section has only one part. For the case where an atomic spin can be defined, the correlation function is given by the expression

$$G^{\alpha\beta}(\vec{r},t) = \langle S^{\alpha}(0,0) S^{\beta}(\vec{r},t) \rangle$$
(18)

where S^{α} , S^{β} are the spin components. The cross-section is given by

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \,\mathrm{d}\epsilon} = \left(\frac{1.91\,\mathrm{e}^2}{\mathrm{m}_0\,\mathrm{c}^2}\right)^2 \frac{1}{2\pi\,\hbar} \frac{\mathrm{k}_1}{\mathrm{k}_0} \,\left|\,\mathrm{F}(\vec{q})\right|^2 \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) \sum_{\mathrm{R}} \int \mathrm{d}t \,\mathrm{e}^{i(q\,\mathrm{r}\,-\,\omega t)} \,\mathrm{G}^{\alpha\beta}(\vec{r},t)$$
(19)

In this formula, e and m_0 represent the charge and mass of the electron respectively, and c the velocity of light. F(q) is the form factor of the

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magnetic electrons and $\epsilon = \hbar \omega$ is the energy transfer between the neutron and the scattering system. This expression contains both the elastic and the inelastic parts of the scattering cross-section. It refers to the case of fixed atoms (no magneto-vibrational contribution). The elastic part of the cross-section is given by the contribution $\langle S(0) \rangle \langle S(r) \rangle$ to the correlation function. This contribution vanishes for $T > T_c$.

Another expression for the cross-section has been given by De Gennes. Writing down a Fourier expansion for the magnetization M(r):

$$M(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} e^{-i \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} M(\vec{\mathbf{q}})$$
(20)

(where V is the volume of the sample), he arrives at the following formula for the scattering cross-section:

$$\frac{d^2\sigma}{d\Omega \ d\epsilon} = \left(\frac{1.91 \ e}{\hbar \ c}\right)^2 \frac{1}{2\pi \ \hbar} \frac{k_1}{k_0} \int dt \ e^{-i \ \omega t} \langle M_{\perp}(q, 0) M_{\perp}(-q, t) \rangle \quad (21)$$

Here $M_{\perp}(q)$ represents the component of M perpendicular to the vector q, and $\dot{M}(\vec{q},t)$ is the corresponding Heisenberg operator. The spin of the magnetic ion does not enter in this expression, which is identical to the proceeding one; formula (21) is extremely useful in the case of a metal, for which it is not possible to define the spin.

As the magnetic case is the case where most of the data have been obtained as yet, we shall concentrate on it. Anyhow, the treatment of neutron scattering by a fluid near its critical point would be very similar. Furthermore, we shall consider only the case of ferromagnets. The special case of anti-ferromagnets and other structure will be considered later on.

We first consider the static approximation. By introducing the concept of susceptibility in an inhomogeneous field, simplifications of the calculation become possible. The definition of the "new" susceptibility, $\chi(Q)$ in the case of an inhomogeneous field is given in the following way. Let us apply a small external excitation which is sinusoidal in space to a spin system; the response of this system will then also be sinusoidal and have the same wavelength. For Q put equal to zero in $\chi(Q)$, the definition of classical susceptibility is regained. It can be shown that for a semiclassical system of spins we have

$$S(S+1) \frac{\chi(Q)}{\chi_0} = \sum_{r} \langle S(0) S(r) \rangle e^{iqr}$$
 (22)

This expression may be regarded as a good approximation for the case of a quantum-mechanical spin. χ_0 is the value which the susceptibility would have in the absence of interactions (free-law susceptibility). Thus, the calculation of the correlation function is now the calculation of this generalized susceptibility. This can be done, e.g., by using the molecular field theory. Substituting this correlation function into (19) and integrating over an infinitely small energy change (static apJACROT

proximation), we find

$$\frac{d\sigma}{d\Omega} = \left(1.91 \frac{e}{\hbar c}\right)^2 \frac{2 k_B TV}{\frac{V}{\chi} + Aq^2 + Bq^4 \dots}$$
(23)

where χ is the static susceptibility, and A and B parameters not varying strongly as functions of temperature. This expression is identical with the original expression of Van Hove [7] which is given by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \sim \frac{1}{r_1^2 \left(\mathrm{K}^2 + \mathrm{q}^2\right)} \tag{24}$$

which introduces explicitly the range of correlation 1/K; r_1 is a measure of the range of direct exchange interaction. Between these variables the following important relationship holds:

$$r_1^2 K^2 = \frac{\chi_0}{\chi}$$
(25)

De Gennes [8] has shown that Eq. (23) can be derived without any assumption of localized spin, on a purely thermodynamic basis. To do this, the thermodynamic potential written down before is used, and terms describing the inhomogeneity due to the magnetization fluctuations are introduced in it. The probability distribution of the magnetization may then be calculated on the basis of the theorem stating that the probability for a quantity x to take a value between x and x + dx is proportional to $\exp(-\Phi(x)/k_BT)$. According to Landau, this kind of treatment is allowed as long as quantum effects can be neglected, which will be the case for

$$\tau \gg \hbar/k_{\rm B}T$$

where T is a time characterizing the evolution of the system. For transition temperatures above 10° K this condition is well fulfilled.

Now we shall try to see what can be said about the inelastic crosssection if the dynamics of the fluctuations are taken into account. The original treatment of Van Hove [7] assumes that for sufficiently large values of t the Fourier component $\varphi_q(t)$ of the correlation function has an exponential decay with a time τ_q given by

$$\frac{1}{\tau_{\rm q}} = \Lambda q^2 \tag{25a}$$

In this theory, the thermodynamic slowing-down mentioned above gives $\Lambda(T_c) = 0$. Further improvement of the theory by Mori and Kawasaki [9] shows a q dependence of the diffusion constant and predicts a q⁴-dependence of τ_q at T_c . These theories are oversimplified in that the exponential decay is considered as the leading phenomenon. As pointed out by Marshall [10], Villain [5], Kawasaki [11], and Resibois [12], this is correct only if the time necessary to establish this exponential decay is short enough so that no other relaxation process takes place during this time. In ferromagnets, however within the range of correlation 1/K some

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kind of collective modes may take place which will speed up the relaxation process. As mentioned above, we should then distinguish two extreme cases, that of q/K much smaller and that of q/K much larger than 1. For q/K \ll 1 we are in the domain of hydrodynamics, the exponential decay is the leading phenomenon and the prediction of the authors is that Eq.(25a) is correct and

$$\Lambda \sim \sqrt{K} \tag{26}$$

In this case the cross-section is given by an expression calculated by Van Hove

$$\frac{d^2 \sigma}{d\Omega \ d\epsilon} = C \frac{1}{\frac{V}{\chi} + Aq^2 + \dots} \frac{Aq^2}{\omega^2 + \Lambda^2 q^4}$$
(27)

with Λ given by (26).

For $q/K \gg 1$, that is to say at T_c and very close to it, we must take into account the relaxation process inside the local domain of magnetization.

The predictions of the behaviour in this domain differ from author to author. Both Villain [5] and Halperin [6] predict that in this domain the time of relaxation should be independent of temperature

$$\frac{1}{\tau_{\rm q}} \sim {\rm q}^{5/2} \tag{28}$$

In this case, the cross-section should be of the form

$$\frac{d^2\sigma}{d\Omega \ d\epsilon} = C \frac{1}{\frac{V}{\chi} + Aq^2} \frac{q^{5/2}}{\omega^2 + q^5}$$
(29)

Case of antiferromagnets and other magnetic structures

The value for the bulk magnetization of an antiferromagnetic material is zero. Consequently, it will not show any critical fluctuation. On the other hand, critical fluctuations may appear in the magnetization of each of the sub-lattices. The preceding theory can easily be extended to such a case even if the structures are rather complex [5, 6, 13]. The following results have to be kept in mind:

a) Critical scattering appears at the position of peaks of super-structure. More particularly, critical scattering will not be observed at small angles. This statement will possibly not be true for a metamagnetic material such as FeCl₂, which can be regarded as a superposition of ferromagnetic planes.

b) In general, the number of parameters required to describe the scattering, is larger than in the case of a ferromagnet. The number of parameters required depends on the type of structure and on the number of sub-lattices.

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The above mentioned authors who have worked out the relaxation in a ferromagnet have also calculated the case of anti-ferromagnets.

For the case of an helical structure, critical scattering will occur when the scattering vector is close to the spiral-wave vector Q. It has been shown [14] that the time of relaxation in the case of a ferromagnetic spiral is

$$\frac{1}{\tau_{q}} = \Gamma(Q, T) + \Lambda(Q, T)q^{2}$$
(30)

where \boldsymbol{q} is the deviation of the scattering vector from the spiral-wave vector $\boldsymbol{Q}.$

This review of the theory of critical neutron scattering is very incomplete; we just tried to give the most important results for analysing the experimental data.

3. EXPERIMENTAL RESULTS

Also in this section the review will not be complete, and only part of the results will be presented.

3.1. Critical scattering by magnetic materials

These experiments have two purposes. The first purpose is to determine the critical parameters, and the second one is to verify the theories of relaxation and obtain information on the dynamics of fluctuations.

a.1) Determination of critical parameters

The determination of the critical parameters makes, above all, use of the static approximation; the inelasticity of the scattering must, however, be taken into account to correct the rough data. So what is measured in this case is the scattered intensity versus the scattering vector I(q). From [24] and [25] we see that this will yield γ , γ' and ν , ν' . The parameter β is also accessible to neutrons by an accurate determination of the intensity of a Bragg peak. In Fig.1 we show typical curves of intensity versus temperature in critical scattering. This has been measured for iron by Bally et al. [18]. We see a very intense peak due to the cancellation of χ at T_c in formula (23). In addition, for very small values of the scattering vector we have an extra peak at lower temperatures due to spin waves [17]. For large values of the scattering vector, the peak is shifted to temperatures higher than T_c . This is a consequence of the fact that for large q the situation is sensitive to shortrange correlation, where the asymptotic formula $(1/r) \exp(-Kr)$ is no longer valid: results can be explained by using a general expression of the form

$$g(r) = \frac{1}{r}e^{-Kr}(1 - e^{-ar})$$
 (31)

which reduces to the asymptotic expression for large r.



FIG.1. Calculated velocity auto-correlation in liquid argon at 85.5°K. Curve A: $\langle \omega^2 \rangle_{av} = 50 \times 10^{24} \text{s}^{-2}$, D = 1.88 × 10⁻⁵ cm² s⁻¹. Curve B: $\langle \omega^2 \rangle_{av} = 45 \times 10^{24} \text{s}^{-2}$, D = 1.88 × 10⁻⁵ cm² s⁻¹ (see Ref. [9]). The circles are from Nijboer, B.R.A., Rahman, A., Physica <u>32</u> (1966) 415.



FIG.2. Determination of critical parameters.

Figure 2 shows a good example of the data of Ref. [15] used for the determination of critical parameters. In this figure we note the following general features:

1) a linear variation of I^{-1} with q^2 , which is in good agreement with relations (23) and (24) which are a direct consequence of a pair correlation in $(1/r)\exp(-Kr)$ at large distances (Ornstein-Zernike expression).

2) a deviation from linearity when the scattering vector becomes larger. This is a direct consequence of the fact that correlation function at small r deviates from the Ornstein-Zernike form.

3) an intercept with the ordinate axis which increases with $(T - T_c)$ and which according to (23) is a measure of the susceptibility.

4) curves which are roughly parallel, but deviate slightly from this parallelism. This indicates that r_1 in (24) varies slowly with temperature. A complete analysis allows us to obtain K as a function of $(T - T_c)$.

To get accurate values of $\chi(T)$ and K(T) we must correct these curves for angular divergence and inelastic effects. The expression for such corrections can be found, e.g., in Ericson's thesis [16]. If one uses neutrons of long wavelengths, the angular divergence correction will be smaller, but the inelastic correction will be larger than if one uses short wavelength neutrons. Obviously, inelastic correction can only be made if the time of relaxation τ_q is known. To our knowledge, this has been done in the case of iron, making use of relation (25) and using values of Λ determined as indicated below. The results for iron are the following:

2ν	γ	Authors
1.28	1.20	Jacrot et al. [17]
-	1.30	Passel et al. [15]
1.38	1.33	Bally et al. [13]
1.27	-	Spooner and Averbach [19]

We note the large dispersion of these results, at least, if we want to check the scaling-law conclusions. A more accurate determination, where, in particular, data of different wavelength ranges should be collected, is still advisable. Results in other ferromagnetic materials are the following:

Nickel	$\gamma \sim 1.30$	Parette [17]
Cobalt	$2\nu = 1.20$ $\gamma = 1.19$	Bally et al. [18]
Terbium (Ferromagnetic spiral)	γ = 1.20	Als-Nielsen et al.[14]

It is interesting to compare these results with data obtained by usual magnetics techniques, which yield

Iron	$\gamma = 1.33$
Nickel	$\gamma = 1.29$ to 1.35
Gadolinium	γ = 1.16 to 1.33
Cobalt	$\gamma = 1.21$
CrO_2	$\gamma = 1.6$

As pointed out by Belov [20], these magnetics measurements have special difficulties. Neutron techniques are the only ones where one really obtains the susceptibility in zero field. As one is interested in the sublattice susceptibility in the case of anti-ferromagnets, only neutrons yield this staggered susceptibility. The results obtained so far are the following:

$\operatorname{Cr}_2\operatorname{O}_3$	$2\nu = 1.34$. Riste et al.[21]
$\rm Fe_2O_3$	$2\nu = 1.26$	Riste et al.[21]
KMnF₃	$\gamma = 1.34$	Cooper et al.[22]
MnF_2	$\gamma = 1.00$	Parette et al.[23]

For these anti-ferromagnets, no corrections have been applied to take account of inelastic correction. But Parette et al. have shown that these results are identical for short and long wavelengths, which indicates that in this case these corrections should be very small.

The parameter β has also been measured in some cases:

D.A.G.	$\beta = 0.41$	Norwelletal. [24]
Terbium	$\beta = 0.25$	Dietrich et al. [25]
KMnF ₃	$\beta = 0.33$	Cooper et al.[22]

We must note that if the result for γ in MnF₂ is correct, a violation of the scaling laws is implied. We know that $\alpha = 0$ and $\beta = 0.33$ in MnF₂. So in this case we have

$$2 - \alpha \neq \gamma + 2\beta = 1.66$$

The last point of the static aspect of critical scattering by magnetic substances which we should mention is the very high sensitivity to applied magnetic fields, even of 10 to 100 Oersted [17].

a.2) Relaxation in critical phenomena

The dynamical aspect of critical phenomena is seen in neutron scattering by the non-elastic character of the scattering. As can be seen from Eq. (27) this fact appears essentially as a line broadening, with a width given approximately by
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A simple analysis from the line broadening is rather inaccurate; mostly, the instrumental width is large compared to this broadening. Thus, the data have to be analysed by fitting the experimental crosssection to expressions as, e.g. (27) or (29).

Iron and Nickel:

In the case of iron, it has been shown in Refs [15, 17] that at the Curie point the scattering is inelastic, which indicates that at this temperature τ_q is finite for $q \neq 0$. The data are not accurate enough to yield any detailed information on $\tau_q(q)$, but one can say that the data can be fitted by an expression of the form of (27), with a value of the dimensionless parameter of $\mu = (2/\hbar)m\Lambda = 11$. This value seems to be constant for $T_c \leq T \leq T_c + 30^\circ$. All data have been obtained for q/K > 1. So this result is in agreement with theoretical predictions given above. The data of Jacrot [17] seem compatible with an expression of the form (29). More accurate measurements must be made. For this purpose, one should use good energy and temperature resolutions and look at $\tau_q(T)$ for a fixed value of q. The width should remain constant and start to increase at temperature where $q \sim K$.

In nickel, the data are poorer [17], but look rather similar to those in iron, with, perhaps, a q⁴ dependence of τ_q [26]. Also here more work is advisable. Drabkin et al. [27] studied the polarization of scattered neutrons and claim to have proved that the scattering was elastic. In our view, the sensitivity of this technique is too small to see parameters Λ of the order that has been observed directly.

Terbium:

We have seen that the time of relaxation should be as indicated in Eq.(30), Als-Nielsen [14] has measured $\Gamma(Q, T)$, by experiments with q=0. The result is shown in Fig.3. This result is explained qualitatively by Villain [5] who assumes in his analysis that at high temperatures where the range of correlation is small the substance behaves like a ferromagnet, and close to T_c where the range of correlation is large compared to the pitch of the screw the relaxation is of the anti-ferromagnetic type.

$RbMnF_3$:

The most interesting study made in this anti-ferromagnetic substance shows the simultaneous existence of a broadened line corresponding to critical fluctuations and of two peaks associated with spin waves. This is true below and just above T_c . These observations are in good agreement with Marshall's [10] prediction, who regards the finite relaxation time observed in iron as being due to unresolved spin wave peaks.

3.2. Critical scattering by non-magnetic materials

The data available in non-magnetic materials are rather limited. In particular, to the knowledge of the author, nothing has been published on scattering by critical fluids. This is due to technical difficulties as usually one works with large beams of neutrons, which are incompatible



FIG.3. Temperature variation of the time-decay parameter $\Gamma(\varphi, T)$. The result of conventional theory is also shown.

with a good definition of critical fluid conditions due to, e.g., gravity effects. In our opinion the existence of high-flux reactors, which allow work with narrow beams, should make these experiments possible and useful. Two kinds of information are expected. First, in hydrogenous material, which has a highly incoherent cross-section, one should be able to measure the self-diffusion coefficient by means of Eq. (17); it must show anomalies at T_c . Secondly, the study of the time of relaxation should complement the laser results, which are always in the hydro-dynamical domain.

In critical binary liquid mixtures, which are quite similar to single critical fluids, a preliminary observation has been made by Wignall and Rainey [29] using a bismuth-gallium mixture. Critical scattering has been clearly observed. The mean magnitude of concentration fluctuation, which is the equivalent of the usual range of fluctuation, has a temperature variation with $2\nu \sim 1$, and the variation of the concentration with chemical activity which is the equivalent of the susceptibility shows a temperature dependence with $\gamma \sim 1$.

As far as order-disorder transitions in alloys are concerned, a systematic study of the β -brass transition has been made by Als-Nielsen and Dietrich [30]. In this case, obviously all times involved are very long (macroscopic) and the static treatment is rigorous. The experiment shows that the correlation of occupation of lattice sites has the shape $(1/r)\exp(Kr)$. The variation of K with temperature is given by $K \sim (T-T_c)^{\nu}$ with $2\nu = 1.30$. One can also define the analogue of the magnetic susceptibility, as an order-disorder transition in an alloy is formally equivalent to an order-disorder transition in an Ising anti-ferromagnet. This susceptibility which is given by $K_1^2 r_1^2$, (intercept of 1/I with the ordinate axis), has a variation with $\gamma = 1.25$. It is also possible to determine the variation of long-range order below T_c by intensity of Bragg peaks. This gives $\beta = 0.305$. We can observe that in this transition we have $\gamma + 2\beta = 1.86$ and $3\nu = 1.95$ such that we are not far from the scaling-law prediction which states equality of these figures.

4. CONCLUSIONS

The potentiality of neutron scattering to provide useful information is fairly large and if the applications have been limited so far, this is mostly for technical reasons. In the future, careful work will make it possible to handle these technical difficulties.

The greatest difficulty with neutrons is, so far, the low intensities of the available fluxes which are much smaller than in the case of X-rays. But, on the other hand, neutrons have considerable advantages:

- 1) The large available range of the scattering vector.
- The possibility of reducing multiple scattering by reducing the thickness of the sample (this cannot be done with light, whose wavelength is too large, so that thin samples give rise to refraction).
- 3) The transparency to neutrons of nearly all materials. We must notice that, on the other hand, the incoherent cross-section makes it difficult to work on hydrogenous materials with neutrons.
- 4) The magnetic moment of the neutron which makes it a unique tool to study magnetic transitions.

For the study of the dynamics of transitions, at first sight neutrons have a very strong competition with laser. This competition seems to be hopeless for neutrons as laser can see a broadening of 1 cycle/second. This is 10^5 more sensitive than what can be done now with neutrons. But with laser the wavelength is nearly always larger than the correlation range (q/K \ll 1) so that we observe only the hydrodynamic process of relaxation. Neutrons allow us to observe both hydrodynamic and real critical processes.

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INVESTIGATIONS OF MAGNETIC MATERIALS USING NEUTRON SCATTERING

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Abstract

1. Basic formulae: 1.1. Introduction 1.2. Bragg scattering 1.3. Spin waves; 2. Magnetic moment distribution in metals, alloys and transition ion complexes: 2.1. Ferromagnetic metals; 2.2. Transition ion complexes; 2.3. Disordered alloys; Shull-Wilkinson model; dilute alloys; 3. Paramagnetic and critical scattering by ferromagnets: 3.1. Formulae for paramagnetic and critical scattering; 3.2. The inelasticity of the scattering; 3.3. Theoretical discussion for T approaching T_c ; 3.4. Recent experiments at temperatures very close to T_c .

1. BASIC FORMULAE

1.1. Introduction

The purpose of these lectures is to give some idea of the power of neutron scattering methods to investigate magnetic solids. We shall see that neutrons can tell us a great deal about magnetic systems and that most of the information could not have been obtained by using any other technique. In principle, neutron scattering methods can be used to answer almost any question about the structure or dynamics of a magnetic system and it is probably fair to claim that neutrons provide us with the most powerful single technique for investigating magnetic solids which is known today. Perhaps it is as well that the experiments are so valuable, because they are certainly expensive.

The general idea of the experiments is very simple. Thermal neutrons emerge from a nuclear reactor, are collimated into a beam and velocity selected and then allowed to fall on the sample. The intensity of scattered neutrons is measured as a function of scattering angle and for inelastic experiments an energy analysis is made using time-of-flight or other techniques. Figures 1 and 2 show schematic diagrams of a Bragg scattering apparatus and a time-of-flight apparatus for inelastic experiments. They are self-explanatory.

We must now decide how to relate the observations to properties of the scattering sample. It is convenient to define the wave-vector change \vec{K} and the energy loss h ω of the neutron as follows

$$\vec{\mathbf{K}} = \vec{\mathbf{k}} - \vec{\mathbf{k}}^{\dagger} \tag{1.1}$$

$$\hbar \omega = E - E' = \frac{\hbar^2}{2m_0} (k^2 - k'^2)$$
 (1.2)

^{*} The paper was presented by G.G. Low.



FIG. 1. A schematic diagram of a Bragg scattering apparatus.



FIG. 2. Schematic diagram of a time-of-flight apparatus.

In terms of these quantities the magnetic cross-section per unit solid angle per unit energy interval is

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega^{\prime}\mathrm{d}E^{\prime}} = \frac{\mathrm{N}}{\mathrm{h}} \left(\frac{\mathrm{e}^{2}\gamma}{\mathrm{mc}^{2}}\right)^{2} \frac{\mathrm{k}^{\prime}}{\mathrm{k}} \left|\mathrm{F}(\vec{\mathrm{K}})\right|^{2} \times \left\{1 - \hat{\mathrm{K}}_{z}^{2}\right) \mathrm{S}^{zz}(\vec{\mathrm{K}},\omega) + \left(1 - \hat{\mathrm{K}}_{x}^{2}\right) \mathrm{S}^{xx}(\vec{\mathrm{K}},\omega) + \left(1 - \hat{\mathrm{K}}_{y}^{2}\right) \mathrm{S}^{yy}(\vec{\mathrm{K}},\omega)\right\} \quad (1.3)$$

where N is the number of atoms in the crystal, $\gamma = 1.91$ is a measure of the neutron's magnetic moment, \hat{K} is the unit vector in the direction of \vec{K} ; $F(\vec{K})$ is a form factor defined as the Fourier transform of the spin density associated with an individual ion or atom

$$\mathbf{F}(\vec{\mathbf{K}}) = \mathbf{S}^{-1} \int d\vec{\mathbf{r}} \, \mathbf{e}^{\,\mathbf{i}\,\vec{\mathbf{K}}\cdot\,\vec{\mathbf{r}}} \, \rho_{\mathbf{S}}\left(\vec{\mathbf{r}}\right) \tag{1.4}$$

The inclusion of the total spin S in the equation ensures that F(0) is unity. Equation (1.3) assumes_only scalar interactions between the spins.

The quantities $S^{xx}(\vec{K}, \omega)$, sometimes called the scattering law, are related to correlation functions by

$$S^{XX}(\vec{K},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sum_{\vec{R}} e^{i(\vec{K}\cdot\vec{R}-\omega t)} \langle S_{0}^{X}(0) S_{\vec{R}}^{X}(t) \rangle$$

$$= \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle S^{X}(-\vec{K},0) S^{X}(\vec{K},t) \rangle$$
(1.6)

where

$$S^{X}(\vec{K},t) = \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} S^{X}_{\vec{R}}(t)$$
(1.7)

In these formulae $\vec{S}_{\vec{R}}(t)$ is the spin at site \vec{R} and time t. The correlation functions used in Eqs (1.5) and (1.6) are important because they give a very complete and simple description of the sample. In part of section 2 we will examine what information can be obtained from the form factor $F(\vec{K})$, but most of the time we will discuss the quantities $S^{xx}(\vec{K},\omega)$, etc. It should be noted that it can be shown that

$$S^{XX}(\vec{K},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}\cdot i\omega t} \langle S_{0}^{X}(0) S_{\vec{R}}^{X}(t) \rangle$$
$$= \frac{1}{4} \left(e^{\beta h\omega} - 1 \right)^{-1} i \left[g(\vec{K},\omega) - g(-\vec{K}, -\omega) \right]$$
(1.8)

where $g(\vec{K},\omega)$ is the difference between the retarded and advanced Green functions along the real axis of ω . The Green functions are defined in Zubarev's notation [1]:

$$G_{\overrightarrow{nm}}(t) = \ll S_{\overrightarrow{n}}(t); \quad S_{\overrightarrow{m}}^{+}(0) \gg$$
$$= \mp i\theta (\pm t) \langle [S_{\overrightarrow{n}}(t), S_{\overrightarrow{m}}^{+}(0)] \rangle \qquad (1.9)$$

1.2. Bragg scattering

From (1.3) we notice that scattering which is strictly elastic must have a contribution proportional to $\delta(\omega)$ and therefore we first ask for this. Expressions (1.5) and (1.6) show this is related to the correlation functions at infinite time. But at infinite time there can be no correlations between spin fluctuations. Hence

$$S_{\text{Bragg}}^{\text{xx}}(\vec{K},\omega) = \frac{1}{2\pi} \int_{\vec{K}}^{\infty} dt \sum_{\vec{R}} e^{i(\vec{K}\cdot\vec{R}-\omega t)} \langle S_{0}^{x}(0) S_{\vec{R}}^{x}(\omega) \rangle$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sum_{\vec{R}} e^{i(\vec{K}\cdot\vec{R}-\omega t)} \langle S_{0}^{x} \rangle \langle S_{\vec{R}}^{x} \rangle$$

$$= \delta(\omega) \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} \langle S_{0}^{x} \rangle \langle S_{\vec{R}}^{x} \rangle$$

$$= \delta(\omega) \frac{1}{N} \left| \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} \langle S_{\vec{R}}^{x} \rangle \right|^{2} \qquad (1.10)$$

The remainder of the scattering is called "inelastic" and, for example,

$$\mathbf{S}_{\text{inel.}}^{\text{xx}} (\vec{K}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sum_{\vec{R}} e^{i(\vec{K} \cdot \vec{R} - \omega t)} \langle \langle \mathbf{S}_{0}^{\text{x}}(0) \mathbf{S}_{\vec{R}}^{\text{x}}(t) \rangle - \langle \mathbf{S}_{0}^{\text{x}} \rangle \langle \mathbf{S}_{\vec{R}}^{\text{x}} \rangle \rangle$$
(1.11)

In many magnetic materials the spin patterns are very simple with the time average spin always along a single direction. Conventionally, this direction is labelled the z-axis. Then

$$S_{Bragg}^{xx}(\vec{K},\omega) = 0 = S_{Bragg}^{yy}(\vec{K},\omega)$$
 (1.12)

In a ferromagnet all spins are equivalent; hence (1.10) gives

$$S_{\text{Bragg}}^{zz}(\vec{K},\omega) = \delta(\omega) \langle S \rangle^{2} \frac{1}{N} \left| \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} \right|^{2}$$
$$= \delta(\omega) \langle S \rangle^{2} \frac{(2\pi)^{3}}{v_{0}} \sum_{\vec{\tau}} \delta(\vec{K}-\vec{\tau}) \qquad (1.13)$$

where v_0 is the unit cell volume and $\vec{\tau}$ is the reciprocal lattice vector. Substituting into (1.3) gives the Bragg cross-section

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega^{2}} = \frac{(2\pi)^{3}}{\mathrm{v}_{0}} \operatorname{N}\left(\frac{\mathrm{e}^{2}\gamma}{\mathrm{mc}^{2}}\right)^{2} \left| \mathrm{F}(\vec{\mathrm{K}}) \right|^{2} \langle \mathrm{S} \rangle^{2} (1 - \hat{\mathrm{K}}_{z}^{2}) \sum_{\vec{\tau}} \delta(\vec{\mathrm{K}} - \vec{\tau}) \qquad (1.14)$$

This vanishes above T_c , where $\langle S \rangle$ is zero, and is usually recognized with the help of a magnetic field which is able to orient the ferromagnetic domains in various directions, i.e. the "z-axis" is along \vec{H} . In the absence of \vec{H} the orientation factor $(1 - \hat{K}_z^2)$ must be averaged over domains. In a cubic crystal it is simply 2/3. The last factor of (1.14) is very restrictive, it tells us that scattering can only occur if \vec{K} coincides with a reciprocal lattice vector. This factor is the same as that occurring in X-ray diffraction and the experimental techniques for observation are identical in principle so we will not discuss them here.

In a simple anti-ferromagnet

$$\langle S_{\vec{R}}^{z} \rangle = (\pm)_{\vec{R}} \langle S \rangle$$
 (1.15)

where $\langle S \rangle$ is the time-averaged spin on a sub-lattice. In place of (1.14) we then get

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega^{\dagger}} = \frac{(2\pi)^3}{\mathrm{v}_0} \operatorname{N}\left(\frac{\mathrm{e}^2\gamma}{\mathrm{m}\mathrm{c}^2}\right)^2 \left| \mathbf{F}(\mathbf{K}) \right|^2 \langle \mathbf{S} \rangle^2 \left(1 - \hat{\mathbf{K}}_2^2\right) \sum_{\vec{\tau}} \delta(\vec{\mathbf{K}} - \vec{\tau}) \left| \mathbf{F}_{\mathrm{c}}(\vec{\tau}) \right|^2 \qquad (1.16)$$

where

$$\mathbf{F}_{c}(\vec{\tau}) = \sum_{\vec{\rho}} e^{i\vec{K}\cdot\vec{\rho}}(\pm)\vec{\rho}$$
(1.17)

where v_0 is the volume of the magnetic unit cell (frequently larger than the chemical unit cell) and the sum over $\vec{\rho}$ includes all the magnetic ions in one unit cell. This formula (1.16) can be used to deduce the spin pattern of anti-ferromagnets. To see how this is done we look at only one example, MnF_2 .

The chemical structure of MnF_2 is well known. The position of each unit cell is given by

$$\vec{n} = (n_1 a, n_2 a, n_3 c)$$
 (1.18)

and the unit cell volume, v_0 , is $a^2\,c$ and contains 2 Mn atoms and 4 F ions. The reciprocal lattice is

$$\vec{\tau} = 2\pi \left(\frac{t_1}{a}, \frac{t_2}{a}, \frac{t_3}{c} \right)$$
(1.19)

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where t_1 , t_2 , t_3 are integers. Within the unit cell we have

Mn⁺⁺ at(0,0,0) and
$$\left(\frac{a}{2}, \frac{a}{2}, \frac{c}{2}\right)$$

and F^{-} at {a(1-u), a(1-u), 0}; {a(0.5+u), a(0.5-u), $\frac{c}{2}$ }
{au, au, 0}; {a(0.5-u), a(0.5+u), $\frac{c}{2}$ } (1.20)

where $u \approx 0.31$. Hence the nuclear scattering has

$$F_{nuc} (\vec{\tau}) = b_{Mn} \{ 1 + \exp[i\pi (t_1 + t_2 + t_3)] \}$$

$$+ b_F \{ \exp[i2\pi u (t_1 + t_2)] + \exp[i2\pi (1 - u) (t_1 + t_2)] \}$$

$$+ \exp[i\pi (t_1 + t_2 + t_3) + i2\pi u (t_1 - t_2)]$$

$$+ \exp[i\pi (t_1 + t_2 + t_3) + i2\pi u (t_2 - t_1)] \}$$

$$= 2b_{Mn} + 4b_F \cos 2\pi u t_1 \cos 2\pi u t_2 \quad \text{if } t_1 + t_2 + t_3 \text{ is even}$$

$$= -4b_F \sin 2\pi u t_1 \sin 2\pi u t_2 \qquad \text{if } t_1 + t_2 + t_3 \text{ is odd.} \quad (1.21)$$

In these formulae ${\rm b}_{Mn}$ and ${\rm b}_F$ are the coherent scattering amplitudes of Mn and F nuclei, respectively. Hence for the first few reciprocal lattice vectors

$$F_{nuc}(100) = 0$$

$$F_{nuc}(001) = 0$$

$$F_{nuc}(110) = 2b_{Mn} + 4b_F \cos^2 2\pi u$$

$$F_{nuc}(101) = 2b_{Mn} + 4b_F \cos 2\pi u, \text{ etc.} \qquad (1.22)$$

Nevertheless, below the Néel temperature, a Bragg peak at (100) is observed together with magnetic peaks at.(111), (210) and (201). We first note that these are indexed on the same unit cell, i.e. in this case the magnetic and chemical unit cells have the same volume. There

are two Mn atoms per cell which must have opposite spins. Hence

$$F_{c}(\vec{\tau}) = 1 - \exp[i\pi(t_{1} + t_{2} + t_{3})]$$

= 0 if $t_{1} + t_{2} + t_{3}$ is even
= 2 if $t_{1} + t_{2} + t_{3}$ is odd. (1.23)

We notice that we expect a magnetic peak at both (100) and (001) but the latter does not appear in an experiment. It follows that for this peak the orientation factor $(1 - \hat{K}_z^2)$ must be zero. Hence the spins are directed along the z axis and the spin pattern of the crystal has been completely determined.

The example just chosen is very simple but all determinations of anti-ferromagnetic and ferromagnetic ordering use simple extensions of the formulae given here. Notice that we cannot switch on or off the



FIG. 3. Powder diffraction patterns for MnO (Schull, Strauser and Wollan, Phys. Rev. 83 (1951) 333. Figure reproduced from Neutron Diffraction by G. E. Bacon by courtesy of the author and the Clarendon Press.)



FIG. 4. Spin pattern in MnO. (Figure reproduced from Neutron Diffraction by G. E. Bacon by courtesy of the author and the Clarendon Press.)

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magnetic scattering of an anti-ferromagnet because, except in special cases, the anti-ferromagnetic domains do not respond to an external magnetic field. However, anti-ferromagnetic peaks are easily noticed by comparing diffraction patterns below and above the Néel temperature. An example is shown in Fig. 3 for MnO, together with the spin pattern determined from the results (Fig. 4).

1.3. Spin waves

The elementary excitations present in ferromagnets and antiferromagnets at low temperatures are called spin waves. Figure 5 shows an "instantaneous snapshot" of a spin wave in a ferromagnet,



FIG. 5. Schematic diagram of spin waves in a ferromagnet.

each spin precesses and the phase of the precession varies through the crystal according to the wave vector \vec{q} of the spin wave. In order to calculate the appropriate cross-sections we must use spin wave theory to calculate the correlation functions in (1.9). To do this we use the familiar Heisenberg model with a Hamiltonian

$$\mathcal{H} = -2J \sum_{\vec{n},\vec{m}} \vec{S}_{\vec{n}} \cdot \vec{S}_{\vec{m}}$$
(1.24)

where the sum runs over nearest neighbour pairs only. If we use the Holstein-Primakoff transformation we have, to leading order,

$$S_{\vec{n}}^{z} = -S + a_{\vec{n}}^{*}a_{\vec{n}}$$

$$S_{\vec{n}}^{+} = \sqrt{2S} a_{\vec{n}}^{*} \qquad S_{\vec{n}}^{x} = \sqrt{\frac{S}{2}} (a_{\vec{n}}^{*} + a_{\vec{n}}) \qquad (1.25)$$

$$S_{\vec{n}}^{-} = \sqrt{2S} a_{\vec{n}} \qquad S_{\vec{n}}^{y} = -i \sqrt{\frac{S}{2}} (a_{\vec{n}}^{*} - a_{\vec{n}})$$

where $a_{\vec{n}}$ and $a_{\vec{n}}^*$ are Bose annihilation and creation operators for site \vec{n} . Using the Fourier transforms

$$a_{\vec{n}} = \frac{1}{\sqrt{N}} \sum_{\vec{q}} e^{+i\vec{q}\cdot\vec{n}} b_{\vec{q}}$$

$$a_{\vec{n}}^* = \frac{1}{\sqrt{N}} \sum_{\vec{q}} e^{-i\vec{q}\cdot\vec{n}} b_{\vec{q}}^*$$
(1.26)

where $b_{\vec{q}}$ and $b_{\vec{q}}^*$ annihilate and create spin waves of vector \vec{q} , it is found that \mathscr{H} is diagonalized to leading order and becomes

 $\hbar\omega_{\rightarrow} = 2JSr(1 - \gamma_{\rightarrow})$

$$\mathscr{H} = -JNrS^{2} + \sum_{\vec{q}} \hbar \omega_{\vec{q}} n_{\vec{q}}$$
(1.27)

where

$$\gamma_{\vec{q}} = \frac{1}{r} \sum_{\vec{p}} e^{i \vec{q} \cdot \vec{p}}$$

$$n_{\vec{q}} = a_{\vec{q}}^* a_{\vec{q}} \qquad (1.28)$$

and r is the number of nearest neighbours. From (1.25)

$$S_{\vec{n}}^{\mathbf{X}}(t) = \sqrt{\frac{s}{2}} \left\{ a_{\vec{n}}^{*}(t) + a_{\vec{n}}(t) \right\}$$
$$= \left(\frac{s}{2N} \right)^{\frac{1}{2}} \sum_{\vec{q}} \left\{ e^{\cdot i \vec{q} \cdot \vec{n}} b_{\vec{q}}^{*}(t) + e^{i \vec{q} \cdot \vec{n}} b_{\vec{q}}^{*}(t) \right\}$$
$$= \left(\frac{s}{2N} \right)^{\frac{1}{2}} \sum_{\vec{q}} \left\{ e^{-i \vec{q} \cdot \vec{n} + i\omega \vec{q}^{t}} b_{\vec{q}}^{*} + e^{i \vec{q} \cdot \vec{n} - i\omega \vec{q}^{t}} b_{\vec{q}} \right\}$$
(1.29)

Hence

$$\langle S_0^{\mathbf{x}}(0) S_{\overline{n}}^{\mathbf{x}}(t) \rangle = \frac{S}{2N} \sum_{\overrightarrow{q}} \{ e^{-i\overrightarrow{q}\cdot\overrightarrow{n}+i\omega_{\overrightarrow{q}}t} (\overrightarrow{n}_{\overrightarrow{q}}+1) + e^{i\overrightarrow{q}\cdot\overrightarrow{n}-i\omega_{\overrightarrow{q}}t} \overrightarrow{n}_{\overrightarrow{q}} \}$$
(1.30)

where we have introduced the thermal expectation values

$$\bar{n}_{\vec{q}} = \frac{1}{e^{Bh\omega}\vec{q} - 1}$$
(1.31)

Similarly, we can show that

$$\langle S_0^y(0) S_{\vec{n}}^y(t) \rangle = \langle S_0^x(0) S_{\vec{n}}^x(t) \rangle$$
 (1.32)

Hence from (1.11)

$$S_{\text{inel}}^{\text{xx}} (\vec{K}, \omega) = \frac{S}{2} \frac{(2\pi)^3}{v_0} \sum_{\vec{\tau}, \vec{q}} \{\delta(\vec{K} - \vec{q} - \vec{\tau}) \ \delta(\omega - \omega_{\vec{q}})(\vec{n}_{\vec{q}} + 1) + \delta(\vec{K} + \vec{q} + \vec{\tau}) \ \delta(\omega + \omega_{\vec{q}}) \ \vec{n}_{\vec{q}}\}$$
(1.33)

and substituting into (1.3) gives

$$\frac{d^{2}\sigma}{d\Omega' dE'_{inel, spin-wave}} = \frac{N}{\hbar} \left(\frac{e^{2}\gamma}{mc^{2}}\right)^{2} \frac{k'}{k} |F(\vec{K})|^{2} \{1 + \hat{K}_{2}^{2}\} \times \frac{S}{2} \frac{(2\pi)^{3}}{v_{0}}$$

$$\times \sum_{\vec{\tau},\vec{q}} \{\delta(\vec{K} - \vec{q} - \vec{\tau}) \delta(\omega - \omega_{\vec{q}})(\vec{n}_{\vec{q}} + 1)$$

$$+ (\vec{K} + \vec{q} - \vec{\tau}) \delta(\omega + \omega_{\vec{q}})(\vec{n}_{\vec{q}})$$

$$= \frac{N}{\hbar} \left(\frac{e^{2}\gamma}{mc^{2}}\right)^{2} \frac{k'}{k} |F(\vec{K})|^{2} \{1 + \hat{K}_{2}^{2}\} \frac{S}{2} \frac{(2\pi)^{3}}{v_{0}}$$

$$\times \sum_{\vec{\tau}} \{\delta(\omega - \omega_{\vec{\tau} + \vec{K}})(\vec{n}_{\vec{\tau} - \vec{K}} + 1) + \delta(\omega + \omega_{\vec{\tau} - \vec{K}})(\vec{n}_{\vec{\tau} - \vec{K}}) + 1 + \delta(\omega + \omega_{\vec{\tau} - \vec{K}})(\vec{n}_{\vec{\tau} - \vec{K}})$$

$$(1.35)$$

The first term corresponds to spin wave creation, the second to spin wave annihilation. To study spin wave scattering the cross-section is observed as a function of ω and, at fixed \vec{K} , this shows two maxima, one for positive ω corresponding to neutron energy loss and spin wave creation, the other for negative ω corresponding to annihilation. The observations give the spin wave frequency corresponding to the appropriate \vec{K} value.



FIG.6. Spin wave dispersion in fcc Co Q. S2 Fe 0.08 (Sinclair, Brockhouse, Phys. Rev. 120 (1960) 1638).

In this way many spin wave spectra have been determined. A few examples are given in the diagrams. Figure 6 shows ω_q as a function of q for f.c.c. $Co_{0.92}Fe_{0.08}$ and Fig.7 for b.c.c. Fe. Figure 8 shows results for Fe_3O_4 , Fig.9 for MnF_2 .



FIG.8. Spin wave dispersion in Fe₃O₄ (Brockhouse, B.N., Watanabe, H. in Inelastic Scattering of Neutrons in Solids and Liquids (Proc. Symp. Chalk River, 1962), 2, IAEA, Vienna (1963) 297.

0.0

008

0.0

0.0

0.02

ENERGY TRANSFER the (eV)

FIG.9. Spin wave dispersion in MnF₂ (Low, Okazaki, Turberfield, Stevenson, J. Appl. Phys. 35, (1964) 998).

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2. MAGNETIC MOMENT DISTRIBUTIONS IN METALS, ALLOYS AND TRANSITION ION COMPLEXES

2.1. Ferromagnetic metals

We have seen how Bragg scattering involved the form factor $F(\vec{K}\,)$ which was defined as

$$F(\vec{K}) = S^{-1} \int d\vec{r} e^{i\vec{K}\cdot\vec{r}} \rho_{S}(\vec{r}) \qquad (2.1)$$

where $\rho_{s}(\vec{r})$ is the spin density and S the total spin associated with each atom. Because $\rho_{s}(\vec{r})$ in total is a periodic function, (2.1) can be inverted so as to lead to

$$\langle \rho_{\rm S}(\vec{r}) \rangle = \frac{\langle {\rm S} \rangle}{v_0} \sum_{\vec{\tau}} e^{i\vec{\tau} \cdot \vec{t}} F(\vec{\tau})$$
 (2.2)

giving the time-averaged spin density in terms of the experimental quantities $\langle S \rangle F(\vec{\tau})$. From this formula it follows that from the intensity of Bragg peaks we can deduce $\langle \rho_{s}(\vec{r}) \rangle$ throughout the unit cell. $\langle \rho_{s}(\vec{r}) \rangle$ is best represented as a contour map.

In fact it turns out that there are considerable advantages to be gained by carrying out Bragg scattering measurements on ferromagnetic specimens with a beam of polarized neutrons. Interference between nuclear and magnetic scattering then gives rise to a cross term in the cross-section which is absent for an unpolarized incident beam. Thus, if we write the magnetic scattering length as

$$p = \frac{\gamma e^2}{mc^2} F(\vec{\tau}) \langle S \rangle$$
 (2.3)

and the nuclear length as b, for a suitable scattering geometry we have cross-sections of $(b \pm p)^2$, dependent on whether the neutrons are polarized parallel or antiparallel to the magnetization of the specimen. Measurements can easily be made for both incident neutron polarizations by the use in the experimental apparatus of a suitable polarization "flipper" based on the radiofrequency resonance technique. The ratio between these measurements gives the ratio of p/b, i.e.

$$R = \left(\frac{b+p}{b-p}\right)^2$$
(2.4)

or

$$\frac{p}{b} \sim \frac{R-1}{4} \tag{2.5}$$

for $p \ll b$ as is usually the case. The polarized neutron method enables the magnetic scattering to be accurately and easily measured in the presence of the nuclear Bragg peaks (unpolarized neutrons are scattered with an intensity proportional to $b^2 + p^2$ and the small p^2 term cannot be separated off with any great precision). Additionally, it is unnecessary to measure the integrated intensity by tracking across a Bragg peak: all that is required is a single pair of measurements at the point of maximum intensity, together with an accurate background count.



FIG. 10. Magnetic moment density in Fe (Shull, Yamada, J. phys. Soc. Japan 17, (1962) Supplement B-3, 1).

Figures 10 and 11 show contour maps obtained in this way by Shull and collaborators for metallic Fe and Ni. Notice that between the Fe atoms the spin density is negative. A careful discussion by Shull has shown this to be a real effect and it was the first clear cut evidence that the 4s electrons in Fe are polarized in the opposite direction to the 3d electrons. A similar situation seems to exist also for Ni. Notice also that the results do not have resolution enough to show up the fall of the spin density near the Fe and Ni nuclei - this must in fact happen because 3d electrons have no amplitude at a nucleus.



FIG. 11. Moment density in Ni (Mook, Phys. Rev. 149 (1966) 495).

2.2. Transition ion complexes

The same idea is easily extended to anti-ferromagnets. Figure 12 shows a contour map for NiO determined by Alperin. The figure clearly shows up that the Ni⁺⁺ ion does not have a spherical spin distribution but, as we would expect, has the magnetic moment distributed in E_g orbitals. Actually it turns out that experiments such as these can give important information on covalency effects in transition ion complexes. This possibility has been examined in detail by Hubbard and Marshall (see Ref. [2]).

The existence of a degree of covalency in a nominally ionic compound corresponds to the return of some part of the electron charge which would be donated from the cation to the anion in the fully ionic situation. In the case of a magnetic material, this back-transfer of electrons to the cation will usually have associated with it an outward transfer of unpaired spin on to the ligands. The total amount of unpaired spin associated with an isolated ion complex will often remain unaffected: the change in its spatial distribution may, however, be quite pronounced and should in many cases be observable in neutron diffraction experiments. Such measurements would thus lead to quantitative information on the degree of covalency present. In fact, in concentrated materials where antiferromagnetism occurs some cancellation of spin takes place also, as we shall see.

A convenient framework within which a lot of the discussion of covalency has been carried on is the linear combination of atomic orbitals (LCAO) approximation. The wavefunctions describing the outer electrons



FIG. 12. Moment density in NiO (Alperin, J. phys. Soc. Japan 17 (1962), Supplement B-2, 12).

associated with a transition metal ion and its surrounding ligands are written in the form:

$$\psi_a = N_a(\phi - AX) \tag{2.6}$$

$$\psi_{\rm b} = N_{\rm b} (X + B\phi) \tag{2.7}$$

where ϕ is an atomic orbital of the central metal ion and X is a suitable combination of ligand orbitals having the same overall symmetry as ϕ . N_a and N_b are normalization factors and A and B are the admixture parameters which are small numbers for the nominally ionic compounds. As a consequence of orthogonality between the molecular orbitals, i.e. $(\psi_a \mid \psi_b) = 0$, we have the relationship

$$B = \frac{A - (\phi \mid x)}{1 - A(\phi \mid x)}$$
(2.8)

between A and B. (The $(\alpha | \beta)$ are overlap integrals.)

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From the above comments we see that ψ_b has predominantly the nature of the ligand orbitals while ψ_a closely resembles an orbital of the metal ion. In the case of ψ_b , the plus sign has the effect of increasing the electron density in the region between the metal ion and the ligand nuclei and thus lowering the energy of an electron in this orbital relative to that of an electron in a pure atomic orbital either on the metal ion or on a ligand atom. Conversely, the energy of an electron in ψ_a is increased. Thus ψ_b is known as a "bonding" orbital and ψ_a as an "anti-bonding" orbital. In the case of the nominally ionic compounds we shall be discussing in detail below, it may be assumed that the bonding orbitals are full. Thus, they have no net unpaired spin associated with them and all we need consider in connection with neutron scattering and other magnetic properties are the anti-bonding orbitals.

Let us now write down the explicit form of the anti-bonding orbitals corresponding to a d-ion surrounded by a regular octahedron of F or O ligands. ϕ in Eq.(2.6) becomes one of the five functions d_{3z²-r²}, d_{x²-y²}, d_{xy}, d_{yz} or d_{zx}. For X we form linear combinations of the s and p orbitals of the ligands having corresponding overall symmetries. The resulting molecular orbitals are either the σ orbitals formed from wavefunctions of e_g symmetry, i.e.

$$\psi_{3z^{2}-r^{2}} = N_{\sigma} \left\{ d_{3z^{2}-r^{2}} - A_{\sigma}(p_{3}^{\sigma} + p_{6}^{\sigma} - \frac{1}{2} p_{1}^{\sigma} - \frac{1}{2} p_{2}^{\sigma} - \frac{1}{2} p_{2}^{\sigma} - \frac{1}{2} p_{4}^{\sigma} - \frac{1}{2} p_{5}^{\sigma} \right\} - A_{s}(s_{3} + s_{6} - \frac{1}{2} s_{1} - \frac{1}{2} s_{2} - \frac{1}{2} s_{4} - \frac{1}{2} s_{5}) \right\}$$

$$(2.9)$$

$$\psi_{x^{2}-y^{2}} = N_{\sigma} \left\{ d_{x^{2}-y^{2}} - \frac{\sqrt{3}}{2} A_{\sigma} (p_{1}^{\sigma} + p_{4}^{\sigma} - p_{2}^{\sigma} - p_{5}^{\sigma}) - \frac{\sqrt{3}}{2} A_{s} (s_{1} + s_{4} - s_{2} - s_{5}) \right\}$$
(2.10)

or the π orbitals formed from wavefunctions of t_{2g} symmetry

$$\psi_{xy} = N_{\pi} \{ d_{xy} - A_{\pi} (p_1^y + p_2^x - p_4^y - p_5^x) \}$$
(2.11)

$$\psi_{yz} = N_{\pi} \{ d_{yz} - A_{\pi} (p_2^z + p_3^y - p_5^z - p_6^y) \}$$
(2.12)

$$\psi_{zx} = N_{\pi} \{ d_{zx} - A_{\pi} (p_1^{z} + p_3^{x} - p_4^{z} - p_6^{x}) \}$$
(2.13)

The subscript numbers on the p and s functions refer to the ligand positions according to the convention shown in the diagram (see Fig. 12a). The superscript on a p function shows the direction of its positive lobe; σ indicates. that it points towards the central d-ion. A diagrammatic representation of ψ_{zx} is given to illustrate these points (Fig. 12b).



FIG. 12a. Conventional subscripts for p and s functions.



FIG. 12b. Diagrammatic representation of ψ_{zx} .

The normalization factors are given by

$$N_{\sigma}^{-2} = 1 + 3 A_{\sigma}^{2} - 6 A_{\sigma} S_{\sigma} + 3 A_{s}^{2} - 6 A_{s} S_{s}$$
 (2.14)

$$N_{\pi}^{2} = 1 + 4A_{\pi}^{2} - 8A_{\pi}S_{\pi}$$
 (2.15)

where the overlap integrals are defined as

$$S_{\sigma} = (d_{3z^2 - r^2} | p_3^{\sigma})$$
 (2.16)

$$S_s = (d_{3z^2 - r^2} | s_3)$$
 (2.17)

$$S_{\pi} = (d_{2x} | p_3^x)$$
 (2.18)

The magnetic moment density associated with an isolated d-ion plus its octahedral array of ligands is given by the sum of the squares of the wavefunctions (2.9) to (2.13) which contain unpaired electrons. Thus, for example, if the d-ion is Ni⁺⁺ where we have 2 unpaired electrons in the e_{σ} molecular orbitals we would have

$$\rho(\vec{r}) = \left| \psi_{3z^2 - r^2}(\vec{r}) \right|^2 + \left| \psi_{x^2 - y^2}(\vec{r}) \right|^2$$
(2.19)

Now $p(\vec{r})$ can be expressed as the sum of three parts, i.e.

$$\rho(\vec{r}) = \rho_{\rm d}(\vec{r}) + \rho_{\rm d1}(\vec{r}) + \rho_{\rm l}(\vec{r})$$
(2.20)

where $\rho_d(\vec{r})$ and $\rho_l(\vec{r})$ depend only on wavefunctions associated with the d-ion and the ligands respectively and $\rho_{d1}(\vec{r})$ depends on products con-

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taining both these types of wavefunction. We have immediately that

$$\rho_{\rm d}(\vec{r}) = N_{\sigma}^2 \{ \left| d_{3z^2 - r^2} \right|^2 + \left| d_{x^2 - y^2} \right|^2 \}$$
(2.21)

and that

$$\rho_{d1}(\vec{r}) + \rho_{1}(\vec{r}) = \left[\left\{ \left| \psi_{3z^{2} - r^{2}} \right|^{2} + \left| \psi_{x^{2} - y^{2}} \right|^{2} \right\} - N_{\sigma}^{2} \left\{ \left| d_{3z^{2} - r^{2}} \right|^{2} + \left| d_{x^{2} - y^{2}} \right|^{2} \right\} \right] \quad (2.22)$$

It follows straight away that

$$\int d\vec{r} \{ \rho_{d1}(\vec{r}) + \rho_1(\vec{r}) \} = 2(1 - N_{\sigma}^2) \sim 2(3A_{\sigma}^2 - 6A_{\sigma}S_{\sigma} + 3A_s^2 - 6A_sS_s)$$
(2.23)

so that

$$\int d\vec{r} \rho_{dl}(\vec{r}) \sim -12 (A_{\sigma}S_{\sigma} + A_{s}S_{s}) \qquad (2.24)$$

$$\int d\vec{r} \,\rho_1(\vec{r}) \sim 6 \,(A_{\sigma}^2 + A_s^2) \tag{2.25}$$

In fact if we now consider the situation in a concentrated Ni salt such as NiO or KNiF₃ where magnetic ordering occurs and examine the distribution of magnetic moment in the anti-ferromagnetic phase we see that an interesting cancellation has taken place. For the types of antiferromagnetic structure found in both of these systems the ligands lie at the centre of straight lines joining pairs of neighbouring d-ions of opposite spin direction. The $\rho_1(\vec{r})$ corresponding to a pair of d-ions having opposed spins will have opposite signs too and thus cancellation will result and for the anti-ferromagnetic situation

$$\int d\vec{r} \,\rho(\vec{r}) = \int d\vec{r} \,\{\rho_{d}(\vec{r}) + \rho_{d1}(\vec{r})\}$$
$$= 2\{N_{\sigma}^{2} - 6(A_{\sigma}S_{\sigma} + A_{s}S_{s})\} \sim 2(1 - 3A_{\sigma}^{2} - 3A_{s}^{2}) \qquad (2.26)$$

This means that the intensity of the anti-ferromagnetic reflections will be less than one would calculate in the absence of covalency. In the forward direction the magnetic form factor will be diminished by the factor $(1 - 3A_{\sigma}^2 - 3A_s^2)$ in Eq.(2.26). Thus, a careful study of the absolute intensities of the low index reflections can lead to a determination of this quantity and hence provide quantitative information on the degree of covalency. Nathans et al. [3] were the first to follow this approach and estimate covalency parameters using data from careful powder measurements on a range of anti-ferromagnets. Other measurements have been made by Fender, Jacobson and Wedgwood at Harwell[4].

It is easy to see that, whereas the fractional loss of magnetic moments found above for an e_σ orbital is

$$3A_{g}^{2} + 3A_{s}^{2}$$
 (2.27)

that for a t_{2g} orbital is

 $4A_{\pi}^2$ (2.28)

Although the above discussion covers a number of the most important anti-ferromagnets, e.g. NiO, MnO, KNiF_3 , KMnF_3 etc., in general the surroundings of the ligands in anti-ferromagnets do not have the simple symmetry necessary for the cancellation effects described. In principle, it is then necessary to work with the squares of the full wavefunctions given in Eqs (2.9) to (2.13). However, because the ligands are spaced so far from the central d-ion, their effects in the scattering do not appear until quite small values of scattering vector are reached. Thus, for simple structures the lowest-angle Bragg peak will probably have a diminished intensity roughly in accord with the formulae quoted above. A table of results from neutron diffraction experiments of this sort is given (Table I).

2.3. Disordered alloys

Important information about the electronic structure of alloys can be obtained by studying the elastic diffuse scattering. To examine this we return to section 1 and note that

$$S_{elastic}^{zz}(\vec{K},\omega) = \delta(\omega) \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} \langle S_0^z \rangle \langle S_{\vec{R}}^z \rangle$$
(2.29)

and substituting into (1, 3) gives

$$\frac{d\sigma}{d\Omega'_{elastic}} = \frac{N}{4} \left(\frac{e^2 \gamma}{mc^2}\right)^2 |F(\vec{K})|^2 (1 - \hat{K}_z^2) \sum_{\vec{k}} \mu_0 \mu_{\vec{k}} e^{i\vec{K}\cdot\vec{R}}$$
(2.30)

where we have introduced the magnetic moment $\mu_{\vec{R}}$ at \vec{R} (in units of the Bohr magneton). The formula (2.30) is better to use than the corresponding one involving $\langle S_{\vec{R}}^z \rangle$ because it takes better account of any orbital moment which is unquenched.

The value of (2.30) depends on whether or not there are fluctuations in $\mu_{\vec{R}}$ from site to site: it is understood that the origin atom 0 is arbitrary. We define the mean moment as

$$\bar{\mu} = \frac{1}{\bar{N}} \sum_{\vec{R}} \mu_{\vec{R}}$$
(2.31)

Configuration	Ion	Material	Result	
d³	Cr ³⁺	LaCrO ₃	$A_{\pi}^{2} \sim 3.5\%$	Nathans et al.
d ⁵	Fe ³⁺	LaFeO3	$A_{\sigma}^{2} + 2 A_{\pi}^{2} + A_{s}^{2} \sim 8\% $	Nathans et al.
	Mn ²⁺	MnF ₂	$A_{\sigma}^{2} + 2 A_{\pi}^{2} + A_{s}^{2} \sim 3.3\%$	Nathans et al.
		MnO	$A_{\sigma}^{2} + 2 A_{\pi}^{2} + A_{s}^{2} = 3.5\%$	Fender et al.
		MnS	$A_{0}^{2} + 2 A_{\pi}^{2} + A_{s}^{2} = 7.6\%$	Fender et al.
		MnCO3	Cation moment loss ~ 10%	Brown & Forsyth
d ⁸	Ni ²⁺	NiO	$A_G^2 + A_S^2 \sim 4\%$	Alperin Fender et al.

TABLE I.	COVALENCY	PARAMETERS	FROM	NEUTRON
DIFFRACT	ION			

Note: The values of the covalency parameters given above have all been roughly corrected for the effects of zero-point motion in an anti-ferromagnet. Because of these corrections those values marked with an asterisk differ from the figures originally published.

and the corresponding cross-section is the Bragg term

$$\frac{d\sigma}{d\Omega'_{\text{Bragg}}} = \frac{N}{4} \left(\frac{e^2 \gamma}{mc^2}\right)^2 |F(\vec{K})|^2 (1 - \hat{K}_2^2) \, \bar{\mu}^2 \, \frac{(2\pi)^3}{v_0} \sum_{\vec{\tau}} \delta(\vec{K} - \vec{\tau})$$
(2.32)

The remainder is the elastic-diffuse scattering

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega'_{\mathrm{elas, diff.}}} = \frac{\mathrm{N}}{4} \left(\frac{\mathrm{e}^{2}\gamma}{\mathrm{m}\,\mathrm{c}^{2}} \right)^{2} \left| \mathrm{F}(\vec{\mathrm{K}}) \right|^{2} (1 - \hat{\mathrm{K}}_{z}^{2}) \frac{1}{\mathrm{N}} \sum_{\vec{\mathrm{n}},\vec{\mathrm{m}}} \mathrm{e}^{\mathrm{i}\vec{\mathrm{K}}\cdot(\vec{\mathrm{n}}-\vec{\mathrm{m}})} \langle (\mu_{\vec{\mathrm{n}}}^{2} - \bar{\mu})(\mu_{\vec{\mathrm{m}}}^{2} - \bar{\mu}) \rangle$$

$$(2.33)$$

where the brackets $\langle \rangle$ now mean that we take an ensemble average. Obviously, there is no elastic diffuse scattering if the sample is pure with all $\mu_{\vec{n}}$ equal to $\bar{\mu}$. But in a binary alloy $\mu_{\vec{n}}$ varies from site to site. To evaluate (2.33) we look at several special cases.

Shull-Wilkinson model

Suppose the alloy has atoms of type A and concentration (1-c); of type B with concentration c. And suppose all atoms A have the same moment μ_A and all B atoms have μ_B ; this is a crude assumption but gives

(A)

a simple model. If we define

$$p_{\rightarrow} = 0$$
 if atom A is at n
n
(2.34)
 $p_{\rightarrow} = 1$ if atom B is at n

Then

 $\langle \mathbf{p}_{\vec{n}} \rangle = c$ $\langle \mathbf{p}_{\vec{n}} \mathbf{p}_{\vec{m}} \rangle = c^{2} + c(1 - c) \stackrel{\delta \rightarrow \rightarrow}{nm}$ (2.35)

In this model

$$\mu_{\vec{n}} = (1 - p_{\vec{n}}) \mu_{A} + p_{\vec{n}} \mu_{B}$$
$$= \mu_{A} + p_{\vec{n}} (\mu_{B} - \mu_{A})$$
$$\bar{\mu} = \mu_{A} + c (\mu_{B} - \mu_{A}) \qquad (2.36)$$

$$\langle \mu_{\vec{n}} \mu_{\vec{m}} \rangle = \langle \{ \mu_{A} + p_{n} (\mu_{B} - \mu_{A}) \} \{ \mu_{A} + p_{\vec{m}} (\mu_{B} - \mu_{A}) \} \rangle$$

$$= \bar{\mu}^{2} + c (1 - c) (\mu_{B} - \mu_{A})^{2} \delta_{\vec{n} \vec{m}}$$

$$(2.37)$$

Hence (2.33) is

$$\frac{d\sigma}{d\Omega'_{el, diff.}} = \frac{N}{4} \left(\frac{e^2 \gamma}{mc^2}\right)^2 \left| F(\vec{K}) \right|^2 (1 - \hat{K}_z^2) c(1 - c)(\mu_B - \mu_A)^2 \qquad (2.38)$$

This is the well known Shull-Wilkinson formula. It describes a background scattering which varies with scattering angle only through the form factor $F(\vec{K})$. It has frequently been used to determine the magnitude of $(\mu_B - \mu_A)$. This coupled with a magnetization measurement to give $\bar{\mu}$ then enables us to calculate μ_A and μ_B separately. A knowledge of $\bar{\mu}$, μ_A and μ_B is essential to understand the electronic structure of these alloys.

Dilute alloys

We now attempt a more precise theory. Suppose the concentration c is only a few per cent. Most of the A atoms will have a moment μ_A because they are far from a B atom. The atom B itself will have μ_B . The A atoms near to B will have their moment disturbed from μ_A : suppose this disturbance is $g(\vec{R})$ at the distance \vec{R} , then

$$\mu_{\vec{n}} = \mu_{A} + p_{\vec{n}}(\mu_{B} - \mu_{A}) + \sum_{\vec{m}} p_{\vec{m}} g(\vec{m} - \vec{n})$$
(2.39)

so

Defining

$$G(\vec{K}) = \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} g(\vec{R})$$
(2.40)

(note $g(0) \equiv 0$)

$$\bar{\mu} = \mu_{A} + c \{ \mu_{B} - \mu_{A} + G(0) \}$$
(2.41)

and substituting (2.39) into (2.33) gives eventually

$$\frac{d\sigma}{d\Omega'} = \frac{N}{4} \left(\frac{e^2 \gamma}{mc^2} \right)^2 |F(\vec{K})|^2 (1 - \hat{K}_z^2) c(1 - c) \{\mu_B - \mu_A + G(\vec{K})\}^2 (2.42)$$

To see roughly how this varies with \vec{K} consider the example where g(\vec{R}) is confined to nearest neighbours at positions $\vec{\rho}$. Then

$$G(\vec{K}) = g_1 \sum_{\vec{\rho}} e^{i\vec{K}\cdot\vec{\rho}}$$
(2.43)

which in a spherical approximation we replace by

$$G(K) \rightarrow rg_1 \frac{\sin K\rho}{K\rho}$$
 (2.44)

Hence

$$\left\{\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega'_{\mathrm{el. diff.}}}\right\}^{\frac{1}{2}} \sim f(\mathrm{K}) \left\{\mu_{\mathrm{B}} - \mu_{\mathrm{A}} + \mathrm{rg}_{1} \frac{\mathrm{sin } \mathrm{K}\rho}{\mathrm{K}\rho}\right\}$$
(2.45)

The behaviour of this is shown schematically in Fig. 12c.



We see that at large K we recover the Shull-Wilkinson results. At small K a structure appears which enables us to determine $G(\vec{K})$ and hence $g(\vec{R})$. A special apparatus has been developed at Harwell for this experiment.

A few of the Harwell results are shown in the Figs 13, 14, 15, 16, 17 and 18. Notice that the Fe-based and Ni-based alloys are quite different. These experiments have led to new theoretical models which have advanced our qualitative understanding of metals and alloys. The



FIG. 13. Diffuse scattering lengths for alloys based on Fe (Collins and Low).



FIG. 14. Sketch of $\rho'(t)$ for alloys based on Fe – the plots (a) and (b) correspond to transition element solutes to the left and to the right of Fe in the periodic table respectively.



FIG. 15. Diffuse cross-sections for alloys based on Ni (Low, Collins, J. appl. Phys. 34 (1963) 1195).



FIG. 16. Sketch showing qualitative behaviour of the magnetic disturbance for alloys based on Ni.



FIG. 17. Diffuse cross-sections for alloys based on Pd (Low, Holden).



FIG. 18. Polarization around Fe and Co solute atoms in Pd (Low, Holden).

plots in real space in the figures are in terms of the magnetic-moment density disturbance $\rho'(\vec{r})$ rather than $g(\vec{R})$. In the solvent metal

$$F(\vec{K}) G(\vec{K}) = F(\vec{K}) \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} g(\vec{R}) = \sum_{\vec{R}}^{R \neq 0} e^{i\vec{K}\cdot\vec{R}} F(\vec{K}) \int_{\text{Unit cell at } \vec{R}} d\vec{r} \rho'(\vec{r})$$
$$= \sum_{\vec{R}}^{R \neq 0} e^{i\vec{K}\cdot\vec{R}} \int_{\text{Unit cell at } \vec{R}} d\vec{r} \rho'(\vec{r}) e^{i\vec{K}\cdot\vec{(r-\vec{R})}} (2.46)$$

Thus from Eq.(2.42)

$$\frac{d\sigma}{d\Omega^{\dagger}_{el,}} \sim \left| \mathbf{F}(\vec{K}) \left\{ \mu_{B} - \mu_{A} + \mathbf{G}(\vec{K}) \right\} \right|^{2}$$

$$= \left| \sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}} \int_{\text{Unit cell at }\vec{R}} d\vec{r} \,\rho^{\dagger}(\vec{r}) \,e^{i\vec{K}\cdot(\vec{R}-\vec{r})} \right|^{2}$$

$$= \left| \int_{\text{All space}} d\vec{r} \,\rho^{\dagger}(\vec{r}) \,e^{i\vec{K}\cdot\vec{r}} \right|^{2} \qquad (2.47)$$

3. PARAMAGNETIC AND CRITICAL SCATTERING BY FERROMAGNETS

3.1. Formulae for paramagnetic and critical scattering

Using Eqs (1.6) and (1.10) we have that

$$S_{\text{inel.}}^{\alpha\alpha}(\vec{K},\omega) = S^{\alpha\alpha}(\vec{K},\omega) - S_{\text{Bragg}}^{\alpha\alpha}(\vec{K},\omega)$$
$$= \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \{\langle S^{\alpha}(-\vec{K},0) \ S^{\alpha}(\vec{K},t) \rangle - \langle S^{\alpha}(-\vec{K}) \rangle \langle S^{\alpha}(\vec{K}) \rangle \}$$
(3.1)

from which we notice that

~

$$\int_{-\infty}^{\infty} d\omega S_{\text{inel.}}^{\alpha \alpha}(\vec{K},\omega) = \frac{1}{N} \{\langle S^{\alpha}(-\vec{K},0) S^{\alpha}(\vec{K},0) \rangle - \langle S^{\alpha}(-\vec{K},0) \rangle \langle S^{\alpha}(\vec{K},0) \rangle \}$$
(3.2)

In the limit $K \rightarrow 0$ (3.2) is proportional to the mean square fluctuation in magnetization which, by elementary thermodynamics, is proportional to the magnetic susceptibility. Hence

$$\lim_{K \to 0} \int_{-\infty}^{\infty} d\omega \, S_{\text{inel.}}^{\alpha \alpha} (\vec{K}, \omega) = kT \, \chi^{\alpha \alpha} / g^2 \mu^2$$
(3.3)

where the susceptibility $\chi^{\alpha\alpha}$ is defined in the usual way. For the correct choice of principle axes, $\chi^{\alpha\alpha}$ has two values χ^{zz} and χ^{xx} = χ^{yy} below T_c , and one value, χ^{zz} = χ^{xx} = χ^{yy} , above T_c .

The form of (3.3) suggests that we seek a more general relation, valid at all \vec{K} , by introducing the quantity $\chi^{\alpha\alpha}(\vec{K})$ which describes the response to a field of wave vector \vec{K} . We introduce a relaxation function

$$R^{\alpha\alpha}(\vec{K},t) = \int_{0}^{\beta} d\lambda \langle e^{\lambda \mathscr{X}} S^{\alpha}(-\vec{K},0) e^{-\lambda \mathscr{X}} S^{\alpha}(\vec{K},t) \rangle - \beta \langle S^{\alpha}(-\vec{K},0) \rangle \langle S^{\alpha}(\vec{K},t) \rangle \quad (3.4)$$

It can then be shown that

$$S^{\alpha\alpha}(\vec{K},\omega) - S^{\alpha\alpha}(\vec{K},\omega)_{Bragg} = \frac{\hbar\omega}{1 - e^{-\hbar\omega\beta}} \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \ R^{\alpha\alpha}(\vec{K},t)$$
(3.5)

and also that

$$X^{\alpha\alpha}(\vec{K}) = \frac{g^2\mu^2}{N} R^{\alpha\alpha}(\vec{K}, 0) \qquad (3.6)$$

Hence

$$S^{\alpha\alpha}(\vec{K},\omega) - S^{\alpha\alpha}(\vec{K},\omega)_{Bragg} = \frac{kT}{g^2\mu^2} \chi^{\alpha\alpha}(\vec{K}) \frac{\hbar\omega\beta}{1 - e^{-\hbar\omega\beta}} F^{\alpha\alpha}(\vec{K},\omega)$$
(3.7)

where

$$\mathbf{F}^{\alpha\alpha}(\vec{\mathbf{K}},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ \mathrm{e}^{-\mathrm{i}\omega t} \ \mathrm{f}^{\alpha\alpha}(\vec{\mathbf{K}},t)$$
(3.8)

and

$$f^{\alpha\alpha}(\vec{K},t) = \frac{R^{\alpha\alpha}(\vec{K},t)}{R^{\alpha\alpha}(\vec{K},0)} = \frac{g^2\mu^2}{N\chi^{\alpha\alpha}(\vec{K})} R^{\alpha\alpha}(\vec{K},t)$$
(3.9)

By definition $f^{\alpha\alpha}(\vec{K}, 0)$ is unity and hence, from (3.8)

$$\int_{\infty}^{\infty} d\omega F^{\alpha\alpha}(\vec{K},\omega) = 1$$
 (3.10)

Therefore (3.7) gives

$$\frac{kT}{g^{2}\mu^{2}} \chi^{\alpha\alpha}(\vec{K}) = \int_{-\infty}^{\infty} d\omega \frac{1 - e^{-\hbar\omega\beta}}{\hbar\omega\beta} \{S^{\alpha\alpha}(\vec{K},\omega) - S^{\alpha\alpha}(\vec{K},\omega)_{Bragg}\}$$
(3.11)

This is an important relation because it is the generalization of (3,3) and because it unambiguously relates the observed cross-sections to a quantity of theoretical interest. Whether or not we understand the full ω dependence of the cross-section we can deduce $\chi^{\alpha\alpha}(\vec{K})$ provided the experimental results are known with sufficient accuracy to evaluate the integral on the right-hand side of (3.11).

Frequently, it is more convenient to measure the total count rate at a fixed scattering angle instead of the full $S(\vec{K},\omega)$; to deduce $X(\vec{K})$ from such measurements involves two approximations. The integral in (3.11) should be performed at fixed \vec{K} , not at fixed scattering angle. The error introduced by this is small if the incident neutron energy is large compared with the energy changes, $\hbar\omega$. Second, the count rate is not weighted with the factor $(1 - e^{-\hbar\omega\beta})/\hbar\omega\beta$ and therefore we require that $\hbar\omega \ll kT$. If this last condition is satisfied the factor becomes unity and the experiments give $\chi^{\alpha\alpha}(\vec{K})$ directly.

The molecular field theory for a ferromagnet above T_c predicts $X(\vec{K})$ to have the form:

$$\chi^{xx}(\vec{K}) = \chi^{zz}(\vec{K}) = \frac{\chi_c}{r_1^2(\kappa_1^2 + q^2)}$$
 (3.12)

where

$$\vec{K} = \vec{\tau} + \vec{q}$$
(3.13)

and $\vec{\tau}$ is the nearest reciprocal lattice vector,

$$\chi_{c} = g^{2} \mu^{2} S(S+1)/3 kT_{c}$$
 (3.14)

 r_1^2 gives a measure of the range of the exchange interaction

$$\mathbf{r}_{1}^{2} = \frac{1}{6} \frac{\sum_{R} J(R) R^{2}}{\sum_{R} J(R)}$$
(3.15)

and $\kappa^{}_1$ is an inverse correlation range defined above $T^{}_{\! C}$ by

$$r_1^2 \kappa_1^2 = \frac{\chi_c}{\chi^{2Z}(0)} = \frac{T - T_c}{T_c}$$
(3.16)

Other simple theories of ferromagnets give results qualitatively similar.

These predictions have been tested by Passell et al.([9], see Fig.19) by neutron experiments on metallic iron. They conclude that the general form (3.12) is correct within the limits of experimental error but that $r_1^2 \kappa_1^2$ does not have a linear variation with T - T_c, as predicted by (3.16)

but instead

$$r_1^2 \kappa_1^2 \sim (T - T_c)^{4/3}$$
 for $T \sim T_c$ (3.17)

This 4/3 law is in agreement with recent theoretical work by Domb [5] and by Gammell, Marshall and Morgan [6] who found a 4/3 law for the divergence of χ^{zz} (0) using the mathematical technique of successive Padé approximants.



FIG. 19. Temperature dependence of $r_1^2 \kappa_1^2$ in Fe (Passell, Klinowski, Brun and Nielsen, 1965, Phys. Rev. 139, A1866).

Below T_c the molecular field theory again gives the general form (3.12), but with

$$r_{1}^{2}\kappa_{1z}^{2} = 2 \frac{T_{c} - T}{T_{c}}$$

for $T < T_{c}$ (3.18)
 $\kappa_{1x}^{2} = 0$

Since this simple theory gives the incorrect power law above T_c we would expect it also to be incorrect below T_c but, to date, no experimental results of sufficient accuracy are available below T_c . A theory due to Elliott and Marshall [7] gives results virtually identical with (3.12) to (3.18) with the one important difference that they predict a non-zero κ_{1x}^2 below T_c . The precise reason why the theories differ in this way is not yet understood; non-interacting spin waves also give $\kappa_{1x}^2 = 0$ and therefore it appears that in the theory of Elliott and Marshall a diffusive-like behaviour is built into the perpendicular correlation function $\langle S_0^{\alpha}(0) S_p^{\alpha}(t) \rangle$. We will return to this point in the next section.

3.2. The inelasticity of the scattering

To consider this problem we concentrate our attention on $F^{xx}(\vec{K},\omega)$. Above T_c this is identical with $F^{zz}(\vec{K},\omega)$ and therefore gives a complete description of the ω -dependence, while below T_c it gives the single spin wave scattering. We are not able to calculate $F^{xx}(\vec{K},\omega)$ rigorously

but we can get some information about its moments of it. We first note that

$$\frac{\partial}{\partial t} \mathbb{R}^{xx}(\vec{K},t) = \frac{i}{\hbar} \langle [S^{x}(-\vec{K},0), S^{x}(\vec{K},t)] \rangle \qquad (3.19)$$

Hence

$$\frac{\partial^2}{\partial t^2} \mathbf{R}^{\mathbf{x}\mathbf{x}}(\vec{\mathbf{K}},t) = \frac{i}{\hbar} \langle [\mathbf{S}^{\mathbf{x}}(-\vec{\mathbf{K}},0), \frac{\partial}{\partial t} \mathbf{S}^{\mathbf{x}}(\vec{\mathbf{K}},t)] \rangle$$

and

$$\frac{\partial^{n}}{\partial t^{n}} \operatorname{R}^{xx}(\vec{K}, t) = \frac{i}{n} \langle [S^{x}(-\vec{K}, 0), \frac{\partial^{n-1}}{\partial t^{n-1}} S^{x}(\vec{K}, t)] \rangle \qquad (3.20)$$

It is easy to show that $F^{xx}(\vec{K},\omega)$ is even in ω so only the even moments are non-zero. Then

$$\langle \omega^2 \rangle = \int_{-\infty}^{\infty} d\omega \ \omega^2 F^{xx}(\vec{K}, \omega) = -\left\{ \frac{\partial^2}{\partial t^2} f^{xx}(\vec{K}, t) \right\}_{t=0}$$

$$= \frac{-g^2 \mu^2}{N \chi^{xx}(\vec{K})} \left\{ \frac{\partial^2}{\partial t^2} R^{xx}(\vec{K}, t) \right\}_{t=0}$$
(3.21)

and similarly

$$\langle \omega^4 \rangle = \frac{g^2 \mu^2}{N \chi^{xx}(\vec{K})} \left\{ \frac{\partial^4}{\partial t^4} R^{xx}(\vec{K}, t) \right\}_{t=0}$$
 (3.22)

If we now assume a nearest-neighbour model these two expressions can be evaluated. We find, using (3.20) and (3.21),

$$\langle \omega^2 \rangle = \frac{2g^2 \mu^2 J}{\hbar^2 \chi^{xx}(\vec{K})} (\gamma_0 - \gamma_K) \langle S^y S^y_a + S^z S^z_a \rangle$$
(3.23)

where

$$\gamma_{\vec{K}} = \sum_{\vec{p}} e^{i\vec{K}\cdot\vec{p}}$$
(3.24)

The expression for $\langle \omega^4 \rangle$ is very long and will not be repeated here. It is of a similar form to (3.23) with a denominator $\chi^{XX}(\vec{K})$ and a numerator involving correlation functions between four spins which are close together. This numerator is also proportional to $(\gamma_0 - \gamma_K)$, as is (3.23).

From these remarks we can now reconstruct the general character of the moments $\langle\omega^n\rangle$ as a function of n.

(a) $\langle \omega^0 \rangle$ is unity.

(b) $\langle \omega^2 \rangle$, $\langle \omega^4 \rangle$ and all higher moments are inversely proportional to $\chi^{xx}(\vec{K})$.

(c) $\langle \omega^2 \rangle \langle \omega^4 \rangle$ and all higher moments are proportional to $(\gamma_0 - \gamma_K)$. This follows as a general rule from the remark that $f^{xx}(\vec{K}, t)$ is independent of t in the limit $K \to 0$.

(d) $\langle \omega^2 \rangle, \langle \omega^4 \rangle$ etc. are proportional to correlation functions between spins which are close together. This follows from (3.19), (3.20) which involve a commutator, and therefore reduce, at t = 0, to shortrange correlation functions.

We now note that effect (d) cannot produce important qualitative effects near the critical temperature. For example we note that (3.23) can be re-written, above T_c , as

$$\langle \omega^2 \rangle = \frac{-2 g^2 \mu^2}{3 \hbar^2 \chi(\vec{K})} (\gamma_0 - \gamma_{\vec{K}}) E(T)$$
 (3.25)

where E(T) is the thermal energy for a typical pair of spins

$$E(T) = -2J\langle \vec{S} \cdot \vec{S}_{a} \rangle \qquad (3.26)$$

We know that the specific heat has a weak singularity (probably logarithmic) at T_c , and hence E(T) is continuous, but with an infinite slope, at T_c . This is a weak singularity compared to the divergence in $\chi(0)$; this essential difference is because any short range correlation function can have only weak singularities whereas $\chi(\vec{K})$ involves long-range correlation functions. We conclude that effect (d) produces numerical factors slowly varying with T.

Effect (b), the thermodynamic slowing down of fluctuations, shows that the scattering becomes more nearly elastic near T_c . Effect (c), the kinematic effect, shows that long wavelength fluctuations are slow.

At infinite temperature the discussion is straightforward. From (3.12) and (3.16) we get

$$\chi(\vec{K}) \rightarrow \chi_{c}T_{c}/T = g^{2}\mu^{2}S(S+1)/3kT = \chi_{0}$$
 (3.27)

where we use X_0 to stand for the Curie susceptibility. The short range correlation functions appearing in the moment formulae are also inversely proportional to T and a tedious calculation gives the results

$$\langle \omega^2 \rangle \rightarrow \left(\frac{2J}{\hbar}\right)^2 \frac{2}{3} S(S+1) (\gamma_0 - \gamma_K)$$
 (3.28)

$$\langle \omega^4 \rangle \rightarrow \left(\frac{2J}{\hbar}\right)^4 \frac{4}{9} \{S(S+1)\}^2 (\gamma_0 - \gamma_K) \left\{\frac{7}{2} \gamma_0 - \frac{3}{2} \gamma_K - 2 - \frac{3}{4S(S+1)}\right\}$$
 (3.29)

In the forward direction¹ we notice, since both $\langle \omega^2 \rangle$ and $\langle \omega^4 \rangle$ are proportional to K², that $\langle \omega^4 \rangle$ is much larger than $\langle \omega^2 \rangle^2$. It follows that although the half width at half height of $F(\vec{K}, \omega)$ must be small the shape must have large wings to it, i.e. $F(\vec{K}, \omega)$ must be something like a cut-off Lorentzian. We therefore assume

$$F(\vec{K},\omega) = \frac{1}{\pi} \frac{\Gamma_{K}}{\omega^{2} + \Gamma_{K}^{2}} \text{ for } |\omega| < s$$

$$= 0 \quad \text{for } |\omega| > s \quad (3.30)$$

where

$$\Gamma_{\rm K} = \frac{\pi}{2\sqrt{3}} \left\{ \frac{\langle \omega^2 \rangle^3}{\langle \omega^4 \rangle} \right\}^{\frac{1}{2}}$$
(3.31)

and

$$s = \left\{\frac{3\langle\omega^4\rangle}{\langle\omega^2\rangle}\right\}^{\frac{1}{2}}$$
(3.32)

are chosen to give the second and fourth moments correctly. Substituting from (3.28) and (3.29) gives, to leading order in K^2 ,

$$\Gamma_{\rm K} = \frac{J\pi}{3\hbar} (\gamma_0 - \gamma_{\rm K}) \left[\frac{{\rm S}({\rm S}+1)}{\{{\rm r}-1-3/16~{\rm S}\,({\rm S}+1)\}} \right]^{\frac{1}{2}}$$
(3.33)

$$s = \frac{4J}{\hbar} \left[S(S+1) \right]^{\frac{1}{2}} \left[r - 1 - 3/16 S(S+1) \right]^{\frac{1}{2}}$$
(3.34)

where r is the number of nearest neighbours. If we write

$$\Gamma_{\rm K} = \Lambda \,{\rm K}^2$$
 at T = ∞ (3.35)

and use molecular field theory to give J in terms of ${\rm T_c}$, we can now evaluate A. For Fe we find

$$2 m_0 \Lambda/\hbar = 19$$
 at $T = \infty$ (3.36)

The factors on the left hand side of (3.36) are convenient and give a dimensionless number. Equation (3.36) is only a rough estimate because we have used a nearest-neighbour Heisenberg model to represent metallic

¹ At large values of K and especially for a polycrystalline sample, deGennes has shown that, in the infinite temperature limit, a Gaussian curve approximates the energy distribution quite well. The fitting of a Gaussian function to experimental measurements of high temperature paramagnetic scattering has allowed the exchange parameters in a number of salts (MnF_2 , MnO, $KMnF_3$, $NaMnF_3$, $LaCrO_3$, $LaMnO_3$, $LaFeO_3$, $RbMnF_3$) to be evaluated. This work is reviewed by Collins in the Proceedings of the Boston Magnetism Congress [8].
Fe and furthermore we used molecular field theory to relate J to T_c . Nevertheless it should be of the correct order of magnitude. It should be noted that the only significant singularities of (3.30) are poles on the imaginary axis, at $\omega = \pm i \Gamma_K$.

At low temperatures the discussion is also straightforward. In a ferromagnet the last factor of (3.23) becomes S² and both molecular field theory and spin wave theory give

$$\chi^{xx}(\vec{K}) = \frac{g^2 \mu^2}{2J(\gamma_0 - \gamma_{\vec{k}})}$$
(3.37)

Hence

$$\langle \omega^2 \rangle \rightarrow 4 \, \mathrm{J}^2 \, \mathrm{S}^2(\gamma_0 - \gamma_{\vec{k}}) / \hbar^2 \quad \text{at } \mathrm{T} = 0$$
 (3.38)

The general expression for $\langle \omega^4 \rangle$ can be used to give

$$\langle \omega^4 \rangle = \langle \omega^2 \rangle^2$$
 at T = 0 (3.39)

The only distribution which satisfies (3.21) is a δ -function. Hence (3.38) and (3.39) together give

$$\mathbf{F}^{\mathbf{xx}}(\vec{K},\omega) = \frac{1}{2} \,\delta(\omega - \omega_K) + \frac{1}{2} \,\delta(\omega + \omega_K) \quad (\mathbf{T} = 0) \tag{3.40}$$

where

$$\omega_{\rm K} = 2 \, \mathrm{J} \, \mathrm{S} \left(\gamma_0 - \gamma_{\rm K} \right) / \hbar \tag{3.41}$$

is the correct spin wave frequency. As the temperature is raised the spin waves get damped and the δ -functions of (3.40) become broadened into cut-off Lorentzians, i.e. the singularities of $\mathbf{F}^{xx}(\vec{K},\omega)$ move slightly off the real axis.

As the temperature is raised still further the spin wave interactions result in an energy renormalisation. It is well known that at low temperatures this energy renormalisation follows a $T^{5/2}$ law. Up to, say 0.8 T_c, it is probably reasonable to use (3.23) directly to give a rough estimate of the spin wave energy. Hence, very roughly,

$$\omega_{\rm K} \sim 2 \, J \, (\gamma_0 - \gamma_{\vec{\rm K}}) \, \left\{ \left\langle {\rm S}^{\, y} {\rm S}^{\, y}_{\, a} + \, {\rm S}^{z} \, {\rm S}^{\, z}_{\, a} \right. \right\}^{\frac{1}{2}} / \hbar \qquad {\rm for} \, \, 0 < \, {\rm T} < \, 0.8 \, {\rm T_c} \qquad (3.42)$$

In the neighbourhood of T_c we expect

$$\langle S^{y}S^{y}_{a} \rangle \sim \langle S^{y}S^{z}_{a} \rangle \sim \frac{S(S+1)}{3(r-1)}$$
 (3.43)

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Henċe

$$\omega_V = A K^2 \tag{3.44}$$

where

$$A \sim (2J a^2 r/6\hbar) \{2 S(S+1)/3(r-1)\}^{\frac{1}{2}}$$
 (3.45)

Substituting for J as before we find for Fe [S=1, r=8] the result

$$2m_0 A/\hbar \sim 30$$
 (3.46)

This last estimate is rough because we have made no real attempt to calculate the renormalized ω_K within, say, a factor of 2. Nevertheless, within this kind of uncertainty it should be satisfactory up to about 0.8 T_c and beyond that temperature the spin wave interaction problem is too difficult to discuss here.

We now notice by comparing (3.35) and (3.46) that the separation between the spin wave peaks at about 0.8 T_c is roughly the same as the width of the scattering curve at infinite temperature. The shape of $F^{xx}(\vec{K},\omega)$ is very different at the two temperatures but the scale of the dependence on ω is roughly the same.

We now turn to a discussion of $F^{xx}(\vec{K},\omega)$ near T_c . Because of the weak T dependence of effect (d), near but just above T_c we may estimate moments as

$$\left\langle \omega^2 \right\rangle_{\mathrm{K},\mathrm{T}} \sim \left\langle \omega^2 \right\rangle_{\mathrm{K},\infty} \, x_0 / x \, (\vec{\mathrm{K}},\mathrm{T})$$

$$\left\langle \omega^4 \right\rangle_{\mathrm{K},\mathrm{T}} \, \sim \left\langle \omega^4 \right\rangle_{\mathrm{K},\infty} \, x_0 / x \, (\vec{\mathrm{K}},\mathrm{T})$$

$$(3.47)$$

where χ_0 is the Curie susceptibility. By comparison with the discussion of $F(\vec{K},\omega)$ at infinite temperature we see this has the effect of replacing K^2 by $K^2 \chi_0 / \chi(\vec{K},T)$. The ratio $\langle \omega^4 \rangle / \langle \omega^2 \rangle^2$ is now even larger than at infinite temperature because $\chi(\vec{K},T)$ is large near T_c . In the absence of any other information about $F(\vec{K},\omega)$ we assume it is a cut-off Lorentzian just as at infinite temperature; by analogy to (3.35) we get immediately

$$\Gamma_{\rm K} = \frac{\Lambda \, {\rm K}^2 \, {\rm x}_0}{{\rm x} \, ({\rm \vec{K}},{\rm T})} = \Lambda \, {\rm K}^2 {\rm r}_1^2 (\kappa_1^2 + {\rm K}^2) \, {\rm T}_{\rm c} \, / \, {\rm T}$$
(3.48)

From either (3.16) or (3.17) we see that $r_1^2 \kappa_1^2$ is small near T_c and in typical neutron experiments on ferromagnets the observations are made at angles such that $q^2 = K^2 \sim \kappa_1^2$. Thus, for an experimental situation such as that used by Passell et al. [9] the expression (3.48) is some two orders of magnitude smaller than the appropriate expression for infinite temperature, (3.35). Hence the theoretical prediction is that there is a very substantial narrowing of the scattered neutron distribution as the temperature is reduced towards T_c . However in the experiments by Passell et al. [9] and in others by Jacrot et al. [10], none of the features of (3.48) are observed. In particular, these earlier experiments suggest:

(1) The order of magnitude of $\Gamma_{\!K}$ is given by an expression like (3.35) with

$$2 m_0 \Lambda/\hbar \sim 11.4$$
 [Experiment T \sim T,] (3.49)

This is about two orders of magnitude larger than (3.48).

(2) $\Gamma_{\rm K}$ is approximately independent of temperature. This is in contrast with (3.48) which varies sensitively with T because of the $r_1^2 \kappa_1^2$ dependence.

(3) $\Gamma_{\rm K}$ is proportional to K² within experimental error. No term proportional to K⁴, as predicted by (3.48), is observed.

We are forced to conclude that the conventional theory as we have just summarized it, fails substantially. Therefore, in the next section, we look for an improvement.

3.3. Theoretical discussion for T approaching T_c

The discussion of 3.2 has shown that the inelasticity near T_c is hard to understand and therefore in this section we shall discuss the qualitative features which it now appears a good theory of the critical region must have.

We first note that the calculation for infinite temperature (3.36), the spin wave calculation at about 0.8 T_c, i.e. (3.46), and experiment just above T_c, (3.49), all give results roughly in agreement as regards the dependence of $F^{xx}(\vec{K},\omega)$ on ω . This suggests that, apart from a very narrow temperature region right at T_c which we shall discuss in 3.4 below, the ω scale of $F^{xx}(\vec{K},\omega)$ does not in fact change significantly from 0.8 T_c up to infinite temperature but that the shape of $F^{xx}(\vec{K},\omega)$ changes considerably from two distinct spin wave peaks below T_c into a single Lorentzian at infinite temperature. But calculations which rely upon moment calculations are quite unable to give sensitive information on shapes and therefore the theory as described in 3.2 is suspect.

We now examine more carefully the behaviour of (3.47). Using (3.12) it gives

$$\left<\omega^{2}\right>_{K,T} = \left<\omega^{2}\right>_{K,\infty} (r_{1}^{2}\kappa_{1}^{2} + r_{1}^{2}K^{2}) T_{c}/T$$
 (3.50)

$$\langle \omega^4 \rangle_{K,T} = \langle \omega^4 \rangle_{K,\infty} (r_1^2 \kappa_1^2 + r_1^2 K^2) T_c / T$$
 (3.51)

(3.50) is proportional to K^2 at infinite temperature, because $\langle \omega^2 \rangle_{K,\infty}$ is proportional to K^2 but as the temperature is lowered (3.50) becomes smaller and becomes proportional to K^4 at temperatures sufficiently close to T_c that $\kappa_1^2 \ll K^2$. If we assume that $F^{xx}(\vec{K},\omega)$ remains a cut-off Lorentzian we are immediately led to (3.48). But the above behaviour is quite consistent with a gradual change of shape in $F^{xx}(\vec{K},\omega)$ from a Lorentzian at infinite temperature to one which is dominated by two peaks at $\omega = \pm A K^2$ for temperatures such that $\kappa_1^2 \ll K^2$. These peaks would make

a negligible contribution themselves to $\langle \omega^4 \rangle$ and the higher moments. Such peaks, if they existed, would have the obvious interpretation of quasi-spin waves above T_c . However we notice that a rectangular distribution bounded by $\omega = \pm A K^2$ would serve equally well as a dominant distribution near T_c . We also recall that, above T_c , $F^{xx}(\vec{K},\omega)$ and $F^{zz}(\vec{K},\omega)$ are identical and we cannot possibly associate single spin wave processes with $F^{zz}(\vec{K},\omega)$. Nevertheless the general point remains valid, it is quite consistent with (3.50) and (3.51) for any curve whether double peaked or not, to be sharply confined to limits $\omega = \pm A K^2$ provided it also has weak "tails" which can give large values to $\langle \omega^4 \rangle$ and higher moments.

This argument can be summarized as follows:

(i) The moment calculations are sensitive to the tails of the distribution $F^{xx}(\vec{K},\omega)$ whereas the neutron experiments measure only the central portion of $F^{xx}(\vec{K},\omega)$.

(ii) Apart from a very narrow range of temperature right at T_c which we discuss in 3.4 below, this central portion has a width, $\sim A K^2$, roughly independent of T from 0.8 T_c to infinite temperature but with a shape varying from a double peak (representing spin waves) at the lower limit to a single peak at high T. This central portion always contains the major part of the area of $F^{xx}(\vec{K}, \omega)$.

(iii) The tails of the distribution $F^{xx}(\vec{K},\omega)$ are sensitive to T and vary so as to give agreement with the moment calculations. They are difficult to observe experimentally.

(iv) Above T_c , $F^{zz}(\vec{K},\omega)$ is identical with $F^{xx}(\vec{K},\omega)$ but below T_c does not show distinct spin wave peaks. However the ω -scale is roughly similar,

The above conclusions appear to be dictated by the experimental results which were obtained for the general range $K \sim \kappa_1$. For either $K \ll \kappa_1$ or $K \gg \kappa_1$ the neutron experiments give no information and therefore it is possible that in these regions the ω dependence is qualitatively different.

The clearest way of describing the situation is in terms of the singularities of $F^{xx}(\vec{K},\omega)$ in the complex ω plane. We have already remarked that the high temperature theory, (3.35), gives two significant poles at $\pm i\Lambda K^2$; the other singularities of $F^{xx}(\vec{K},\omega)$, [which are needed to describe the cut-off procedure for $|\omega| > s$], are distant $\sim J/h$ from the origin. The conventional theory, (3.48), near T_c tells us that the two significant poles have moved along the imaginary axis to $\pm i\Lambda K^2 \chi_0 / \chi(\vec{K}, T)$ and the other singularities of $F^{xx}(\vec{K},\omega)$ remain at a long distance from the origin. However, the neutron experiments insist that this is not correct, there must be singularities of some type distributed at distances $\sim \Lambda K^2$ from the origin; the poles predicted by (3.48) may or may not exist but if they do exist they must have a weight small compared to those at distances $\sim \Lambda K^2$.

The form of $\mathbf{F}^{xx}(\vec{K},\omega)$ below \mathbf{T}_c is of special interest. Well below \mathbf{T}_c we know that $\mathbf{F}^{xx}(\vec{K},\omega)$ is dominated by two spin wave peaks centred at $\pm \omega_K$, where ω_K is the renormalized spin wave energy, and with a width dependent in the spin wave lifetime. As the temperature is raised does $\mathbf{F}^{xx}(\vec{K},\omega)$ retain this form or does a distinct diffusive mode appear in addition? We may speculate that an analogy to the classical fluid may exist. A classical fluid, at small K, may be described by the usual

equations of hydrodynamics. In the absence of any dissipative effects. viscosity or thermal conductivity, the relaxation function [equivalent to $F^{xx}(\vec{K},\omega)$] has two δ -function peaks at + c_sK where c_s is the velocity of sound. The introduction of viscosity or thermal conductivity damps these sound waves and simultaneously a diffusive mode also appears in the relaxation function. In other words, in the complex ω plane, as soon as the sound wave poles move off the real axis, a new pole appears on the imaginary axis. In suitable cases therefore, the relaxation function as measured by experiment as a function of real ω , can have three maxima. one at $\omega = 0$ and two symmetrically placed either side at the appropriate renormalised frequencies. In the magnetic system the same phenomena might take place as the spin waves are damped. This possibility is intimately linked with the problem of the energy renormalisation of spin waves very close to T_c and in view of the extremely speculative nature of this particular discussion we shall not pursue it further other than to remark that it is also connected with the behaviour of κ_{1x}^2 below T_c (this problem was mentioned in 3.1).



FIG. 20. Possible singularities of $F^{XX}(\vec{K}, \omega)$ in the complex ω -plane (Marshall).

The discussion of this section is most clearly summarized in Fig. 20 which shows the positions of the singularities of $\mathbf{F}^{XX}(\vec{K},\omega)$ in the complex ω plane according to the conventional theory and also two possibilities which would be consistent with the neutron results. In this figure singularities which are a long distance $\sim J/\hbar$ from the origin are not shown. Figure 20a gives the conventional theory, Fig. 20 b the theory we would expect by

analogy to hydrodynamics and Fig. 20c the theory we might expect if no "diffusive" mode appears below T_c . At the present time we are not able to tell whether possibility, (b) or (c) is correct.



FIG. 21. Inelastic scattering at $q = 0.2 \text{ Å}^{-1}$ in RbMnF₃ (Néel point 82.65 ± 0.07°K) (according to Nathans, Menzinger, Pickart).

3.4. Recent experiments at temperatures very close to T_c

Figure 21 shows the striking neutron results obtained by Nathans, Menzinger and Pickart on the anti-ferromagnetic crystal $RbMnF_3$. The persistence of two outer peaks at $\omega \neq 0$ up to temperatures appreciably above T_c is clearly demonstrated. (Below T_c the $\omega = 0$ peak must not necessarily be taken as evidence that the diagram in Fig. 19b above is the correct one. $RbMnF_3$ has cubic symmetry and consequently the neutron measurements were carried out with a mixture of domains present which would allow scattering from both longitudinal and transverse excitations, i.e. the central peak may come from $F^{ZZ}(\vec{K}, \omega)$ not $F^{XX}(\vec{K}, \omega)$.)

The discussion in 3.3 concerning inelasticity near T_c must be extended in view of recent results which indicate that very close indeed to T_c thermodynamic slowing down does take place, at least under some conditions. Experiments on Ni by Drabkin, Zabidarov, Kasman and Okorokov [11] and on Tb by Als-Nielsen, Dietrich, Marshall and Lingard [12] show the energy width narrowing rapidly as T approaches T_c (see Fig. 22). Narrowing is also observed for RbMnF₃ by Nathans et al. [13] when $q = |\vec{K} - \vec{r}| = 0$. In fact, a common feature in all these observations is the small value of q involved. Thus except right at T_c or T_N , we probably have a situation where $q \ll \kappa_1$, and the scattering in effect samples distances large compared with the correlation length in real space, and is rather insensitive to short-range fluctuations within the regions of correlated spin, such as would correspond to "spin wave" excitations. In terms of Fig.20, the appearance of thermodynamic slowing down in a very narrow temperature range near T_c suggests that at $T \sim T_c$ the singularities on the imaginary axis are close to the origin and dominate the susceptibility and neutron scattering properties. As T is increased these singularities move away very rapidly and the situation is once more controlled by the "spin wave" singularities indicated in Fig.20.



FIG. 22. Temperature variation of the inelasticity in the scattering from Tb (Als-Nielsen, Dietrich, Marshall, Lingard, Solid State Communications 5 (1967) 607).

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SELECTED TOPICS IN NEUTRON SPECTROMETRY

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Abstract

1. Neutron spectroscopy and electrical conductivity in liquid metals: 1.1. Introduction; 1.2. Structure factor and radial distribution function; 1.3. Structure factor, direct correlation function and ion-ion potential; 1.3.1. The results of the Born and Green theory; 1.3.2. The results of the Percus-Yevick theory; 1.3.3. The ion-ion potential in liquid zinc; 1.4. Structure factor and electrical conductivity of liquid metals.

2. Applications of elastic diffraction of neutrons to solids and liquids: 2.1. Introduction: 2.2. Physical meaning of the method of elastic diffraction of neutrons; 2.3. Applications of the method of elastic diffraction of neutrons to the study of liquids; 2.3.1. The growth of the Debye-Waller cloud in a simple liquid; 2.3.2. Accurate determination of the structure factor; 2.4. Applications of the method of elastic diffraction of neutrons to the study of solids; 2.4.1. Accurate determination of the Debye-Waller factor; 2.4.2. Diffuse disorder scattering and thermal diffuse scattering; 2.4.3. Elastic diffraction of neutrons and crystal structure analysis of hydrogenous compounds; 2.5. Summary and conclusions.

1. NEUTRON SPECTROSCOPY AND ELECTRICAL CONDUCTIVITY IN LIQUID METALS

1.1. Introduction

In this seminar I would like to present the connections existing between the information obtainable by diffraction of neutrons and other radiations in liquid metals, and the transport properties of the electrons in the metal itself.

My task has really been made easier by the courses given by professors Ziman, March, Garcia-Moliner, and Lloyd; I refer to their comprehensive lecture notes for the background underlying the matter covered in this seminar. In order to discuss the connection between the structure factor S(Q) and i) the radial distribution function g(r), ii) the direct correlation function c(r) and the ion-ion potential $\phi(r)$ and iii) the electrical conductivity of liquid metal, I will make also use of some experimental results recently obtained in Ispra on liquid zinc, in collaboration with Drs Corchia and Rizzi.

1.2. Structure factor and radial distribution function

We shall assume that the connection between S(Q) and g(r) is well known to the participants such that we shall only give a summary survey of the situation. We shall first study the simplest case, the diffraction of radiation by a pair of atoms at a distance \vec{r} , and then generalize to ordinary monatomic systems. The ingoing plane wave \vec{k}_0 associated with the incident radiation (neutrons, X-ray, etc.) is scattered by the atomic centres according to the Huygens principle, and the resulting amplitude $A(\vec{Q})$ of the outgoing wave \vec{k} is proportional to:

$$A(\vec{Q}) \propto a\left(1 + e^{i\vec{Q} \cdot \vec{r}}\right)$$
 (1.1)

where (see Fig. 1.1) a is the scattering amplitude or form factor of the scattering centre and $\vec{Q} \equiv \vec{k} - \vec{k}'$ is the wave vector transfer. The intensity $I(\vec{Q})$ associated with the scattering process is then given by:

$$\left|A(\vec{Q})\right|^{2} \propto 4 a^{2} \cos^{2} \frac{Qr\cos\alpha}{2}$$
(1.2)



FIG. 1. 1. The scattering process by a pair of atoms.

and for an isotropic system it turns out to be proportional to the average of $|A(Q)|^2$ over the solid angle 4π :

$$I(Q) \propto 2a^2 \left(1 + \frac{\sin Qr}{Qr}\right)$$
(1.3)

Let us now think of the liquid as an ensemble of N-1 pairs of atoms isotropically distributed around anyone of the N atoms taken as the origin. The scattered neutron intensity is then given by:

$$I(Q) \propto Na^{2} \left(1 + \sum_{s=2}^{N} \frac{\sin Qr_{s}}{Qr_{s}}\right)$$
(1.4)

 \mathbf{or}

$$I(Q) \propto Na^{2} \left(1 + 4\pi \rho \int_{0}^{\infty} g(r) \frac{\sin Qr}{Qr} r^{2} dr \right)$$
(1.5)

In Eq.(1.5) ρ and ρ g(r) are the average and the local number density of atoms in the liquid, respectively.

Putting:

$$\frac{I(Q)}{Na^2} = \frac{I(Q)}{I(\infty)} \equiv S(Q) \equiv i(Q) + 1$$
(1.6)

one obtains from Eq.(1.5) a formula equivalent to Eq.(1.10) of Professor March's notes:

Q(S(Q) - 1) =
$$4\pi\rho \int_{0}^{\infty} (g(r) - 1) \sin Qr r dr$$
 (1.7)

The difference between (1.5) and (1.7) comes from the term

$$4\pi\rho\int\limits_{0}^{R}\sin \mathbf{Qr} \mathbf{r} d\mathbf{r}$$

on the right-hand side of (1.7), which, as can be shown, would add contributions to the scattered intensity only at wavevector transfers comparable with the reciprocal of the macroscopic dimensions R of the sample container. Neglecting these contributions, which are only important in an experimentally inaccessible region, we see from Eq.(1.7) and its Fourier inverse:

$$r\rho(g(r)-1) = \frac{1}{2\pi^2} \int_{0}^{\infty} Q(S(Q)-1) \sin Qr \, dQ \qquad (1.8)$$

that Q times the fluctuations of the scattered intensity around its asymptotic value and r times the local fluctuations of the atomic number density around its average value are connected via a Fourier transform: the knowledge of the structure factor S(Q) of a monatomic liquid is perfectly equivalent to the knowledge of its distribution function g(r). g(r) gives a description of the system at a microscopic level in ordinary space, S(Q) gives an equivalent description in reciprocal or wave-vector space and, so to speak, defines the amount of pleasure the system finds in the process of exchanging a wavevector Q or momentum hQ with the impinging radiation. S(Q) is independent of the nature of the radiation used, being a characteristic of the system: it is the same for X-rays, neutrons, electrons in a metal, etc.

The experimental behaviour of the structure factor S(Q) for zinc at 470°C, as obtained by neutron diffraction in our laboraroty at Ispra, is shown in Fig. 1.2 (taken from Ref.[1]). This behaviour, mostly confirmed by independent neutron measurements performed at about the same temperature in England [2] and in the Philippines [3], appears in strong contrast with that obtained in 1941 by X-ray diffraction [4]: the X-ray data, corrected for the atomic form factor a(Q), (see Fig. 1.3) show an anomalous bump in the region $Q \sim 1.5 \text{ Å}^{-1}$ and, furthermore, S(Q) as obtained by X-rays oscillates around unity in a rather unusual and unsatisfactory way. Furthermore, the radial distribution function g(r) obtained by Fourier inversion of the neutron diffraction data matches the interatomic distances between near neighbours in the crystal, whereas this is not true for the X-ray data.

1.3. Structure factor, direct correlation function and ion-ion potential

In his lectures Professor March has shown in detail the connections between S(Q), g(r), the direct correlation function, c(r), and the ion-ion



FIG. 1.2. Neutron diffraction pattern of liquid zinc at 470°C, corrected for the contribution of the quartz container and the transmission of the sample, but not for multiple scattering (this figure is taken from Ref.[1]).

potential, $\phi(\mathbf{r})$, according to the theories of Born and Green, and Percus and Yevick. It is, therefore, sufficient to summarize the theoretical background and to present thereafter the general behaviour of the ion-ion potential as obtained experimentally.

1.3.1. The results of the Born and Green theory

From the definition of the ion-ion potential $\phi(\mathbf{r})$ in terms of the potential of the mean force $U(\mathbf{r}) = K_B T \ln g(\mathbf{r})$ and the three-atom correlation function $\rho^{(3)}$ $(\vec{r}_1, \vec{r}_2, \vec{r}_3)$:



FIG. 1.3. X-ray diffraction pattern of liquid zinc (this figure deduced by Professor Harrison from the data in Ref. [4], is taken from Ref. [7], page 154).

and by using the Kirkwood superposition approximation for $\rho^{(3)}$:

$$\rho^{(3)}(\vec{r}_{1},\vec{r}_{2},\vec{r}_{3}) = \rho^{3} g(r_{12}) g(r_{23}) g(r_{31})$$
(1.10)

and Abe's approximation for the evaluation of the integral on the righthand side of Eq.(1.9), we obtain:

$$\ln g(r) + \frac{\phi(r)}{K_{\rm p}T} = (g(r) - 1) - c(r) \qquad (1.11)$$

where c(r) is the Ornstein-Zernike direct correlation function, accessible by neutron experiments as will be seen below (see Eq. 1.24).

1.3.2. The results of the Percus-Yevick theory

Using the Fourier components of the density

$$\rho_{Q} = \frac{1}{N} \sum_{s} e^{i\vec{Q}\cdot\vec{r}_{s}}$$
(1.12)

as the Lagrange coordinates of the system, expressing the kinetic and pairwise potential energy of the Hamiltonian in terms of the ρ_Q 's and their conjugated momenta, and noting that, by definition of $g(\vec{r})$, the quantity:

$$S(Q) - 1 \equiv i(Q) = \rho \int e^{i\vec{Q} \cdot (\vec{r_s} - \vec{r_{s'}})} (g(\vec{r_s} - \vec{r_{s'}}) - 1) d(\vec{r_s} - \vec{r_{s'}})$$
(1.13)

can be regarded as N times the average of exp[$i \vec{Q} \cdot (\vec{r}_s - \vec{r}_s)$]:

$$i(Q) = N \langle e^{i\vec{Q} \cdot (\vec{r}_{s} - \vec{r}_{s'})} \rangle$$
(1.14)

we can write i(Q) in terms of the ρ_Q and compute the corresponding ensemble average. By long and nonelementary algebra Percus and Yevick find it possible to connect i(Q) and $\phi(r)$ as follows:

$$i(Q) + i(Q) \frac{N\nu(Q)}{K_BT} + \frac{N\nu(Q)}{K_BT} = 0$$
 (1.15)

$$\frac{N\nu(Q)}{K_{B}T} = \left[\left(e^{\frac{\phi(r)}{K_{B}T}} - 1 \right) g(r) \right]$$
(1.16)

via a quantity $\nu(Q)$, which is directly accessible through the diffractional data:

$$\frac{N\nu(Q)}{K_{\rm B}T} = -\frac{i(Q)}{1+i(Q)}$$
(1.17)

The Fourier transform of $\nu(Q)$ is connected with the direct pair correlation function, c(r), as is verified by Fourier transforming Eq.(1.15). In fact, putting

$$c(\mathbf{r}) = -\left[\frac{N\nu(Q)}{K_{B}T}\right]$$
(1.18)

and

$$h(r) \equiv g(r) - 1$$
 (1.19)

we obtain (see Fig. 1.4):

$$h(\vec{r}_{1} - \vec{r}_{2}) = c(\vec{r}_{1} - \vec{r}_{2}) + \rho \int c(\vec{r}_{1} - \vec{r}_{3}) h(\vec{r}_{3} - \vec{r}_{2}) d\vec{r}_{3}$$

$$= c(\vec{r}_{1} - \vec{r}_{2}) + \rho \int c(\vec{r}_{1} - \vec{r}_{3}) \left\{ c(\vec{r}_{3} - \vec{r}_{2}) + \rho \int c(\vec{r}_{3} - \vec{r}_{4}) h(\vec{r}_{4} - \vec{r}_{2}) d\vec{r}_{4} \right\} d\vec{r}_{3} \qquad (1.20)$$

$$= c(\vec{r}_1 - \vec{r}_2) + \rho \int c(\vec{r}_1 - \vec{r}_3) c(\vec{r}_3 - \vec{r}_2) d\vec{r}_3 + \rho^2 \int c(\vec{r}_1 - \vec{r}_3) c(\vec{r}_3 - \vec{r}_4) c(\vec{r}_4 - \vec{r}_2) d\vec{r}_3 d\vec{r}_4 + \dots$$

giving the pair correlation function in terms of "direct" interactions between pairs of atoms in the liquid.

By Fourier-transforming both sides of Eq.(1.16) and remembering Eqs (1.17) and (1.18), we find the desired connection between $\phi(\mathbf{r})$ and the diffractional data:



FIG. 1.4. Pair correlation function h(r) = g(r)-1 and "direct" correlation function c(r).

Summarizing we obtain as the most important results of (1.3.1) and (1.3.2): the Born-Green equation (in the "hyper-chain" approximation:

$$\ln g(r) + \frac{\phi(r)}{K_{\rm B}T} = h(r) - c(r) \qquad (1.22)$$

the Percus-Yevick equation:

$$\frac{\phi(\mathbf{r})}{K_{B}^{T}} = \ln\left(1 - \frac{c(\mathbf{r})}{g(\mathbf{r})}\right)$$
(1.23)

and

$$\mathbf{r}\rho \mathbf{c}(\mathbf{r}) = \frac{1}{2\pi^2} \int_0^{\infty} \mathbf{Q} \frac{\mathbf{i}(\mathbf{Q})}{1 + \mathbf{i}(\mathbf{Q})} \sin \mathbf{r} \, \mathbf{Q} \, \mathrm{d}\mathbf{Q} \tag{1.24}$$

When used together with Eqs (1.8) and (1.24), Eqs (1.22) and (1.23) allow us to obtain the ion-ion potential $\phi(\mathbf{r})$ directly from the diffractional data.

1.3.3. The ion-ion potential in liquid zinc

The ion-ion potential $\phi(\mathbf{r})$ in liquid zinc, as obtained in the Ispra Laboratory according to the Percus-Yevick theory from Eq.(1.23) and the experimental data of Fig.(1.2), is shown in Fig.(1.5). This form of $\phi(\mathbf{r})$ shows a marked minimum at a distance corresponding to that of nearest neighbours in the liquid and a well-defined maximum at larger distances. $\phi(\mathbf{r})$ tends then rather rapidly to zero without exhibiting strong Friedel-type oscillation. A similar behaviour had been previously found in our laboratory for liquid gallium [5]. The absolute depth of the minimum, which for



ION-ION POTENTIAL IN LIQUID ZINC AT 470°C

FIG.1.5. Ion-ion potential in liquid zinc, according to the Percus and Yevick theory (this figure is taken from Ref. [8]).

liquid zinc does not seem to be large enough to avoid evaporation, is strongly affected by the low Q behaviour of the structure factor. We think that, with some improvement in the accuracy of the experimental data, it will be possible to obtain, from neutron diffraction in liquid metals, as good a basis for a reliable determination of $\phi(\mathbf{r})$ as the one represented by the analysis of the dispersion curves in the corresponding solid.

1.4. Structure factor and electrical conductivity of liquid metals

It is known (see for instance the lectures by Garcia-Moliner and Lloyd) that, within the framework of the relaxation-time approximation, the electrical conductivity σ in a liquid metal is given by:

$$\sigma = \frac{e^2}{3\pi^2 \hbar^2} \tau (k_F) k_F^2 \left(\frac{\partial \epsilon}{\partial k} \right)_F$$
(1.25)

In Eq.(1.25) k_F is the radius of the Fermi sphere, ϵ is the electron energy, and the relaxation time $\tau(k_F)$ is defined as follows:

$$\frac{1}{r(k_{\rm F})} = \frac{V}{2\pi\hbar} \frac{k_{\rm F}^2}{\left(\frac{\partial\epsilon}{\partial k}\right)_{\rm F}} \int_0^{\pi} (1 - \cos\vartheta) \left|\langle \vec{k} + \vec{Q} | W | \vec{k} \rangle\right|^2 \sin\vartheta \,d\vartheta \tag{1.26}$$

In Eq.(1.26) V is the volume of the liquid, $(1-\cos \vartheta)$ is the percentage of the forward momentum conserved as a result of the collision, $k_F^2 \sin \vartheta d\vartheta$ is the element of the Fermi surface representing possible final states associated with elastic scattering of electrons, and the strength of the interaction is represented by the quantity:

$$\left|\left\langle \vec{k} + \vec{Q} \right| | W \right| | \vec{k} \rangle \right|^2 \tag{1.27}$$

The matrix element of the pseudopotential W felt by an electron in the liquid, connects electron states \vec{k} and $\vec{k} + \vec{Q}$. If the pseudopotential W(r) can be described in terms of a sum of pseudopotentials w due to all ions in the liquid, i.e.

$$W(r) = \sum_{s} w(r - r_{s})$$
 (1.28)

we easily obtain

$$\langle \vec{\mathbf{k}} + \vec{\mathbf{Q}} \mid \mathbf{W} \mid \vec{\mathbf{k}} \rangle = \frac{1}{V} \int e^{-i(\vec{\mathbf{k}} + \vec{\mathbf{Q}})} \sum_{s} \mathbf{w}(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{s}) e^{i\vec{\mathbf{k}} \cdot \vec{\mathbf{r}}} d\vec{\mathbf{r}}$$
$$= \frac{1}{N} \sum_{s} e^{i\vec{\mathbf{Q}} \cdot \vec{\mathbf{r}}_{s}} \frac{1}{V_{0}} \int e^{-i\vec{\mathbf{Q}} \cdot \vec{\mathbf{r}} - \vec{\mathbf{r}}_{s}} \mathbf{w}(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{s}) d(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{s})$$
(1.29)

In (1.29) V_0 is the atomic volume. (1.29) can then be written as follows:

$$\langle \vec{\mathbf{k}} + \vec{\mathbf{Q}} | \mathbf{W} | \vec{\mathbf{k}} \rangle = \rho_0 \mathbf{w}(\mathbf{Q})$$
 (1.30)

The matrix element of the pseudopotential giving the amplitude of the strength of the electron-ion interaction is the product of the Fourier components of the density, ρ_Q , and the form factor, w(Q). Substitution of (1.30) into (1.25) and (1.26) eventually leads to the well known expression for the resistivity:

$$\frac{1}{\sigma} = \frac{6\pi}{\hbar} \frac{mV_0}{e^2} \frac{1}{E_F} \int_0^1 S(Q|w(Q)|^2 \left(\frac{Q}{2k_F}\right)^3 d\left(\frac{Q}{2k_F}\right)$$
(1.31)

The very presence of the structure factor S(Q) in the formula for the resistivity¹ represents a strong connection between neutron spectrometry

¹ As a matter of fact it can be shown that similar expressions containing the structure factor and the form factor hold for other transport properties of electrons in liquid metals, such as the thermoelectric power, etc.

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and the transport properties of electrons in liquid metals. Another less direct link between these two fields could originate from the quantity w(Q): in principle, the ion-ion potential, as measurable, e.g., by neutron diffraction, is due to a short-range repulsive interaction, a direct Coulomb interaction between the bare ions and an indirect interaction between the ions via the conduction electrons. This last contribution is certainly related to the form factor w(Q), although it is not easy to build models for the pseudopotentials capable of reproducing the measured ion-ion potential.

Finally, we want to mention that some of the comparisons between computed and experimental values of the resistivity of liquid metals, considered "satisfactory" in recent literature on the theory of pseudopotential, are really not encouraging: for example, in the case of liquid zinc, the use of the structure factor obtained by X-ray diffraction, together with the Heine-Abarenkov form factor led to a computed value of the resistivity of 44 μ ohmcm, compared to an experimental value of 37 μ ohmcm, while the use of the above model for the pseudopotential together with the experimental data obtained in Ispra [1] and in the Philippines would lead to a theoretical value of about 22 μ ohmcm [6] and 19 μ ohmcm [3], respectively.

2. APPLICATIONS OF ELASTIC DIFFRACTION OF NEUTRONS TO SOLIDS AND LIQUIDS

2.1. Introduction

I shall now present and discuss some of the possible applications of the method of elastic diffraction of neutrons to the physics of condensed matter [9-16].

This method has been developed for several years in our laboratory at Ispra.² Although in the language currently used in the literature conventional diffraction is often confused with elastic scattering, these two processes are basically different both in the nature of the information they provide and the experimental arrangement.

Conventional diffraction consists of the determination of the intensity of monochromatic neutrons scattered in the sample under investigation. Usually, measurements are made by a two-axis spectrometer (see Fig. 2.1a), recording the diffracted neutron intensity at any scattering angle and ignoring any energy transfer undergone by the neutron as a result of the scattering process.

Elastic diffraction consists of the determination of the intensity of monochromatic neutrons, elastically scattered in the sample under investigation. Usually, to this end, a three-axis spectrometer is utilized, whose analysing spectrometer, centered at the wavelength of the impinging radiation, records, at any scattering angle, only those among the diffracted neutrons which have an energy equal, within the spectrometer resolution, to that of the impinging neutrons (see Fig. 2.1.b).

In section 2.2. the physical meaning of the method of elastic diffraction will be discussed. In sections 2.3. and 2.4. some of its applications to the physics of liquids and solids respectively, will be presented. Finally, a summary will be given in section 2.5.

² It is a pleasure to acknowledge the contributions to the work presented here given at different times by M. Antonini, P. Ascarelli, G. Borgonovi, F. Pompa, and D. Tocchetti.

2.2. Physical meaning of the method of elastic diffraction of neutrons

It is well known that any measure of conventional diffraction can be regarded as a collection of instantaneous pictures of the system being studied: ignoring possible energy transfers between the system and the radiation is equivalent, according to the Heisenberg principle, to sharply defining the collision time. When, instead, the scattered radiation is allowed to give contributions to the recorded intensity only if its energy





b) A three-axis spectrometer prepared for elastic diffraction of neutrons. In this arrangement only diffracted neutrons of energy equal (within the instrumental energy resolution) to the energy of the neutrons impinging on the sample are allowed to be Bragg-reflected in the analysing spectrometer and to reach the BF_3 counter.

is equal to that of the impinging radiation within an instrumental energy resolution ΔE (which can easily be kept down to ~ 2 meV), the experimenter is left with information which can be conceived as a collection of pictures of the system, each one taken during a time Δt which is inversely proportional to ΔE .

In fact, the differential cross-section $d\sigma/d\Omega_{el}$ of a system of N supposedly identical atoms, for a process of elastic diffraction, is:

$$\frac{\mathrm{d}\,\sigma}{\mathrm{d}\Omega}\Big|_{\mathrm{el}} = \frac{a_{\mathrm{coh}}^2}{2\pi} \int \mathrm{S}(\vec{Q},\,\omega)\,\mathrm{R}(\omega)\,\mathrm{d}\omega \qquad (2.1)$$

where a_{cob} is the (coherent) scattering amplitude; the "scattering law"

$$S(\vec{Q}, \omega) = N \int e^{i(\vec{Q} \cdot \vec{r} - \omega t)} G(\vec{r}, t) d\vec{r} dt$$
 (2.2)

is the Fourier transform of the van Hove space-time pair correlation function $G(\vec{r}, t)$, and the instrumental energy resolution function

$$R(\omega) = R_0 e^{-4\ln 2 \left(\frac{\hbar\omega}{\Delta E}\right)^2}$$
(2.3)

is the probability of recording a neutron undergoing an energy transfer $\hbar\omega$; for the sake of simplicity, this probability is supposed here to be a Gaussian function of $\hbar\omega/\Delta E$.

Also the Fourier transform R(t) of $R(\omega)$ is a Gaussian function of t. Its full width at half maximum Δt is connected with the experimental energy resolution ΔE by:

$$\Delta t = (8 \ln 2)\hbar/\Delta E \tag{2.4}$$

(The time Δt happens to be of the order of 1.8×10^{-12} s when $\Delta E \sim 2$ meV). Substitution of (2.2), (2.3) and (2.4) into (2.1) eventually leads to:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \bigg|_{el} = \mathrm{R}_{0} \mathrm{Na}_{\mathrm{coh}}^{2} \int \mathrm{e}^{i\vec{Q}\cdot\vec{r}} \mathrm{d}\vec{r} \frac{2(\ln 2)^{\frac{1}{2}}}{\sqrt{\pi}} \bigg\{ \frac{1}{\Delta t} \int \mathrm{G}(\vec{r},t) \, \mathrm{e}^{\frac{4\ln 2}{(\Delta t)^{2}}t^{2}} \mathrm{d}t \bigg\}$$
(2.5)

It is then verified that the expression in $\{ \}$ in Eq.(2.5) is a time average of the space-time pair correlation function performed over R(t), i.e. during time of observation Δt given by Eq.(2.4) (see Refs [9, 12]).

2.3. Applications of the method of elastic diffraction of neutrons to the study of liquids

In this section we shall show that the elastic diffraction of neutrons can be profitably used to investigate the properties of a liquid in two instances:

- a) the study of the freedom of movement of an atom in the relaxed structure of the liquid during the time of observation Δt defined in Eq.(2.4) [9].
- b) the precision determination of the structure factor S(Q) [14].

2.3.1. The growth of the Debye-Waller cloud in a simple liquid

In order to easily comprehend the main features of a pattern of elastic diffraction of neutrons in a liquid, it might be appropriate to remember that, at least within the frame of the convolution approximation [16], the differential cross-section of a liquid for (coherent) scattering, $d^2\sigma_{\rm coh}/d\Omega dE$, can be written as the product of the structure factor S(Q), which expresses the instantaneous correlations between atomic positions, and the Fourier transform S_s(\vec{Q}, ω) of the "self"-space-time pair correlation function, which describes the energy spread of the scattered neutrons caused by atomic motions. The general behaviour of S(Q) is well known (see, for example, the previous seminar); a 3-dimensional sketch of S_s(\vec{Q}, ω) is shown in Fig.2.2, where the portion bounded by the dotted line represents the fraction of S_s(Q, ω) accepted by a supposedly Q-independent instrumental energy resolution function R(ω) associated with the three-axis spectrometer

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prepared for elastic diffraction. For example, referring for the sake of simplicity to a condensed system characterized by a strong structural disorder $(S(Q) \sim 1)$ and by dynamical properties similar to those of a perfect gas, it may be proved that substitution of the appropriate $S_s(\vec{Q}, \omega)$ in Eq.(2.1) would lead to the following expression:



FIG.2.2. Sketch of the Fourier transform, $S_S(\vec{Q}, \omega)$, of the "self" space-time pair correlation function, $G_S(\vec{r}, t)$. The dotted lines indicate the supposedly Q-independent instrumental energy resolution function $R(\omega)$ associated with the three-axis spectrometer prepared for elastic diffraction.

FIG.2.3. Elastic diffraction pattern of liquid bromine. The full line is a fit of the experimental data according to the vacancy theory of liquids. It is found that the mean square amplitude of the solid-like motions of a bromine atom in the liquid during an observation time of the order of 1.3×10^{-12} sec is 0.39 Å². (This figure is taken from Ref. [1]).

The elastic scattering cross section would then decrease as a function of the wave vector transfer Q, by an amount depending on the most probable length $v_0\Delta t$ that an atom of mass M and velocity $v_0 = (2 K_B T/M)^{\frac{1}{2}}$ travels during the time of observation Δt .

Actually, the pattern of elastic diffraction of neutrons in a liquid happens to be of the type shown in Fig. 2.3. This pattern is remarkably different from that obtainable in a conventional diffraction experiment (see, for example, Fig. 1.1), especially at high wave vector transfers where the downward slope can be explained, as suggested above, in terms of the Debye-Waller cloud built by the atomic motion during the time of observation. It becomes then possible to fit experimental data of this kind to suitable models for the dynamics of the liquid and, accordingly, to obtain interesting information (see Fig. 2.3) on the freedom of motion of an atom in the relaxed structure of the liquid [9].

2.3.2. Accurate determination of the structure factor

These features of the elastic diffraction of neutrons in a liquid might be of interest in some cases also for an accurate determination of the structure factors [14]. For example, the very fact that the elastic component of a neutron diffraction pattern in a liquid differs so much from the total intensity, stimulates some discussions on the reliability of the static approximation; this approximation implies that, since the time taken by a neutron to proceed along distances between near neighbours is short



FIG. 2.4. Conventional neutron diffraction in laboratory and wave vector space. (This figure is taken from Ref. [6]).

compared to the time necessary for the occurrence of major changes in the local configuration of the liquid, possible energy transfers in the scattering are small enough to allow a single value of the wavevector transfer, $4\pi \sin \theta / \lambda_0$ (λ_0 being the wavelength of the monochromatic beam), to be uniquely associated with any scattering angle 20.

On the basis of this hypothesis, the measured and the true values of the structure factor, given by:

$$\frac{d\sigma}{d\Omega} = \int_{L} \frac{d^2 \sigma_{coh}}{d\Omega dE} dE \qquad (2.7)$$

and

$$S(Q) = \int \frac{d^2 \sigma_{coh}}{d\Omega dE} dE \qquad (2.8)$$

respectively, should be equal (see Fig.2.4). In order to appreciate how much these quantities actually differ, we may compute their difference (within the frame of the convolution approximation) in the case of a liquid described again by a gas-like behaviour of $S_s(Q, \omega)$.

One then finds, to a good approximation [14]:

$$\frac{d\sigma_{coh}}{d\Omega} - S(Q) = Na_{coh}^2 \frac{3}{32} \frac{K_B T \frac{\hbar^2 Q^2}{2M}}{E_0^2} \frac{1}{S(Q)} \frac{d^2 S(Q)}{dQ^2} Q^2$$
(2.9)

The information obtained by a measurement of conventional diffraction, $d\sigma_{coh}/d\Omega$, differs from the one required, S(Q), by a term increasing with the sample temperature T, the recoil energy $\hbar^2 Q^2/2M$ and the local curvature of the structure factor, and decreasing, as expected, with the impinging neutron energy E_0 . It has, in fact, been verified experimentally that an efficient way of obtaining more resolved patterns is to increase E_0 , notwithstanding the loss of experimental resolution generally accompanying the reduction of the wavelength used [6].



FIG. 2.5. Conventional neutron diffraction: the pattern of a powder sample of NH_4Br . (This figure is taken from Ref. [7]).

Another suggested possibility of improving the experimental situation is to use the elestic diffraction arrangement with poor energy resolution (i.e. $R(\omega) \simeq \text{constant}$). By a procedure discussed in detail elsewhere [14] it is possible, in some cases, to arrange the spectrometer for quasielastic diffraction so as to enable it to perform instrumentally the integration indicated in Eq. (2.1) (or, under conditions of poor resolution, Eq. (2.7), along a line very close to the line characterized by Q = constant and required by definition (Eq. (2.8)). Under these conditions, it is possible to obtain well resolved patterns. Up to now, the instrumental energy resolution used in this kind of problems has been too narrow to decide whether the improvement of resolution obtained should be attributed to the truncation effectively operated on the integration (2.1) by the steep $R(\omega)$ adopted so far or to the more correct orientation of the instrumental path of integration provided by the elastic arrangement. In any case, the bumps found in regions of the patterns of elastic diffraction in liquid bromine and gallium where only inflection points appear in the corresponding patterns of conventional diffraction (see Fig. 2.5), suggest that further study along these lines could lead to an improvement of the quality and reliability of structure factor data.

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2.4. Applications of the method of elastic diffraction of neutrons to the study of solids

In this section, three possible cases where elastic diffraction of neutrons has been profitably used to improve the quality of the experimental information will be presented:

- a) the determination of the Debye-Waller factor; [10, 11, 12, 17]
- b) the analysis of the static-like component of the structural disorder in some crystals [11] or glasses [2];
- c) the crystal structure analysis of hydrogenous compounds [15].

2.4.1. Accurate determination of the Debye-Waller factor

It is well known that an accurate measurement of the Debye-Waller factor in a solid is only possible if the elastic and inelastic (or thermal diffuse) components of the intensity in the Bragg reflections can be separated. Usually, both in X-ray and conventional neutron diffraction, the essentially inelastic contributions associated with thermal motions are eliminated by setting the base of the Bragg peak along the linearly interpolated line at the background level. This procedure can be only in part justified by the fact that the radiation inelastically scattered by phonons associated with the (normal) modes of vibration in the crystal acquires besides the wavevector transfer $2\pi\tau$ of the nearest reciprocal lattice point, an additional amount of wavevector transfer, \vec{q} , the wavevector of the interacting phonon; and, consequently, like a collection of pairs of Lyman ghosts, it is located away from the Bragg node. Nevertheless, an important portion of the inelastic component unfortunately lies just beneath the Bragg peak since it is due to production or annihilation of phonons of small wavevector. Among these phonons, of course, the acoustic ones have a very small energy $\hbar\omega_{q} \sim \hbar cq$ (c being a measure of the sound velocity). Since the neutron scattering cross-section is proportional to the mean square amplitude of the wave associated with the interacting phonon - and therefore, in the classical limit, to the square of the inverse of the relative frequency - the inelastic component of the intensity, appropriately weighted over the scattering surface, has a maximum exactly at the reciprocal lattice vector (logarithmic singularity smoothened by the finite angular resolution and by the fact that the number of normal modes is actually finite [10]). This result has been proved directly by Mössbauer experiments (see Refs [19, 20, 21]) and, accordingly, it is difficult to subtract correctly the thermal diffuse component from the essentially elastically Bragg-scattered neutron radiation, unless use is made of the method of elastic diffraction.

Actually, it turns out [10] that the efficiency of the method of elastic diffraction of neutrons depends on the relative values of the instrumental energy resolution ΔE (in practical cases ΔE can be kept down to about 1 meV [12, 13]) and the energies heq associated with the phonon lines building up the thermal diffuse component of the scattered intensity. The effectiveness of the filtering action exerted by the analysing spectrometer on the scattered neutron energies becomes smaller as \vec{q} is decreased, that is where it is more needed. Nevertheless, the possibility of eliminating, at least, part of the thermal diffuse intensity beneath the Bragg reflections and the whole of it in regions of wavevector space between reciprocal

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lattice nodes, the improvement in resolution and the reduction of the effects of second order contamination in the monochromatic beam due to the presence of the analysing spectrometer, make the method of elastic diffraction of neutrons an attractive one especially in connection with powder samples of low crystal symmetry or in cases where an accurate value of the Debye-Waller factor is needed.

Measurements performed in our laboratory in white tin [11] and aluminium [13] samples gave results consistent with those reported in the literature.

2.4.2. Diffuse disorder scattering and thermal diffuse scattering

It is well known that any reason for disorder in an ideally periodic crystal structure leads to removal of intensity from the ideally sharp Bragg reflections. We have just indicated that when the disorder is dynamical in nature, besides additional wave vector transfers, also energy transfers are experienced by the radiation probe. If, instead, the disorder is staticlike (we refer here especially to lattice distortions, vacancies, etc. in crystals possibly undergoing structural modifications, or to amorphous solids) – in the sense that an appreciable variation of its configuration takes a time much longer than the time of observation (Eq. (2.4)) associated with a typical instrumental energy resolution – neutrons accordingly removed from Bragg reflections are not allowed to experience perceptible energy transfers, and give rise to an essentially elastic component of the scattered intensity which we might call diffuse disorder scattering.

While X-ray and conventional neutron diffractions do not distinguish between elastically and inelastically scattered radiation and at any wavevector transfer furnish a scattered intensity due to both thermal and staticlike disorder, elastic diffraction of neutrons is associated only with the diffuse disorder component of the scattering; consequently, the method of elastic diffraction of neutrons appears to be the only available tool for separating in a direct way diffuse disorder scattering from thermal diffuse scattering [22].

As an example of the application of the suggestions reported here, reference is made to the elastic diffraction pattern of the region around the (002) forbidden reflection of white tin [11].

2.4.3. Elastic diffraction of neutrons and crystal structure analysis of hydrogenous compounds

It is well known that one of the most important fields of application of conventional neutron diffraction is the determination of the hydrogen position in inorganic and organic compounds. To this end, nevertheless, due to the high value of the proton cross-section for incoherent scattering, crystal-lographers have been forced either to make recourse to single crystal work or to use deuterated samples. It is also known that the best way of estimating extinction corrections in the intensity data from single crystals is to compare those with the corresponding data from powder samples. So far, it has in general been impossible to obtain by conventional neutron diffraction reliable intensity data from non-deuterated hydrogenous compounds in powder form: the background associated with the incoherent scattering cross-section of hydrogen, $\sigma_{\rm incoherent}(H) \sim 80$ barn, overwhelms



FIG. 2. 6. Elastic diffraction of neutrons: the pattern of a powder sample of NH4Br. (This figure is taken from Ref. [7]).



FIG. 2.7. Conventional diffraction pattern of NH4Br.

the Bragg signal associated with the coherent scattering cross-section, $\sigma_{coherent}(H) \sim 1.8$ barn (see, for example, Fig.2.6).

Fortunately, a close examination of this problem makes it possible to ascertain that while, as discussed in section 2.4.1., the contribution of hydrogen to the <u>coherently</u> scattered intensity at the Bragg reflections is associated with processes which are basically <u>elastic</u>, the corresponding <u>incoherent</u> contributions responsible for most of the background are associated with processes which are basically inelastic.

The amount of the mean square energy transfer in a process of incoherent scattering – determined by the second moment of $S(Q,\omega)$ – is of the order of the geometrical average of the thermal energy K_BT and the recoil energy $\hbar^2Q^2/2M_H$; for not too low temperatures of operation and wavevector transfers, these energies are large enough, with respect to the instrumental energy resolution of a three-axis spectrometer, to justify a careful investigation of the possibilities offered by the method of elastic diffraction of neutrons for enhancing the (elastic) signal to (inelastic) background ratio in the powder patterns of nondeuterated hydrogenous compounds.

Preliminary experimental results along this line, together with a more detailed discussion of the dynamics of the scattering process of a neutron in a crystal containing hydrogen, are reported in Ref. [15]. Here it will be sufficient to compare the elastic and conventional diffraction pattern of $\rm NH_4Br$ (see Figs 2.6 and 2.7) and deduce that the method of elastic diffraction of neutrons enables the experimentalists to eliminate instrumentally most of the undesired background whenever the origin of the latter is due to the presence of hydrogen in the sample under investigation.

2.5. Summary and conclusions

In conclusion it seems possible to state that the method of elastic diffraction of neutrons can be used to advantage in several cases. Its applications to the physics of liquids, to an accurate determination of the Debye-Waller factor, to the analysis of the static-like disorder in crystals and amorphous solids, and to the crystal structure analysis of hydrogenous compounds seem very promising if one considers the experimental evidence obtained so far in the Ispra laboratory.

$\mathbf{R} \to \mathbf{F} \to \mathbf{R} \to \mathbf{N} \to \mathbf{C} \to \mathbf{S}$

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MAGNETIZATION DENSITY IN FERROMAGNETIC METALS

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The problem of obtaining information on the charge density in solids (i.e. on the function $\rho(\vec{r})$) has been of great importance from the very beginning of the study of solid state physics as it throws some light on the electron wavefunctions. It is well known that, in principle, such information is given by X-ray scattering, by means of the relationship:

$$\rho(\mathbf{x}, \mathbf{y}, \mathbf{z}) = \frac{1}{\mathbf{V}} \sum_{\substack{hkl \\ hkl}}^{+\infty} \mathbf{F}(hkl) \exp\left[-2\pi i \left(\frac{h\mathbf{x}}{a} + \frac{k\mathbf{y}}{b} + \frac{l\mathbf{z}}{c}\right)\right]$$
(1)

where $\rho(x, y, z)$ is the charge density at any point x, y, z in the unit cell and F(hkl) is the structure factor for the reflection (hkl). The sum is extended over all the (hkl) which implies that structure factors for all reflections must be measured [1]. This is, of course, impossible; however, X-ray experimentalists have been able to get from Eq.(1) information suitable for solving chemical structures. As far as the problem of electron wave functions in solids is concerned, X-ray scattering has been of little help, so far. All electrons contribute to the scattering, and it is not simple to separate the contributions from different shells. Furthermore, only recently the experimental problem of high-precision scattering factor measurements in single crystals has been faced [2]. On the other hand, in magnetic neutron scattering Eq.(1) can be used as well: in this case $\rho(x, y, z)$ is the magnetization density and F(hkl) the magnetic structure factor. Also in neutron scattering termination problems in calculating ρ from experimental data arise; however, it can be shown that reasonable accuracy can be obtained also for a maximum $(\sin \theta)/\lambda$ value of about 1 Å⁻¹ provided proper use of the averaging method suggested by Marshall and developed by Moon and Shull [3, 4] is made.

Furthermore, higher sensitivity in determining the magnetic structure factors can be obtained for ferromagnets and some anti-ferromagnets by means of polarized neutrons and finally neutrons do interact with magnetic electrons only, so that information on wave functions of outer electrons can be obtained, whose contribution to X-ray scattering is usually heavily masked by all other electrons of the atom. It is well known that for a single atom the neutron magnetic form factor in electron units is determined in the case of complete quenching of the orbital moment, by the unpaired spin density and is given by

$$\mathbf{f}(\vec{\mathbf{k}}) = \int \left[A\rho_{\uparrow}(\vec{\mathbf{r}}) - B\rho_{\downarrow}(\vec{\mathbf{r}}) \right] e^{i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}} d\tau$$
(2)

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where $\rho_{\uparrow}(\vec{r})$ and $\rho_{\downarrow}(\vec{r})$ are the charge densities per electron for electrons of spin up and spin down, respectively, $\vec{k} = \vec{K} - \vec{K}_0$ is the scattering vector and the integral is extended over the whole space. It can be shown that if the one-electron charge density is spherically symmetric, Eq.(2) reduces to

$$f(k) = \int_{0}^{\infty} r^{2} \left[R_{\uparrow}^{2}(r) - R_{\downarrow}^{2}(r) \right] \frac{\sin kr}{kr} dr$$
(3)

where R^2 is the radial part of the charge density. In other words, if the charge distribution is spherically symmetric the form factor is independent of the direction of \vec{K} which from an experimental point of view means that form factors measured at different \vec{K} values must fall on the same smooth curve, and furthermore any pair of reflections of the same \vec{K} must give an identical form factor.

The first measurements made with unpolarized neutrons indicated for experimental magnetic form factors a behaviour in general agreement with free-atom one-electron calculations, but did not permit many details to be seen, until in 1959 the first polarized-neutron measurements [5] were able to give evidence of the departure of 3d electrons from spherical symmetry in cobalt, iron and nickel. This was interpreted in terms of a deviation of the $\ensuremath{\,\mathrm{T_{2g}}}$ and $\ensuremath{\mathrm{E}_g}$ sublevel population from the statistical values of 60% and 40%, respectively. In other words, within the one-electron approximation and keeping for convenience the separability condition of the 3d electrons wavefunction into radial and orbital parts, we can directly calculate from the experimental form factor values how 3d electrons accommodate between the two sublevels (three-fold and doubly degenerate, respectively), which would maintain the cubic symmetry of the charge distribution. In Fig. 1, the experimental form factor of cubic cobalt is plotted as a function of $(\sin \theta)/\lambda$. The departure from spherical symmetry is evident by examining the reflection pairs which for the same $(\sin \theta)/\lambda$ give different form factor values.

Weiss and Freeman [6,7] were able to show that for $\rm T_{2g}$ and $\rm E_g$ electrons form factors were, respectively, given by

$$f_{T_{2g}} = \langle J_0(kr) \rangle - \frac{1}{3} A \langle J_4(kr) \rangle$$

and

$$f_{E_g} = \langle J_0(kr) \rangle + \frac{1}{2} A \langle J_4(kr) \rangle$$

where A is a simple function of the Miller indices of the reflection only, and

$$\langle J_n(\mathbf{kr}) \rangle = \int_0^{\infty} \mathbf{r}^2 (\mathbf{R}^2_{\dagger} - \mathbf{R}^2_{\downarrow}) J_n(\mathbf{kr}) d\mathbf{r}$$

where $J_n(kr)$ is the nth order spherical Bessel function. To calculate $\langle J_n(kr) \rangle$, for $n \neq 0$, Watson and Freeman [8] used one-electron wave



FIG. 1. Magnetic form factor of fcc cobalt. Taken from Ref. [5]

functions calculated for free atoms by the Hartree-Fock method. In this way the aspherical contributions to the form factor are evaluated.

For the calculation of the spherical part which gives the general trend of the magnetization density unrestricted Hartree-Fock calculations were performed by Wood and Pratt [9], Stern [10], and Watson and Freeman [11].

As is well known, the Hartree-Fock formalism consists of approximating a true many-electron wave function by a single Slater determinant. In practice, this formalism is further modified by the addition of restrictions which have the advantage of simplifying the task of solving the equations, but which also have effects on the final form of the wave functions. These restrictions are:

(1) The spatial part of a ψ_i is assumed to be separable into a radial and an angular part:

$$\psi_i(\mathbf{r}, \theta, \varphi, \sigma) = [\mathbf{U}_i(\mathbf{r})/\mathbf{r}] \mathbf{F}_i(\theta) \mathbf{S}_i(\sigma)$$

where $S_i(\sigma)$ is a spin function with a spin quantum number m_s of $\pm 1/2$. In practice, $F_i(\theta)$ is normally chosen to be a spherical harmonic, or, in other words ψ_i is assumed to be an eigenfunction for a spherical environment (which is true only for atomic S states). The $F_i(\theta, \phi)$ are assigned before the application of the variation principle and only the $U_i(r)$ are obtained variationally. The problem becomes one-dimensional.

(2) Assuming (1), $U_i(r)$ is constrained to be independent of the m_ℓ value associated with ψ_i .

(3) $U_i(r)$ is likewise constrained to be independent of m_s .

The last two restrictions imply a single $U_i(r)$ for any shell (i.e., n and ℓ value) and, in turn, a separate Hartree-Fock equation for the shell rather than a separate equation for the electron. Now it has been shown



FIG. 2. The magnetic form factor of hexagonal cobalt compared with the fcc case. The solid line was drawn to emphasize the smooth decrease in the hexagonal form factor, indicating almost spherical symmetry. Taken from Ref.[3].

by Pratt [12] for an atom with net spin that if orbitals with the same n, ℓ , and m_f values, but different m_s are varied independently, the resulting variational equations have a different form for orbital of different m_s. This difference arises because of the net spin of the atom, there being a different exchange interaction for electrons with m_s of the same spin as the total M_s than for electrons of opposite spin. This effect is described as an exchange polarization and the separate variation with regard to the different m_s values is known as the unrestricted Hartree-Fock method.

As far as the symmetry of surrounding atoms is concerned, it seems that they influence strongly the deviations from spherical symmetry, but affect very little the radial distribution of magnetization as can be inferred from the data of Fe₁ and Fe₁₁ in Fe₃Al and by comparing fcc and hcp data for cobalt as given in Fig.2. We could perhaps conclude that the Hartree-Fock method itself is not very sensitive to the shape of the outer-electron wave function; in other words, self-consistency can be obtained also with an outer-electron distribution deviating appreciably from the real one. Furthermore, the Hartree-Fock equations do not take into proper account the inter-electron distribution.

Therefore, interpreting the form factor measurements in term of Watson and Freeman calculations means to be always within the frame of an approximation. In general, it is much more significant to obtain a three-dimensional magnetization density map which gives a direct insight into the situation. The interpretation of the map in terms of one or another approximation might always be a matter of speculation and of possible



Magnetization in kilogauss

FIG. 3. Model of the magnetization distribution in the body-centred-cubic unit cell of iron. The concentration of the very large positive 3d shell magnetization along the cube edges is overemphasized to show its relationship to the negative magnetization rings. Taken from Ref. [4].

future improvement. Figure 3 shows the magnetization density map of iron found by Shull and Yamada [13]. The interatomic magnetization distribution is characterized by a series of interlocking, negative magnetization rings arranged in a three-dimensional chain structure [4]. Each ring is centred at the midpoint between second-nearest neighbours in the body-centred cubic lattice with the plane of the ring being transverse to the bonding line. There is some variation of the negative field with values ranging as high as -2.0 kG. As the nuclear position is approached the very much larger and positive 3d shell magnetization is encountered with fields as large as +500 kG. It is estimated from the volume of negative magnetization rings that as much as 35% of the unit cell volume is characterized by a negative field. As far as the interpretation of the iron data is concerned a first analysis was made by Shull and Yamada [13] who, together with the spin magnetization, made also allowance for the 3d orbital moment scattering, together with possible form factor contributions from other electron groups. The orbital unquenched moment contribution can be evaluated from the experimental magneto-mechanical ratio which in iron is 1.93. Furthermore, Shull and Yamada calculated the population of the \mathbf{E}_{g} and \mathbf{T}_{2g} sublevels directly from the observed form factor deviations from spherical symmetry and finally introduced a parameter ξ which represents the fraction of the 3d quenched spin magnetization, $(1 - \xi)$ being the orbit-quenched 4s electron contribution so that experimental data provided the following relation:

$$\vec{\mu}\vec{f} = \mu\xi f_{3d} + \mu(1-\xi) f_{4s}$$
 with $\mu_{3d} = \mu\xi$ and $\mu_{4s} = (1-\xi)\mu$

By using the form factor calculations by Watson and Freeman already mentioned and reported in Fig. 4 they were able to obtain the best fit for a ξ value of 1.10 corresponding to a negative magnetization from 4s electrons



FIG. 4. Comparison between experimental and calculated values of magnetic form factor. Solid curve gives the spherical 3d form factor, the broken and dotted curves give 3d orbital and core contribution respectively. Taken from Ref. [13].

of $-0.21 \mu_B$ as is indicated in Fig. 5 which gives the 4s contribution which would have to be added to the f_{3d} for different ξ in order to give the experimental values. We see that for $\xi = 0.9$ and 1 a f_{4s} much higher than the value which is derived from the 4s wave function calculated for iron by Wood and Pratt [9] and is never higher than 0.01 over the region of observation, would have to be added. Of course, one may object that such an interpretation has the same limits of validity as the Watson and Freeman results. However, it must be pointed out that, while the origin of the negative polarization is still under discussion, its presence seems to be beyond any doubt as it is obtained directly from the experimental data. Negative polarization was also found by Moon in hcp cobalt [3], as can be inferred from Fig. 6 and by Mook in Ni as is shown in Fig. 7. Moon and Mook [14] interpreted their experimental data by writing the form factor as

$$f(\vec{k}) = \frac{2}{g} \left[(1+\alpha) f_j^{3d}(\vec{k}) - \alpha \delta(\vec{k}) \right] + \left[\frac{g-2}{g} f_o(\vec{k}) + f_c(\vec{k}) \right]$$
(4)

where the subscripts s, o and c refer to spin, orbital and core respectively. The g factor determines the fraction of the total moment due to spin polarization and the fraction due to unquenched orbital motion. The values



FIG. 5. $f(expt)^{-f}(3d \text{ calc})$ gives the possible contribution from 4s electrons for various ξ values. 4s contribution is expected to be smaller than 0.01 of a unit. Taken from Ref. [13].



FIG. 6. Projection of magnetic moment density on basal plane. Lower right diagram shows projected position of atoms in orthorhombic unit cell. Dashed lines indicate portion of cell shown in density map. Taken from Ref. [3].

for metallic cobalt and metallic nickel are 2.17 and 2.20, respectively, as given by magneto-mechanical measurements [15]. As can be seen from Eq.(4) in the form-factor expression a $\delta(\vec{K})$ function is introduced which only makes a contribution at $\vec{K} = 0$ and thus corresponds to a uniform contribution to the magnetization, that is, by taking into account the constant negative polarization which appears in both the Co and Ni magnetization density maps. On the other hand, it should be pointed out that as was already mentioned for iron, we find that also in Co and Ni the measured form factor is appreciably higher ($\cong 16\%$) than those calculated in the free-atom approximation unless the negative magnetization due to the Fourier


FIG. 7. The magnetic moment distribution in the [100] plane. Taken from Ref. [14].



FIG. 8. Comparison of experimental results of hexagonal Cobalt with free-atom calculation when $\alpha = 0.18$. The free-atom form factor is based on a $3d^74s^2$ spin-polarized Hartree-Fock calculation by Watson and Freeman. Taken from Ref.[3].

inversion of the experimental data is taken into account. Also in these cases the calculated form factors to which the experimental data were fitted are those of Watson and Freeman, and precisely for Co the best fit was found fot the spin-polarized calculations relative to the configuration $3d^74s^2$ shown in Fig. 8, and for Ni with the unrestricted Ni⁺⁺ calculations shown in Fig. 9. From this analysis of the data the following contributions to the magnetization were obtained:



FIG. 9. Comparison of calculated and measured form factors. Taken from Ref. [14].

cobalt 3 spin	+1.86 ±	0.07 $\mu_{\rm B}$	nickel	3d spin	0.656
constant spin	-0.28 ±	$0.07 \mu_{\rm p}$		constant spin	-0.105
3d orbital	+0.13 \pm	0.01 $\mu_{\rm p}^{\rm D}$		3d orbital	0.055
-		Б			
	+1.71	$\mu_{\rm B}$			+0.606 $\mu_{\rm B}$

The good agreement of the free-atom calculations with the experimental data is interpreted by the fact that in cobalt and even more in nickel the unpaired electrons occupy the top of the 3-band where, as was shown by Stern [10] and Wood [16] with tight-binding calculations in iron, the wave functions are expected to be very similar to free-atom wave functions (Fig. 10). Finally, we want to point out the possible contribution to the form factor of the paired electrons. This is due to the different forms of the radial part of the wave function for the two spin states because of the exchange, or as is briefly said, to the polarization exchange. This effect



FIG. 10. The spherically symmetric part of the charge density $\rho(r)$ for 3d electrons in iron is shown for an atomic sphere radius $r_s = 2.66$ Bohr radii. The dashed and solid curves refer, respectively, to the states at the top and at the bottom of the 3d band when the wave vector is at the endpoint of a (110) direction in the Brillouin zone. [See Eqs (13) and (14)]. The dot-dash curve gives the spherically symmetric part of the charge density due to overlapping atomic charges, calculated from the adjusted coefficients. All charge densities are normalized to 4π over the atomic sphere. Note that the vertical scale has been expanded by a factor of 10 for r >1.5. Taken from Ref. [10].

can be seen in Fig. 11. As to the interpretation of the negative magnetization two possible explanations were provided by Mook: (1) the electrons of the conduction band could be polarized oppositely to the 3d electrons according to the hypothesis of Shull and Yamada, (2) the spin polarization effects can account for the negative densities observed in Fourier maps. In the latter case all the scattering would come from the 3d band and it would be unnecessary to include 4s electron effects.

Recently band calculations for ferromagnetic nickel have been performed by Hodges, Ehrenreich and Lang [17]. They use an interpolation scheme in the sense that unhybridized d bands are represented in terms of linear combinations of atomic orbitals and the conduction bands in terms of a four-orthogonalized-plane-wave approximation while the hybridized wave functions $B_{Kn}(r)$ are written as linear combination of L.C.A.O. $b_{K\mu}(r)$ and O. P.W. $b_{K\nu}(r)$

$$\mathbf{B}_{Kn}(\vec{\mathbf{r}}) = \sum_{\mu} \mathbf{a}_{n\mu}(\vec{\mathbf{K}}) \mathbf{b}_{K\mu}(\vec{\mathbf{r}}) + \sum_{\mathbf{k}} \mathbf{a}_{nk}(\vec{\mathbf{K}}) \mathbf{b}_{Kk}(\vec{\mathbf{r}})$$

The Hamiltonian $H = H_{band} + H_{so} + H_{corr}$ where the first term gives the results of ordinary non-relativistic band theory, the second the effects of the spin-orbit interaction and the third correlation effects which are very important in determining the features of ferromagnetic bands, as they provide a change in energy when the system goes from the para- to the ferromagnetic state so that the Hamiltonian which is used is more general than that of the usual one-electron Hartree-Fock scheme. Various parameters enter into the calculation which are adjusted in order to fit the results of Fermi surface experiments, magneto-optical experiments, electronic specific heat, high field susceptibility, etc. Within this frame the calculations indicate a fairly good agreement with the experimental results of Mook. However, the hypothesis of a slight negative polarization



FIG. 11. The net radial spin density of the Argon-like core ρA , i.e., $[\rho(\text{core}^{\dagger}) - \rho(\text{core}_{4})]$ and the Argon core radial charge density $[\rho(\text{core}^{\dagger}) + \rho(\text{core}_{4})]$ for spin polarized Ni⁺². Taken from Ref.[11].

of the conduction electrons is ruled out on the basis of consistency with the Hamiltonian which is being used while an appreciable contribution to the form factor from the paired electrons of the type mentioned above is found as is shown in Fig.12. The discrepancies for the first three reflections are attributed to the fact that no unrestricted conduction-band wave functions have been used, and that it is particularly difficult to obtain a good estimate of the contribution arising from paired electrons since it depends on the exact form of the unrestricted d-band wave function not only at the top of the band where the L. C. A. O. approximation is certainly valid, but through the whole range of d band energies.

Finally it might be worthwhile to mention some measurements of polarized-positron annihilation in Fe and Ni by Mijnarends and Hambro and by Berko and Zuckerman [18], which have also been interpreted as an indication of negative polarization of the conduction band. Precisely Berko has shown that a peak appearing in the experimental plot of $p(\theta) = [N_{t}(\theta) - N_{t}(\theta)] / [N_{t}(\theta) + N_{t}(\theta)]$ as a function of θ can be interpreted on the basis of a very crude model due to the negative polarization of the conduction band electrons. Here N_{t} and N_{t} are the counting rates of the



FIG. 12. Comparison of calculated magnetic form factor of Ni with experimental results of Mook and Shull. Solid line indicates contribution of paired electrons obtained from unrestricted Hartree-Fock atomic wave functions of Watson and Freeman. Taken from Ref. [17].

photons from positron-electron annihilation at the angle θ , with a magnetic field set respectively parallel or antiparallel to the incident positron momentum.

Until now, we have limited our description to the only metals where magnetization comes only or mostly from the electron spin. It might be interesting to examine a case like Tb (see Ref. [19] where the orbital moment is completely unquenched. However, great experimental difficulties arise as, while the form factors of 3d metal have been measured with considerable accuracy by means of polarized neutrons, the same technique was only partially suitable in the case of unquenched orbital moments. As a matter of fact in the 3d case, where the unpaired spins constitute the predominant part of the magnetic moment, the anisotropy of the spin density is not influenced by the application of a magnetic field in the sense that only the spin direction follows the magnetic field, but its spatial distribution determined by the crystalline field does not change. In rare-earth metals, the presence of an unquenched orbital moment determines a spin-orbit coupling which is larger than the crystalline field effects. Consequently, when a large enough magnetic field is applied to align the moment, as is required for the polarized beam experiment, this field direction becomes the unique axis of moment distribution, so that the cloud of the moment distribution turns with the field. Therefore, we can measure with polarized-neutron technique only the projection of the moment density on a plane normal to the zone axis along which the magnetic field is applied. This implies that also unpolarized neutrons without applied field must be used in order to get the form factor and, what is more important, that the two sets of data are not necessarily identical.

Terbium has hcp structure and exhibits helical antiferromagnetism below 230°K and ferromagnetism below 220°K. The saturation moment is of 9.34 $\mu_{\rm B}$ along the easy b axis and the deviation of this number from the free-ion value of 9 $\mu_{\rm B}$ has been attributed to conduction electron polarization.

It can be shown that the Fourier transform of the magnetization density i.e. the form factor of Tb can be expressed in terms of the quantities $Y_m^e(\theta)$, $\langle g_i \rangle$ and $\langle j_i \rangle$, where $Y_m^e(\theta)$ are the spherical harmonics, θ is the angle between the direction of magnetization and the scattering vector, and $\langle g_i \rangle$ and $\langle j_i \rangle$ are radial integrals which have been calculated by Blume, Freeman and Watson [20] using Hartree-Fock wave functions. Also in this case, of course, the form factor can be divided into a spherical and an aspherical part: $f(\vec{K}) = f_s(\vec{K}) - \Delta a$. The experimental data indicated the presence of a non-localized polarization which gave a contribution of 0.48 μ_B /atom, which has been ascribed to conduction-electron polarization and has the right value to explain the difference between the total magnetic moment per atom and the spin and orbital contribution of 4f electrons.

Until now, we have considered magnetization density in metals which are ferromagnetic as pure elements and have a magnetization due essentially to 3d electrons. Recently, some interest has been also devoted to 4d and 5d electrons. None of the 4d and 5d transition metals exhibits a magnetically ordered state as an element, but some of their alloys show bulk magnetization properties which were interpreted as an indication of a contribution of 4d and 5d electrons to the magnetization. We will briefly review the results obtained in the Pd-Fe system. As a general rule, the data were collected by polarized-neutron experiments which provide very accurate values of form factors; these form factors are to be Fourier-inverted for the purpose of drawing magnetization density maps. However, to distinguish between the two components of the system it is usually necessary to perform some extrapolation or some normalization and to make use of two sets of neutron scattering data: fundamental and super-lattice reflections or fundamental reflections only coupled with magnetic diffuse scattering data.

In the Pd₃Fe alloy the Brookhaven group [21] has determined a 0.34 μ_B moment on the Pd while the resulting form factor was slightly higher than that calculated by Watson and Freeman. The collected data did not allow a Fourier inversion to be performed but could be interpreted in terms of a distribution of the d electrons of iron between the E_g and the T_{2g} levels giving a situation of practical perfect spherical symmetry. It might be interesting to compare these results with those obtained with the same experimental technique in the alloys Pd_{0.50}-Fe_{0.50} [22] and in the Pd_{0.987}-Fe_{0.013} [23]. In the former the symmetry appears to be slightly on the E_g side while the latter shows definite evidence of T_{2g} symmetry so that there is a trend from E_g to T_{2g} symmetry as the Fe content is decreased.

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PART III

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LIQUIDS AND MOLECULES

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NEUTRONS AND MOLECULES

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Abstract

1. Introduction. 2. Scattering of neutrons by molecules of a gas; 2.1. Zemach-Glauber Formalism; 2.2. Rahman-Griffing Theory; 2.3. Situation in methane gas; 2.4. Situation in ammonia gas; 2.5. Discussion. 3. Scattering of neutrons by molecules in a solid: 3.1. Dynamics of molecular solids; 3.2. A brief look at the experimental material obtained with neutrons; 3.3. The case of NH₄Cl; 3.4. Situation in solid methane. 4. Scattering of neutrons by molecules in a liquid: 4.1. General remarks; 4.2. Situation in water; 4.3. Situation in liquid methane.

1. INTRODUCTION

From the title of this paper it will be understood that it deals with neutron scattering by molecules of a gas and by what will be called molecular groups in liquids and solids. Molecular groups in solids and liquids are either radicals and/or ions such as NH_4^+ , H_3O^+ , H_2O (water of crystallisation), etc., or entire molecules (e.g. CH_4) bound by weak Van der Waals forces.

For a gas the importance of using an adequate theoretical description of neutron scattering by molecules will be stressed.

For liquids and solids an attempt will be made to understand neutron scattering in terms of molecular dynamics of the substance and hence to deduce information on the dynamics.

The paper gives, of course, a selection of the existing material, both theoretical and experimental. More complete information may be obtained from the References at the end.

2. SCATTERING OF NEUTRONS BY MOLECULES OF A GAS

2.1. Zemach-Glauber Formalism¹

A quantum-mechanical theory of the scattering of neutrons by molecules, which took into account the translational, vibrational, and rotational molecular degrees of freedom as well as spin effects was given by Zemach and Glauber [1]. Following their arguments, we assume that the neutronmolecule interaction potential has the form:

$$U = \frac{2\pi\hbar^2}{m} \sum_{\nu} b_{\nu} \delta(\vec{r}_n - \vec{r}_{\nu})$$
(1)

¹ This section was prepared on the basis of Ref.[3].

where \sum_{ν} denotes summation over all nuclei in the molecule, and suffix n

refers to the neutron; b_{ν} is the scattering amplitude of the ν -th nucleus. We shall denote the initial and final neutron momentum, respectively,

by $\hbar \vec{k}$ and $\hbar \vec{k}'$, the initial and final energy of the molecule by E_i and E_f , and the corresponding molecular wave functions by ψ_i and ψ_f . A quantummechanical formula for the neutron scattering cross-section in which a transition from the i to the f state takes place is (in the laboratory system):

$$\sigma_{\mathrm{fi}}(\theta) = \left(\frac{\mathrm{m}}{2\pi\hbar^{2}}\right)^{2} \frac{\mathrm{k}^{\mathrm{i}}}{\mathrm{k}_{0}} \left| \langle \psi_{\mathrm{f}} \right| \int \mathrm{e}^{-\mathrm{i}(\vec{k}^{\mathrm{i}} - \vec{k}_{0}) \cdot \vec{r}_{\mathrm{n}}} \mathrm{U} \, \mathrm{d}\vec{r}_{\mathrm{n}} \left| \psi_{\mathrm{i}} \right\rangle^{2} \right|$$

$$= \sum_{\mathrm{evel}} \frac{\mathrm{k}^{\mathrm{i}}}{\mathrm{k}_{0}} \langle \psi_{\mathrm{i}} | b_{\nu} \mathrm{e}^{\mathrm{i}(\vec{k}^{\mathrm{i}} - \vec{k}_{0}) \cdot r_{\nu}} \left| \psi_{\mathrm{f}} \right\rangle \langle \psi_{\mathrm{f}} | \mathrm{e}^{-\mathrm{i}(\vec{k}^{\mathrm{i}} - \vec{k}_{0}) \cdot r_{\nu}} \left| \psi_{\mathrm{i}} \right\rangle$$
(2)

We shall further denote by $\hbar \vec{Q}$ the change in neutron momentum $(\vec{Q} = \vec{k}' - \vec{k}_0)$, and by ϵ the change in neutron energy. Of course, we have

$$\epsilon = \frac{\hbar^2}{2m} (k^{2!} - k_0^2) = E_i - E_f$$

To obtain $\sigma_i(\theta)$ we must make in $\sigma_{fi}(\theta)$ a summation over all final states:

$$\sigma_{i}(\theta) = \sum_{f} \int_{-E_{0}}^{\infty} d\epsilon \, \delta \, (E_{i} - E_{f} - \epsilon) \sigma_{fi}(\theta)$$
(3)

where the delta is introduced in order to assure the energy conservation law. Now we introduce formally the parameter τ which we shall interpret as the time parameter:

$$\sigma_{i}(\theta) = \frac{1}{2\pi} \sum_{f} \int_{-E_{0}}^{+\infty} d\epsilon \int_{-\infty}^{+\infty} d\tau \cdot e^{-i\epsilon\tau} e^{i(E_{i} - E_{f})\tau} \sigma_{fi}(\theta)$$
$$= \frac{1}{2\pi} \sum_{f,\nu',\nu} \int_{-E_{0}}^{\infty} \int_{-\infty}^{+\infty} \frac{k!}{k_{0}} e^{-i\epsilon\tau} \langle \psi_{i} | b_{\nu} e^{iH\tau} e^{i\vec{Q} \cdot \vec{r}_{\nu}} e^{-iH\tau} | \psi_{f} \rangle$$
$$\times \langle \psi_{f} | b_{\nu'} e^{-i\vec{Q} \cdot \vec{r}_{\nu'}} | \psi_{i} \rangle d\epsilon d\tau$$

(here we have made use of the formal relation $[\exp(-iE_f\tau)]\psi_f = [\exp(-iH\tau)]\psi_f$ similarly for ψ_i , where H denotes the Hamiltonian) and then immediately:

$$\sigma_{i}(\theta) = \frac{1}{2\pi} \sum_{\nu,\nu'} \int_{-\varepsilon_{0}}^{\infty} \int_{-\infty}^{+\infty} \frac{\mathbf{k}}{\mathbf{k}_{0}} e^{-i\epsilon\tau} \langle \psi_{i} | \mathbf{b}_{\nu} \mathbf{b}_{\nu'} e^{iH\tau} e^{i\vec{Q}\cdot\vec{r}_{\nu}} e^{-iH\tau} e^{-i\vec{Q}\cdot\vec{r}_{\nu'}} | \psi_{i} \rangle d\epsilon d\tau$$

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We see that the differential cross-section $\sigma_i(\theta)$ may be represented as an integral over the energy of the double differential cross-section $\sigma_i(\theta, \epsilon)$:

$$\sigma_{i}(\theta, \epsilon) = \frac{1}{2\pi} \sum_{\nu, \nu'} \int_{-\infty}^{+\infty} \frac{k'}{k_{0}} e^{-i\epsilon\tau} \langle \psi_{i} | b_{\nu} b_{\nu'} e^{iH\tau} e^{i\vec{Q}\cdot\vec{r}_{\nu}} e^{-iH\tau} e^{-i\vec{Q}\cdot\vec{r}_{\nu'}} | \psi_{i} \rangle d\tau \qquad (4)$$

Here the terms with v = v' describe the direct scattering and those with $v \neq v'$ the interference scattering.

We shall further denote the expectation value in (4) by $\chi_{\nu\nu}$ and introduce the time dependence of \vec{r}_{ν} by a formal relation:

$$\vec{\mathbf{r}}_{v}(\boldsymbol{\tau}) = \mathbf{e}^{\mathbf{i}\mathbf{H}\boldsymbol{\tau}} \vec{\mathbf{r}}_{v} \mathbf{e}^{-\mathbf{i}\mathbf{H}\boldsymbol{\tau}}$$

where

$$\vec{\mathbf{r}}_{y} \equiv \vec{\mathbf{r}}_{y}(0)$$

Thus

$$\chi_{\nu\nu'} = \langle \psi_i | b_{\nu} b_{\nu'} e^{i\vec{Q}\cdot\vec{r}_{\nu}(\tau)} e^{-i\vec{Q}\cdot\vec{r}_{\nu'}(0)} | \psi_i \rangle$$
(5)

We make use now of a dependence

$$e^{i\vec{Q}\cdot\vec{r}_{\nu}}\vec{p}_{\nu}e^{-i\vec{Q}\cdot\vec{r}_{\nu}}=\vec{p}_{\nu}-\hbar\vec{Q}$$

which may be easily written in the form:

$$e^{i\vec{Q}\cdot\vec{r}_{\nu}}H(\ldots\vec{p}_{\nu},\vec{r}_{\nu}\ldots)e^{-i\vec{Q}\cdot\vec{r}_{\nu}}=H(\ldots\vec{p}_{\nu}-\hbar\vec{Q},\vec{r}_{\nu},\ldots)=H_{(\nu)}$$

Limiting ourselves to the direct scattering only, we obtain:

$$\mathbf{X}_{\nu\nu'} = \langle \boldsymbol{\psi}_{i} | \mathbf{b}_{\nu}^{2} \mathbf{e}^{i\mathbf{H}\tau} \mathbf{e}^{-i\mathbf{H}(\nu)\tau} | \boldsymbol{\psi}_{i} \rangle$$
(6)

Now we represent the Hamiltonian as the sum of translational, rotational, and vibrational parts:

$$H = H_{tr} + H_{rot} + H_{vib}$$
(7)

and the wave function

$$\psi = \psi_{\text{spin}} \cdot \psi_{\text{tr}} \cdot \psi_{\text{rot}} \cdot \psi_{\text{vib}} \tag{8}$$

We shall not at the moment discuss the spin dependence of the scattering.

The contribution to the translational part of the expectation value may be obtained from a Hamiltonian of a monatomic gas which is:

$$H = \frac{\vec{p}^2}{2M}$$

the H' is then given by:

 $\mathrm{H}^{\prime}=\frac{(\vec{p}-\hbar\vec{Q})^{2}}{2\mathrm{M}}$

and hence:

$$\langle \psi_{i} | e^{iH\tau} e^{-iH'\tau} | \psi_{i} \rangle = e^{i\tau (2\hbar \vec{p} \cdot \vec{Q} - \hbar^{2}Q^{2})/2M}$$
 (9)

As we are not interested in the $\sigma_i(\theta, \epsilon)$ but in its thermal average, we perform an averaging over a Boltzmann distribution of initial states, and obtain (for a monatomic gas):

$$\left\langle \sigma\left(\theta,\epsilon\right)\right\rangle_{\mathrm{T}} = \frac{\mathrm{b}^{2}}{2\pi} \frac{\mathrm{k}^{\mathrm{t}}}{\mathrm{k}_{0}} \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}\tau\left(\epsilon + \frac{\hbar^{2}\vec{Q}^{2}}{2\mathrm{M}}\right) - (\tau^{2}\mathrm{k}_{\mathrm{B}}\mathrm{T}\vec{Q}^{2}\hbar^{2})/2\mathrm{M}} \mathrm{d}\tau$$
$$= \mathrm{b}^{2} \sqrt{\frac{\mathrm{M}}{2\pi\,\mathrm{k}_{\mathrm{B}}\mathrm{T}Q^{2}\hbar^{2}}} \frac{\mathrm{k}^{\mathrm{t}}}{\mathrm{k}_{0}} \mathrm{e}^{-\frac{\mathrm{M}}{2\mathrm{k}_{\mathrm{B}}\mathrm{T}Q^{2}\hbar^{2}}} \left(\epsilon + \frac{\mathrm{Q}^{2}\hbar^{2}}{2\mathrm{M}}\right)^{2}} (10)$$

It is not possible to discuss here, in detail, further (i.e. rotational, vibrational, spin) contributions to the cross-section. The reader may find these details either in original papers [1], [2] or in a monograph [3]. Let us now conclude that the vibrational contribution was calculated (following the Zemach and Glauber method) by Krieger and Nelkin [4], who also calculated the rotational part for classical rotators. The rotational contribution for quantum rotators was calculated by Griffing [5].

2.2. Rahman-Griffing Theory

Griffing applied the Zemach and Glauber theory as a basis, and followed the Krieger and Nelkin method of treating translations and vibrations. Hence, the translatory part of the cross-section, which had the form (10), is now modulated by a Debye-Waller type of vibrational contribution (in which the inelasticity of vibrations is, however, not taken into account). The rotational part of the expectation value is calculated by Griffing following Rahman's method [6]; the resulting double differential crosssection for the methane molecule is:

$$\sigma(\theta, \epsilon) = 4\sigma_{\rm pp}(\theta, \epsilon) + 12\sigma_{\rm pp}(\theta, \epsilon) + 8\sigma_{\rm cp}(\theta, \epsilon) + \sigma_{\rm cc}(\theta, \epsilon)$$
(11)

where

$$\sigma_{pp} = a_{pp} \frac{1}{2\pi} \frac{k!}{k_0} \cdot \sqrt{\frac{2\pi M}{TQ^2}} \cdot e^{-Q^2 \gamma_{pp}} \sum_{j,J} e^{-\frac{(\epsilon + \alpha)^2}{2TQ^2/M}} \frac{2J+1}{2j+1} B_T(j) \sum_{n=|j-J|}^{j+J} j_n^2(Qr_p)$$
(12)

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and similar expressions may be written for $\sigma_{pp'}$, σ_{cp} and σ_{cc} . New notations used in formula (12) are:

$$\gamma_{\nu\nu'} = \sum_{\lambda} \frac{1}{12\omega_{\lambda}} \left[(C_{\nu}^{(\lambda)})^2 + (C_{\nu'}^{(\lambda)})^2 \right]$$

summation over λ means summation over all vibrational modes, ω_{λ} are vibration frequencies and C_{ν} -vibration amplitudes of the ν -th nucleus (normalised in the way explained in the Krieger and Nelkin paper [4]),

$$a_{\nu\nu}$$
, = $A_{\nu}A_{\nu}$, + $\delta_{\nu\nu}$, $C_{\nu}C_{\nu}$,

where A_{ν} and C_{ν} are bound coherent and incoherent scattering amplitudes. $a_{\nu\nu'}$ replaces the b_{ν} and $b_{\nu'}$ scattering amplitudes used in section 2.1, where the spin dependence of the scattering was completely neglected. $j_n(x)$ is the spherical Bessel function, j and J are the quantum numbers for the initial and final rotational states, $B_T(j)$ is the Boltzmann distribution of initial rotational states for a spherical top, and

$$\alpha = \frac{Q^2}{2M} - \frac{j(j+1)}{2I} + \frac{J(J+1)}{2I}$$

where I is the moment of inertia.

2.3. Situation in Methane Gas

Griffing's original calculations were numerically performed in order to explain the experimental results on gaseous methane obtained by Randolph et al. [7]. These results have shown a significant deviation from the theory of Krieger and Nelkin for small energy and momentum transfers, i.e. for a region where the quantum structure of molecular rotation should have been taken into account. Figure 1 presents a comparison of Griffing calculations and experimental results [7]. In calculations, the values of the initial and final quantum numbers from 0 to 20 were taken into account. It is evident that the theory is able to explain the inelastic peak, which arises from rotations, in contrast to the Krieger and Nelkin theory. However, it does not give a proper magnitude of the quasi-elastic peak as seen in Fig.1. The second calculation based on Griffing formulas was performed by Venkataraman et al. [8] in order to explain Webb's experiment with gaseous methane [9]. Here the incident neutron energy was much lower than in Ref. [7], hence the rotational effects are much more clearly visible. Figure 2 shows again that although the general shape of the experimental curve is explained by the theory, there is a small discrepancy qualitatively similar to that pointed out in connection with Fig.1. The third calculation based on Griffing was performed by Otnes [10] in connection with his experiments on the scattering of cold neutrons by gaseous methane. As seen in Fig. 3, a similar disagreement as those from Figs 1 and 2 was obtained.





FIG.1. A comparison of Griffing theory and Krieger-Nelkin theory with experiment [7] for gazeous methane. Solid line - Griffing theory, dotted line -Krieger-Nelkin theory.

FIG.2. A comparison of Griffing theory with experiment [8, 9] for gazeous methane.



FIG.3. A comparison of Griffing theory with experiment [10] for gazeous methane.

To sum up, the situation in gaseous methane may be presented as follows:

The double differential neutron scattering cross-section is in a wide energy and momentum transfer region well described by the Griffing theory and also, for large energy and momentum transfers, by the Krieger and Nelkin theory. However, for small energy and momentum transfers, the Griffing theory seems to be not quite adequate, as there are fewer neutrons - in the quasi-elastic part - in experiment than in theory, if normalization is arbitrarily made in the inelastic region.



FIG. 4. A comparison of Griffing theory with experiment [8, 9] for gazeous ammonia.

2.4. Situation in Ammonia Gas

Venkataraman et al. [8], following the Griffing method, performed calculations for ammonia gas in order to explain Webb's experimental data [9]. Earlier, but much less accurate calculations were made by Czerlunczakiewicz and Kowalska [11]. Figure 4 presents a comparison between the experiment and the theory, taken from Ref.[8]. It is evident that the same small disagreement which was reported in section 2.3. for gaseous methane is also seen for ammonia gas, i.e. there are fewer neutrons obtained experimentally in the quasi-elastic region than the theory predicts, if one arbitrarily normalizes in the inelastic region.

2.5. Discussion

It should be stressed once more that neutron scattering in gases is fairly well understood in terms of the Krieger and Nelkin theory for large energy and momentum transfers and in terms of the Griffing theory in a much wider transfer region covering much smaller transfers where the quantum structure of rotations must be taken into account. However, there is a significant deviation from the theoretical predictions, which is probably localized in the quasi-elastic region. This localization is not quite certain as, in order to make it, it is necessary to have absolute double differential scattering cross-section measurements. From the methane experiments quoted above, only that of Randolph et al. [7] gives absolute values of the cross-section. All other experiments [9, 10] give only figures which are proportional to the cross-section values. In these cases, arbitrary normalizations are necessary, which, of course, do not indicate where the disagreement is.

It should be pointed out that the question of whether the disagreement is in the elastic or inelastic part, is of primary importance for the theory, as the theoretical investigations are entirely different in the two cases.

It should also be stressed that it is very difficult to find any reason for the discussed discrepancy, as it seems that the Griffing theory takes into account all necessary facts. The only possible point which could a priori be criticized lies in the fact that the Griffing theory does not take the so-called spin correlation effect into consideration.

This effect appears in molecules containing identical nuclei and results in a correlation between the space part and the spin part of the molecular wave function. Calculations concerning this effect in gaseous methane were made by Sinha and Venkataraman [12]. For a hypothetical methane gas at 10°K, the effect on the neutron scattering cross-section obtained by them is as large as 30%. For a room temperature methane it is negligible, amounting only to 0.7%. In view of this last value, it is highly improbable that the spin correlation effect might be responsible for the observed discrepancies between the Griffing theory and experiments.

A new attempt to solve this difficulty was made by Fuliński and Zgierski [13]. They analysed the influence of intermolecular interactions on σ_{tr} (θ, ϵ), assuming at the same time that σ_{rot} (θ, ϵ) and σ_{vib} (θ, ϵ) remain uninfluenced. The authors introduce further the form of intermolecular potential, which differs from the generally accepted Lennard-Jones potential, in order to have a finite value at r = 0, for these calculations. The correction obtained is important for small momentum and energy transfers only. Numerical calculations were made for the conditions of the Randolph et al. experiment [7], i.e. the one which was a basis for the original Griffing calculations. The theoretical curve of Fuliński and Zgierski is identical with that of Griffing on both sides of the quasi-elastic peak as a consequence of the assumption that intermolecular interactions influence the σ_{tr} (θ, ϵ), i.e. the quasi-elastic part only. The latter is decreased as compared with the unperturbed case, hence the theory is now closer to the experimental points.

These considerations cannot as yet be treated as definite. It is necessary to perform more extensive numerical calculations and to compare the results of experiments other than those reported in [7].

3. SCATTERING NEUTRONS BY MOLECULES IN A SOLID

3.1. Dynamics of Molecular Solids²

In some crystals it is justifiable to select s groups of atoms in each unit cell and call them molecular groups. The i-th group now contains

 \mathbf{r}_i atoms, and $\sum_{i=1}^s \mathbf{r}_i$ =p equals the total number of atoms in the unit cell.

This procedure allows a classification of the vibrations in the crystal into external vibrations (oscillatory motions of the s groups in a lattice) and internal vibrations (in each group).

Let us denote by ℓ , μ , ν indices numbering unit cells, groups in the unit cell, and atoms in the group, respectively. The displacement of an atom may be represented in the following form:

$$\vec{u} \begin{pmatrix} \ell \\ \mu \\ \nu \end{pmatrix} = \vec{S} \begin{pmatrix} \ell \\ \mu \end{pmatrix} + \vec{\theta} \begin{pmatrix} \ell \\ \mu \end{pmatrix} \times \vec{r} \begin{pmatrix} \mu \\ \nu \end{pmatrix} + \vec{W} \begin{pmatrix} \ell \\ \mu \\ \nu \end{pmatrix}$$
(13)

Here \vec{S} denotes a translational displacement of the $\begin{pmatrix} \ell \\ \mu \end{pmatrix}$ group as a whole, $\vec{\theta}$ is the angle of rotational displacement of the whole group, $\vec{r} \begin{pmatrix} \mu \\ \nu \end{pmatrix}$ is the position of ν -th atom in the μ -th group, and \vec{W} is displacement caused by internal vibration in the group.

The potential energy of the crystal may be written in the form of a series expansion with respect to \vec{S} , $\vec{\theta}$, \vec{W} . Denoting by an index α or β the x, y, z coordinates of these variables, we have

$$U = U_{0} + U_{1} + \frac{1}{2} \sum_{\alpha} \phi_{\alpha\beta}^{(SS)} \begin{pmatrix} \ell \ \ell' \\ \mu \ \mu' \end{pmatrix} S_{\alpha} \begin{pmatrix} \ell \\ \mu \end{pmatrix} S_{\beta} \begin{pmatrix} \ell' \\ \mu' \end{pmatrix}$$
$$+ \frac{1}{2} \sum_{\alpha} \phi_{\alpha\beta}^{(S\Theta)} S_{\alpha} \theta_{\beta} + \dots + \dots + \dots + \dots + \dots + U_{3} + \dots$$
(14)

The U_1 term vanishes since it contains first derivatives of potential energy vanishing as the potential energy has minimum at the equilibrium position. The U_3 and higher terms are assumed to be zero in this so-called harmonic approximation. The ϕ are the so-called force constants; they are, of course, second derivatives of potential energy taken in equilibrium positions.

An expression for the kinetic energy is:

$$T = \frac{1}{2} \sum_{\ell,\mu} M_{\mu} \left[\dot{\vec{S}} \begin{pmatrix} \ell \\ \mu \end{pmatrix} \right]^{2} + \sum_{\ell,\mu} \dot{\vec{\theta}} \begin{pmatrix} \ell \\ \mu \end{pmatrix} \bar{I}_{\mu} \dot{\vec{\theta}} \begin{pmatrix} \ell \\ \mu \end{pmatrix} + \frac{1}{2} \sum_{\ell,\mu,\nu} m \begin{pmatrix} \mu \\ \nu \end{pmatrix} \cdot \left[\dot{\vec{W}} \begin{pmatrix} \ell \\ \mu \end{pmatrix} \right]^{2}$$
(15)

where $M_{\mu} = \sum_{\nu} m \begin{pmatrix} \mu \\ \nu \end{pmatrix}$ is the total mass of the group and \overline{I}_{μ} its inertia tensor.

² This section was prepared on the basis of Ref.[15].

It is now useful to change variables by substitution:

$$\vec{\rho} = \sqrt{M_{\mu}\vec{S}}; \qquad \vec{\eta} = \sqrt{I_{\mu}\vec{\theta}}; \qquad \vec{v} = \sqrt{m\binom{\mu}{\nu}} \cdot \vec{W}$$

We shall now, additionally, assume that forces between groups are small compared with the forces within the groups. This leads to the neglect of all $\phi^{(WW)}$ except for those with $\ell = \ell'$ and $\mu = \mu'$. We shall also assume that the (SW), (W θ), (WS), (θ W) force constants are small compared with (SS), (S θ), (θ S), (θ B).

Taking this into account in writing the equations of motion, we obtain two independent systems of equations:

$$\ddot{\vec{\rho}} \begin{pmatrix} \ell \\ \mu \end{pmatrix} = -\sum_{\ell'\mu'} \frac{1}{\sqrt{M_{\mu}M_{\mu'}}} \vec{\phi}^{(SS)} \begin{pmatrix} \ell\ell' \\ \mu\mu' \end{pmatrix} \vec{\rho} \begin{pmatrix} \ell' \\ \mu' \end{pmatrix} - \sum_{\ell'\mu'} \frac{1}{\sqrt{M_{\mu}I_{\mu'}}} \vec{\phi}^{(SO)} \begin{pmatrix} \ell\ell' \\ \mu\mu' \end{pmatrix} \vec{\eta} \begin{pmatrix} \ell' \\ \mu' \end{pmatrix}$$

$$\ddot{\vec{\eta}} \begin{pmatrix} \ell \\ \mu \end{pmatrix} = -\sum_{\ell'\mu'} \frac{1}{\sqrt{I_{\mu}M_{\mu'}}} \vec{\phi}^{(OS)} \begin{pmatrix} \ell\ell' \\ \mu\mu' \end{pmatrix} \vec{\rho} \begin{pmatrix} \ell' \\ \mu\mu' \end{pmatrix} - \sum_{\ell'\mu'} \frac{1}{\sqrt{I_{\mu}I_{\mu'}}} \vec{\phi}^{(OO)} \begin{pmatrix} \ell\ell' \\ \mu\mu' \end{pmatrix} \vec{\eta} \begin{pmatrix} \ell' \\ \mu' \end{pmatrix}$$

$$(16)$$

$$\ddot{\vec{\nabla}} \begin{pmatrix} \ell \\ \mu \\ \nu \end{pmatrix} = -\sum_{\nu'} \frac{1}{\sqrt{m} \begin{pmatrix} \mu \\ \nu \end{pmatrix} m \begin{pmatrix} \mu \\ \nu' \end{pmatrix}} \vec{\phi}^{(WW)} \begin{pmatrix} \ell\ell \\ \mu\mu \\ \nu\nu' \end{pmatrix} \vec{\nabla} \begin{pmatrix} \ell \\ \mu \\ \nu \end{pmatrix}$$

The first two equations determine external vibrations, which may be either translational or rotational. There are 3(2s-t) solutions of this kind (t denotes the number of groups containing only one atom). The third equation describes internal vibrations of isolated molecular groups. There are 3(p-2s+t) vibration frequencies.

All solutions are supposed to be plane waves:

$$\vec{\rho} \begin{pmatrix} \ell \\ \mu \end{pmatrix} = \vec{\rho}_0 \cdot e^{i \left(2\pi \vec{q} \cdot \vec{R} \begin{pmatrix} \ell \\ \mu \end{pmatrix} - \omega \tau\right)}$$

$$\vec{\eta} \begin{pmatrix} \ell \\ \mu \end{pmatrix} = \vec{\eta}_0 e^{i \left(2\pi \vec{q} \cdot \vec{R} \begin{pmatrix} \ell \\ \mu \end{pmatrix} - \omega \tau\right)}$$

$$\vec{V} \begin{pmatrix} \ell \\ \mu \end{pmatrix} = \vec{V}_0 \cdot e^{i \left(2\pi \vec{q} \cdot \vec{R} \begin{pmatrix} \ell \\ \mu \end{pmatrix} - \omega \tau\right)}$$
(17)

Here $\vec{R}\begin{pmatrix} \ell\\ \mu \end{pmatrix}$ is the position of the centre-of-mass of the group $\begin{pmatrix} \ell\\ \mu \end{pmatrix}$.

Substituting now solutions (17) into Eqs (16) we obtain relations between ω and \vec{q} , i.e. the dispersion curves. There are altogether 3p curves, which may be divided into four groups (phonon branches):

- 1. acoustic (3)
- 2. optical translational (3s 3)
- 3. optical rotational (3(s-t))
- 4. optical internal (3(p-2s+t))

In the approximation under consideration, the frequencies of the 4th group are very well defined, i.e. the corresponding dispersion curves are flat.

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In some cases the rotational curves will also be flat: this should occur when the mass M_{μ} of the molecular group is much larger than I/r_0 (r_0 being the characteristic distance of atoms in the group). In molecular groups containing hydrogen this is very often fulfilled.

3.2. A Brief Look at the Experimental Material Obtained with Neutrons³

The double differential cross-section for incoherent scattering of neutrons by the ν -th atom in the crystal may be written:

$$\sigma_{\nu}^{\text{inc}}(\theta,\epsilon) \equiv \frac{d^2 \sigma_{\nu}^{\text{inc}}}{d\Omega dE} = C_{\nu}^2 \frac{k!}{k_0} \cdot e^{-2W_{\nu}} \cdot \sum_{n=0}^{\infty} \frac{(2W_{\nu})^2}{n!} \cdot G_n^{(\nu)} (E! - E_0)$$
(18)

where E_0 and E' denote the initial and final neutron energy, $\epsilon = E' - E_0$,

$$G_0^{(\nu)}(\epsilon) = \delta(\epsilon)$$

 $G_{1}^{(\nu)}(\epsilon) = G^{(\nu)}(\epsilon) \quad \text{whereas} \quad G^{(\nu)}(\epsilon) = \frac{g_{\nu}(\epsilon)}{\epsilon} \quad \frac{\coth \frac{\epsilon}{2k_{B}T}}{2\gamma_{\nu}(0)}$ $G_{n+1}^{(\nu)}(\epsilon) = \int_{-\infty}^{+\infty} G^{(\nu)}(\epsilon - \epsilon^{\dagger}) G_{n}^{(\nu)}(\epsilon^{\dagger}) d\epsilon^{\dagger}$ $2W_{\nu} = \frac{\hbar^{2}Q^{2}}{2M_{\nu}} \gamma_{\nu}(0)$ $\gamma_{\nu}(0) = \int_{0}^{\epsilon} \frac{\coth \frac{\epsilon}{2k_{B}T}}{\epsilon} g_{\nu}(\epsilon) d\epsilon$ $g_{\nu}(\epsilon) = g(\epsilon) |C_{\nu}(\epsilon)|^{2}$

is a function equal to the frequency spectrum of the crystal modulated by the squared amplitude of displacement of the ν -th atom from the equilibrium position.

Factor $|C_{\nu}(\epsilon)|$, called the polarization factor, is a linear combination of $|\rho_0|$, $|\eta_0|$, $|v_0|$ which correspond to translational, rotational, and internal vibrations. Because of this factor, some frequencies cannot be observed. For hydrogen atoms, this factor is almost zero for acoustic vibrations. Often the difficulties in determining polarization factors complicate the interpretation of inelastic neutron-scattering spectra.

Formula (18) is called the phonon expansion. The term with n = 0 describes elastic scattering. The term with n = 1 describes neutron scattering connected with the excitation or annihilation of a single phonon; this incoherent one-phonon cross-section is proportional to the frequency spectrum of the crystal. The term with n = 2 describes neutron scattering connected with the excitation or annihilation of two phonons (overtones, combination bands), etc.

³ This section was prepared on the basis of Ref.[15].

As the following discussion will be limited entirely to hydrogenous crystals we shall not discuss the coherence effects in neutron scattering. As examples some few substances studied in the Institute of Nuclear Physics in Cracow in cooperation with the Joint Institute for Nuclear Research in Dubna will be discussed. The main reason for this discussion is to compare the INS data with those obtained in IR and Raman spectroscopy.

3.2.1. Methyl Iodide

Solid methyl iodide probably has an orthorhombic structure belonging to the C_{2v} space group. Its molecular dynamics were studied by the INS method by Janik et al. [14, 15] and by spectroscopy methods by Ito [16], Lafferty and Robinson [17] and Dows [13].



FIG. 5. INS spectrum for solid CH₃I [15].

Figure 5 presents the INS spectrum and Fig. 6 the function $g_{\nu}(\epsilon)$ for hydrogen atoms in CH₃I, obtained from the data of Fig. 5 by applying the phonon expansion formula (18) in one-phonon approximation (with the additional assumption that the Debye-Waller factor is equal to **1**[15].



FIG. 6. $g_{H}(\omega)$ function for solid $CH_{3}I[15]$.

Table I gives a comparison of the INS data [15] and those from Raman spectroscopy [16].

There is a very good agreement between the two sets of data in the lowfrequency region, which is certainly the external vibration region of whole $CH_{3}I$ molecules in the lattice. This agreement may be treated as a test of the flatness of corresponding phonon branches in view of the fact that spectroscopic methods give information on the q = 0 region only (i.e. for phonons of very long wavelength) whereas neutrons scan the whole q-region.

There is also a very good agreement in the region of higher frequencies, which are interpreted as internal vibrations in CH_3I .

The intermediate region appears only in neutron data. Broad bands, whose peak values are listed in Table I, are interpreted as arising from two-, three-, and four-phonon contributions which are much less eminent in spectroscopy than in INS. The small marks made in Fig. 6 indicate the positions of such many-phonon peaks, calculated on the basis of singlephonon lattice vibration data. As may be seen, the marks form several groups, which roughly correspond to the bands observed.

3.2.2. Methylene Iodide

The situation for CH_2I_2 is in many respects similar to that for CH_3I . Again there is good agreement between the INS data of J.A. Janik et al. [15] and the Raman data given by Ito [19].

A comparison of these two sets of data is given in Table II. The agreement seen in the external (lattice) vibration region may again be

Janik et al. [15] INS temperature -160°C cm ⁻¹	Ito [16] R temperature -196°C cm ⁻¹	Interpretation	
-	47		
-	58	Translational (T)	
71	84		
97	94		
103	104	Rotational (R)	
108	112		
182	-	two phonons	
212	-		
300	•	three phonons	
387	- ,	four phonons	
508	508	ν of CH I	
	525	-3 or Oli31	
895	888	$\nu_6^{}$ of $CH_3^{}I$	
000		6 01 01131	

TABLE I.	VIBRATION	N FREQUE	NCIES IN	SOLID	CHJ
INS - neutro	on inelastic	incoherent	scatterin	g metho	od
R – Raman	method				

TABLE II. VIBRATION FREQUENCIES IN SOLID $\rm CH_2I_2$ INS – neutron inelastic incoherent scattering method R – Raman method

Janik et al. [15] INS temperature -160°C cm ⁻¹	Ito [19] R temperature -196°C cm ⁻¹	Interpretation
-	42	
-	63	Lattice vibrations (T and R)
115	99	
• .	134	ν_4 of CH_2I_2
230	-	2 x 115
487	487	ν_3 of CH ₂ I ₂
588	575	v_9 of CH_2I_2
723		ν_{γ} of CH_2I_2

considered to be a proof of the flatness of the corresponding phonon branches.

An interesting (although quite natural) fact may be seen in Fig.7, which presents a comparison of INS spectra for the solid and liquid CH_2I_2 :

the high energy parts of the spectra are almost the same in each case, which shows that internal vibrations are not much effected by phase transitions; the low-energy parts, on the other hand, are quite different, and especially the liquid spectrum is completely smeared out, owing to the freedom of molecular motions in the liquid state.





3.2.3. Thiourea

The situation of $CS(NH_2)_2$ may also be regarded as an example in which the INS and the spectroscopic data can be compared. There is good agreement between the INS data obtained by Bajorek et al. [20], and the IR ones [21].

Some additional interesting information on this substance may be obtained from Fig.8, which presents two spectra for hydrogen atoms in $CS(NH_2)_2$ corresponding to the ferroelectric and paraelectric states [20]. As the spectra are practically identical it may be concluded that differences in the dynamics of hydrogen atoms cannot be responsible for the ferroelectric properties of the substance, as was suggested by several authors.



FIG.8. $g_H(\omega)$ functions for non-ferroelectric and ferroelectric thiourea [20].



FIG.9. $g_{H}(\omega)$ function for solid $H_{3}O. NO_{3}[15]$.

3.2.4. Hydronium nitrate

The structure of $H_3O \cdot NO_3$ is orthorhombic; $H_3O \cdot NO_3$ is composed of alternate layers of flat NO_3 ions and slightly pyramidal H_3O^+ ions. There exists hydrogen bonding between the two layers. For this substance molecular dynamics studies were performed by the INS method (J.A. Janik et al. [15], J.M. Janik et al. [22]) and by the IR method (Savoie and Giguere [23], Bethell and Shepard [24]). Figure 9 shows the

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Janik et al. [15] INS temperature -150°C cm ⁻¹	Savoie & Giguère [23] IR temperature -180°C cm ⁻¹	Interpretation
	117	Tz
164		2
206	205	T _x
246	237	ту
321	329	$T_X + T_Z$
758	675	R

TABLE III. VIBRATION FREQUENCIES IN SOLID $H_3O \cdot NO_3$ INS - neutron inelastic incoherent scattering method IR - infrared spectroscopy

 $g_{\nu}(\epsilon)$ function corresponding to hydrogen motions in $H_3O \cdot NO_3$ in crystalline form, obtained from INS data [15]. Table III gives a comparison between the INS [15] and IR [23] results.

We shall restrict ourselves to a discussion of a disagreement which exists for the high-frequency band. The INS result is a broad band with maximum at 758 cm⁻¹, whereas the IR result gives the value of 675 cm⁻¹. A possible explanation may lie in the dispersion of the corresponding phonon branch which leads to a broadening and to a change of frequency of the INS data as compared with the IR data, the latter being limited to the q = 0 region only. Another explanation might be that there are two maxima unresolved in the INS data: one at about 670 cm⁻¹ corresponding to torsional motion R_x and R_y of the H_3O^+ group and another one at higher frequency corresponding to R_z , which is not being seen in IR in view of the selection rules.

3.3. The Case of NH4Cl

We shall discuss this case separately as (apart from the case of methane) the NH_4Cl (structure shown in Fig.10) is the only substance for which some theoretical predictions concerning the molecular dynamics of the NH_4^+ ion could be made. These predictions, made by Parliński [25], will be summarized below.



FIG. 10. Structure of NH Cl.

It should be clear from the theory presented in section 3.1. that to solve a problem of molecular dynamics in a crystal it is necessary to know all force constants $(\phi_{xx}^{(SS)}, \phi_{xy}^{(SS)}, \ldots, \phi_{xy}^{(SS)}, \ldots, etc)$. The total number of force constants of this type is reduced since there exist some mathematical connections between them, in which no additional physical know-ledge of the system is involved. Parliński further obtains some force constants from an electrostatic model, in which the NH₄ ion is approximated by a composition of four electric charges, each + (e/4), situated in the hydrogen positions, whereas in the Cl positions charges -e are placed.



FIG.11. Dispersion relations for NH4C1 [25].

There are still some force constants unknown so it is necessary to take some experimental data into account. These are: the moduli of elasticity of the substance, and the q = 0 values corresponding to translational and rotational vibrations of the NH₄ groups. On this basis it is possible to obtain the remaining force constants, and hence the dispersion relation (phonon branches) for the three important directions in the NH₄Cl crystal (Fig.11). It may be noticed that the phonon branch corresponding to the torsional motion of the NH⁴ group is indeed very flat, as explained in section 3.1. It should give rise to a very sharp peak in the INS spectrum, as is indeed observed at 49 meV in Fig.12 [26]. The peak at 22.3 meV is caused by translational vibrations of the NH₄ group, and those pertaining to higher energies are overtones and combination bands.

3.4. Situation in Solid Methane

We shall discuss only the situation in solid CH_4 near the melting point. At these temperatures carbon atoms form a cubic lattice. The rotational and translational motions of the CH_4 molecules in this lattice are an open problem.

INS measurements with solid methane were made by Stiller and Hautecler [27], Harker and Brugger [28], and Otnes [10].

An attempt to understand the INS results was made by Kosaly and Solt [29] and by Solt [30], who tried to fit their calculations to the conditions of Otnes' experiment. These considerations will be discussed below.



FIG.13. INS spectrum for solid $CH_4[10]$. Solid line - Griffing theory with incident spectrum used in experiment. Dotted line - Griffing theory with monoenergetic incident spectrum.

Otnes [10] tried to understand his results with solid methane in terms of the modified Griffing theory, assuming (as Griffing did for CH₄ gas) that molecular rotations are free in solid CH₄, but translations are completely stopped. Figure 13 presents Otnes' data and their comparison

with this kind of modified Griffing theory. The normalisation was arbitrarily made at the quasi-elastic peak. One may observe a distinct disagreement, as there are more neutrons scattered in the inelastic part than is predicted by theory. Also the shape of the inelastic part is different from that predicted: especially characteristic and not easy to explain is a flat part of the inelastic spectrum in the region of small energy transfers, or, in other words, an inexplicable shallow "valley" between the inelastic and quasi-elastic parts.

Solt [30] introduces rotational hindrance in solid methane by assuming a hindering potential. He introduces $\psi_r(\omega)$, the wave function of the hindered rotator, expanding it in a complete set of the free-rotator eigenfunctions $\varphi_{jmk}(\omega)$:

$$\psi_{\rm r}(\omega) = \sum_{\rm jmk} \alpha_{\rm jmk}^{\rm (r)} \varphi_{\rm jmk} \quad (\omega)$$
 (19)

where r denotes the quantum number of a hindered rotator and α are coefficients of expansion which are to be determined.

We put further:

$$\varphi_{jmk}(\omega) = \sqrt{\frac{2j+1}{8\pi^2}} \cdot \mathscr{D}_{mk}^{j*}(\omega)$$
(20)

as the \mathscr{D} -functions are used in a formula for the hindering potential, which is supposed to be:

$$V(\omega) = \beta \cdot B \left\{ \frac{7}{10} \mathscr{D}_{00}^{4}(\omega) + \sqrt{\frac{7}{40}} \left[\mathscr{D}_{0,-4}^{4}(\omega) + \mathscr{D}_{04}^{4}(\omega) + \mathscr{D}_{40}^{4}(\omega) + \mathscr{D}_{-40}^{4}(\omega) \right] + \frac{1}{2} \left[\mathscr{D}_{44}^{4}(\omega) + \mathscr{D}_{-44}^{4}(\omega) + \mathscr{D}_{4,-4}^{4}(\omega) + \mathscr{D}_{-4,-4}^{4}(\omega) \right]$$
(21)

where B is a rotational constant.

Solt analyses further the role of the β parameter in the shape of predicted INS spectra, assuming the translations to have been stopped, and adjusting all conditions to those in Otnes' experiment. Figure 14 shows the results for $\beta = 0$ (free rotation) and $\beta = 8$ (rather strong hindrance) together with Otnes' data. It is evident that rotational hindrance smears out discrete rotational peaks, but it does not explain the magnitude and flat shape of the observed spectrum. It is clear that further improvements of the model of dynamics in solid methane are needed.

Kosaly and Solt [29] analysed the influence of translational vibrations of CH₄ molecules on the form of the INS spectrum. They showed that if the frequency of such vibrations is low, their influence on the form of the spectrum is quite significant and, as needed, they increase the inelastic part, the "valley" between the elastic and inelastic parts at the same time becoming filled. In Fig.14 this translational contribution is exemplarily shown for $\omega_D = 50 \text{ cm}^{-1}$ and for $\omega_D = 100 \text{ cm}^{-1}$.

It is suggested [30] that a complete understanding of the solid methane INS spectrum may be obtained by assuming an almost free rotation and translational vibrations, the frequency of which is not higher than about 30 cm^{-1} .

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FIG. 14. Comparison of Solt theory [30] with experiment [10] for solid methane. ----hindrance parameter $\beta = 0$. ______ hindrance parameter $\beta = 8$(a) translatory contribution $\omega_D = 50$ cm⁻¹.(b) translatory contribution $\omega_D = 100$ cm⁻¹.

4. SCATTERING OF NEUTRONS BY MOLECULES IN A LIQUID

4.1. General Remarks

We shall not discuss here the very special subject of molecular selfdiffusion in liquids, for whose study neutrons proved to be a very powerful tool. The reader may find general and detailed discussions of this subject, for example, in a monograph edited by Egelstaff [31].

As a matter of fact, apart from the diffusion problem, other problems in molecular liquids are, in principle, the same as in solids, i.e. when investigating liquids by neutrons, we are interested in the frequency distribution of molecular vibrations which, together with diffusion motions, form what is called molecular dynamics.

In the following two sections we shall exemplarily discuss two liquids from the point of view of molecular dynamics, water and liquid methane.

4.2. Situation in Water

The structure of ice was studied by a number of authors who applied different techniques, among which X-ray scattering appears to be the most powerful. In this structure each oxygen atom is connected by tetrahedral

arms to other oxygen atoms with hydrogens separating them. This structure has considerable free space into which some water molecules may be introduced if they are for some reason separated from the hydrogen-bonded structure.



FIG. 16. INS spectrum for liquid CH₄ [10]. Notations the same as in Fig. 13.

This situation stimulated Szkatuła and Fuliński [32] to interpret the INS data for water and ice in the following way:

They observed that the INS spectra for water and ice differ significantly, as shown in Fig.15. Hence the frequency spectra also differ, which must result in a difference of specific heats. If, however, we compare this difference in specific heats with that measured by the calorimetric method we notice that the difference obtained with neutrons is approximately five times less than that known from calorimetry. The authors now make an assumption that the total specific heat (as measured

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in calorimetry) is a composition of dynamical and associational parts, the latter being connected with the energy needed for breaking the hydrogen bonds at melting:

$$C = C^{dyn} + C^{assoc}$$

From the difference between calorimetric and neutron specific heat data the authors are able to obtain information concerning the number of hydrogen bonds broken at melting, and they conclude that about 30% of hydrogen bonds are broken at 0°C.



FIG. 17. INS spectrum for liquid CH₄ [34], [37]. Lines correspond to two models, both with hindered rotation.

4.3. Situation in Liquid Methane

Liquid methane has been investigated by the INS method by several authors. Hautecler and Stiller [33], Harker and Brugger [28], Otnes [10], Dasannacharya and Venkataraman [34] performed measurements with CH_4 liquid, and Venkataraman et al. [35] with liquid CD_4 .

Theoretical attempts to understand the experimental material were performed by Griffing [36] and by Sears [37].

We shall limit our discussion to only a few remarks.

First, it should be noticed that apart from a broadening of the quasielastic peak, which is explicable in terms of self-diffusion, the inelastic part of the neutron spectrum is very similar to that obtained for the solid CH_4 .

A very natural attempt to understand the experimental data is to try to fit them with a modified Griffing theory with free molecular rotations and translations replaced by a simple diffusion. As shown in Fig.16 [10], there is a significant disagreement. If the theory is arbitrarily normalized to the quasi-elastic peak, there are (similarly as for solid CH_4) more neutrons than predicted in the inelastic region, and (again) the "valley" between the quasi-elastic and inelastic parts is inexplicably shallow.

A similar situation was obtained by other authors and for both CH_4 and CD_4 [34, 35].

Some improvement was obtained by Sears [37], who tried to interpret the data of Dassanacharya and Venkataraman [34] by introducing the rotational hindrance. The hindrance was taken into account in a semiempirical way, by using the IR data for liquid CH_4 . Such a treatment was successful in explaining the practical lack of valley between the inelastic and quasi-elastic parts but there are still more neutrons in the inelastic region than theory predicts, as seen in Fig. 17.

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ATOMIC MOTIONS IN LIQUIDS AND NEUTRON SCATTERING

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Abstract

1. Introduction. 2. Correlation functions. 3. Sum rules. 4. Incoherent scattering. 5. Frequency spectrum. 6. Memory function. 7. Theory of self motion. 8. Coherent scattering. 9. Convolution approximation. 10. Quasi-crystalline model. 11. Scattering in liquid helium. 12. Zero sound in liquid ⁴HeI.

1. INTRODUCTION

The dynamical theory of classical liquids is very little understood. We are in a much better situation regarding the theory of the quantum liquids He II and He³. In the last few years inelastic neutron scattering experiments have revealed many interesting features of the atomic motions in liquids. For example, we now have some evidence of the existence of collective motions not only in the very long wavelength and low-frequency region, but also in the very short-wavelength and very-high-frequency region. The single-particle motions as revealed by neutron scattering experiments are more complex than we had hitherto anticipated; they are not governed by the simple Langevin equation. The task of the theorist is to explain these features from first principles. Not being able to do so. he has been forced to propose, during recent years, several models furthering the understanding of neutron scattering results. To a certain extent, these phenomenological models have helped us to understand the nature of atomic motions in liquids, but the basic problem still remains unsolved.

The state of the subject up to the beginning of 1964 has been summarized in two excellent review articles, one by Sjölander and the other by Larsson [1]. In these lectures I shall, therefore, confine myself to what has been done since then, and be mainly concerned with theoretical developments. For the sake of completeness, my first lecture will cover material with which some of you are perhaps fimiliar.

2. CORRELATION FUNCTIONS

We shall begin with the well-known formulae for the coherent and incoherent differential scattering cross-sections first derived by Van Hove [2] using the first Born approximation and the Fermi pseudo-

potential. These are

$$\frac{d^2 \sigma_{\rm coh} x}{d\Omega \, d\omega} = N \frac{\overline{b}^2}{2\pi} \frac{k}{k_0} \int e^{i(\vec{k} \cdot \vec{r} - \omega \, t)} G(\vec{r}, t) \, d\vec{r} \, dt \qquad (1a)$$

and

$$\frac{d^2\sigma_{inc}}{d\Omega \,d\omega} = N \, \frac{\overline{b^2} - \overline{b}^2}{2\pi} \, \frac{k}{k_0} \, \int e^{i(\vec{k}\cdot\vec{r}\cdot\omega t)} \, G_s(\vec{r}, t) \, d\vec{r} \, dt \qquad (1b)$$

where $h\vec{k}$ and $h\omega$ denote, respectively, the momentum and energy transfers in the collision between the neutron and the scattering system and are given by

 $\vec{k} = \vec{k} - \vec{k}_0$ $\hbar\omega = \frac{\hbar^2 k_0^2}{2m} - \frac{\hbar^2 k^2}{2m}$ (2)

and

m is the neutron mass and $\vec{k_0}$ and \vec{k} are, respectively, the initial and final wave vectors of the neutron. \vec{b}^2 and $(\vec{b}^2 - \vec{b}^2)$ are the squares of the usual coherent and incoherent scattering lengths. The correlation functions G are defined by

$$G(\vec{\mathbf{r}},t) = \frac{1}{N} \sum_{i,j} \int d\vec{\mathbf{r}}' \langle \delta(\vec{\mathbf{r}} + \vec{\mathbf{R}}_j(0) - \vec{\mathbf{r}}') \delta(\vec{\mathbf{r}}' - \vec{\mathbf{R}}_i(t)) \rangle$$
(3a)

and

$$\mathbf{G}_{s}(\vec{\mathbf{r}},t) = \frac{1}{N} \sum_{i} \int d\vec{\mathbf{r}}' \langle \delta(\vec{\mathbf{r}} + \vec{\mathbf{R}}_{i}(0) - \vec{\mathbf{r}}') \ \delta(\vec{\mathbf{r}}' - \vec{\mathbf{R}}_{i}(t)) \rangle$$
(3b)

where $\delta(\dots)$ is the Dirac δ -function, $\vec{R}_j(0)$ and $\vec{R}_i(t)$ are the usual Heisenberg operators denoting, respectively, the positions of the jth atom at time t = 0 and that of the ith atom at time t. The bracket $\langle \dots \rangle$ denotes the statistical average corresponding to equilibrium conditions at temperature T.

To understand the physical meaning of the G-functions let us go over to the classical limit where the operators in (3) can be permuted at will. Performing the integration and remembering that the atoms are equivalent, we have

$$G(\vec{r}, t) = \sum_{i} \langle \delta(\vec{r} + \vec{R}_{0}(0) - \vec{R}_{i}(t)) \rangle$$
(4a)

and

$$G_{s}(\vec{r}, t) = \langle \delta(\vec{r} + \vec{R}_{0}(0) - \vec{R}_{0}(t)) \rangle$$
(4b)

where $\vec{R}_0(0)$ is the position at t = 0 of an arbitrarily chosen atom. As a consequence, we have for t = 0

$$G_{s}(\vec{r}, 0) = \delta(\vec{r})$$
 (5a)

$$G(\vec{r}, 0) = \delta(\vec{r}) + \overline{\rho}g(\vec{r})$$
(5b)

ATOMIC MOTIONS

where $g(\vec{r})$ is the static pair-distribution function which gives the instantaneous probability of finding a particle at \vec{r} around a particle at the origin. For $t \to \infty$, $G_s(\vec{r}, \infty) = 0$ and $G(\vec{r}, \infty) = \bar{\rho}$, the mean particle number density. $G(\vec{r}, t)$ thus represents the probability of finding any particle at \vec{r} at time t if there was a particle at the origin at t=0. On the other hand, $G_s(\vec{r}, t)$ gives the probability of finding the particle at \vec{r} at time t if the same particle was at the origin at time t=0. The latter is thus related to the self-diffusion in a liquid. Such a simple interpretation is valid only in the classical limit. In general, these functions are complex whose real and imaginary parts are related through the fluctuation-disipation theorem. Since it has not been possible to calculate these functions rigorously for a liquid, one resorts to model calculations guided by the above mentioned physical considerations.

Writing the density operator $\rho(\vec{r}, t)$ as

$$\rho(\vec{\mathbf{r}},t) = \sum_{i} \delta(\vec{\mathbf{r}} - \vec{\mathbf{R}}_{i}(t))$$
(6)

we can express $G(\vec{r}, t)$ as

$$G(\vec{\mathbf{r}}, t) = \frac{1}{N} \int d\vec{\mathbf{r}} \langle \rho(\vec{\mathbf{r}} - \vec{\mathbf{r}}, 0) \rho(\vec{\mathbf{r}} + t) \rangle$$
$$= \frac{1}{\bar{\rho}} \langle \rho(0, 0) \rho(\vec{\mathbf{r}}, t) \rangle$$
(7)

valid for a homogeneous system. $G(\vec{r}, t)$ thus gives the correlation between the densities at two different positions and times. Equation (7) brings out clearly the collective aspect of the G-function.

Remembering the definitions of the G-functions and taking the Fourier tranforms, Eqs (1a) and (1b) can also be written as

$$\frac{d^2\sigma_{\rm coh}}{d\Omega\,d\omega} = \overline{b}^2 \frac{k}{k_0} \frac{N}{2\pi} \int e^{-i\omega t} F(\vec{k}, t) \,dt$$
(8a)

and

$$\frac{d^2 \sigma_{inc}}{d\Omega \, d\omega} = \left(\overline{b^2} - \overline{b}^2\right) \frac{k}{k_0} \frac{N}{2\pi} \int e^{-i\omega t} F_s(\vec{\kappa}, t) \, dt$$
(8b)

where the intermediate scattering functions F are defined by

$$\mathbf{F}(\vec{\kappa}, t) = \frac{1}{N} \sum_{i,j} \langle \mathbf{e}^{-i\vec{\kappa}\cdot\vec{R}_{j}(0)} \mathbf{e}^{i\vec{\kappa}\cdot\vec{R}_{i}(t)} \rangle$$
(9a)

and

$$F_{s}(\vec{\kappa}, t) = \frac{1}{N} \sum_{i} \left\langle e^{-i\vec{\kappa} \cdot \vec{R}_{i}^{(0)}} e^{i\vec{\kappa} \cdot \vec{R}_{i}(t)} \right\rangle$$
(9b)

Let us define the dynamical structure factor $S(\vec{\kappa}, \omega)$ through the relations

$$S_{coh}(\vec{\kappa}, \omega) = \frac{1}{2\pi} \int e^{-i\omega t} F(\vec{\kappa}, t) dt$$
 (10a)

and

$$S_{inc}(\vec{\kappa},\omega) = \frac{1}{2\pi} \int e^{-i\omega t} F_{s}(\vec{\kappa},t) dt$$
 (10b)

With the above definitions, we see that the coherent and the incoherent differential scattering cross-sections are, respectively, proportional to $S_{\rm coh}(\vec{k},\omega)$ and $S_{\rm inc}(\vec{k},\omega)$. It is these functions which are determined by a scattering experiment. We could not ask for more information than what is provided by these functions. It is complete. In practice such complete information for all \vec{k} and ω values is not available.

3. SUM RULES

The functions $S(\vec{\kappa}, \omega)$ satisfy certain very important sum rules which serve to check the internal consistency of any experiment or a theory. From Eq. (10a) we have

$$\int_{-\infty}^{+\infty} S_{\text{coh}}(\vec{\kappa}, \omega) \, d\omega = S(\vec{\kappa}) = F(\vec{\kappa}, 0)$$
$$= 1 + \Gamma(\vec{\kappa})$$
(11)

where

$$\Gamma(\vec{\kappa}) = \overline{\rho} \int e^{\vec{i}\vec{\kappa}\cdot\vec{r}} (g(r) - 1) d\vec{r}$$
(12)

using Eqs (9a) and (5b). The X-ray scattering experiment usually gives $S(\vec{k})$.

Similarly,

$$\int_{-\infty}^{+\infty} S_{inc}(\vec{k}, \omega) d\omega = F_s(\vec{k}, 0) = 1$$
(13)

From Eq. (10) it follows that

$$\overline{\omega_{\text{coh}}^{n}} \equiv \int_{-\infty}^{+\infty} \omega^{n} S_{\text{coh}}(\vec{\kappa}, \omega) d\omega = (-i)^{n} \left(\frac{d^{n}}{dt^{n}} F(\vec{\kappa}, t)\right)_{t=0}$$
(14a)

and

$$\overline{\omega_{\text{inc}}^{n}} = \int_{-\infty}^{+\infty} \omega^{n} \operatorname{S}_{\text{inc}}(\vec{\kappa}, \omega) \, d\omega = (-i)^{n} \left(\frac{d^{n}}{dt^{n}} F_{s}(\vec{\kappa}, t) \right)_{t=0}$$
(14b)

One can easily show that

$$\overline{\omega'_{\rm coh}} = \frac{\hbar\kappa^2}{2M}$$
(15a)

and

$$\overline{\omega_{\text{inc}}^{\dagger}} = \frac{\hbar \kappa^2}{2M}$$
(15b)

where M is the atomic mass. Notice that the first moment is independent of the interaction between the particles of the system and is the same for both the coherent and the incoherent case. Quantum-mechanical expressions for the higher moments have been given by Rahman et al [3]. Since in this series of lectures we shall be mainly concerned with classical liquids we shall, following De Gennes [4], derive expressions for these moments in the classical limit.

From (11) and (14a) we have

$$\frac{\widetilde{\omega_{\rm coh}}}{\widetilde{\omega_{\rm coh}}} = -\frac{1}{\rm NS}(\kappa) \leq \rho_{\vec{\kappa}}(0) \frac{d^2}{dt^2} \rho_{\vec{\kappa}}(t) >_{t=0}$$
(16)

where

$$\rho_{\vec{k}} = \sum_{i} e^{\vec{k} \cdot \vec{R}_{i}}$$
(17)

which denotes the κ^{th} Fourier component of the density fluctuation $\rho(\vec{r})$. Now

$$\langle \rho_{\vec{k}}(0) \ \vec{\rho}_{\vec{k}}(t) \rangle = \frac{d}{dt} \langle \rho_{\vec{k}}(0) \ \dot{\rho}_{\vec{k}}(t) \rangle$$

$$= \frac{d}{dt} \langle \rho_{\vec{k}}(-t) \ \dot{\rho}_{\vec{k}}(0) \rangle$$

$$= -\langle \vec{\rho}_{\vec{k}}(-t) \ \dot{\rho}_{\vec{k}}(0) \rangle$$

$$= -\langle \dot{\rho}_{\vec{k}}(0) \ \dot{\rho}_{\vec{k}}(t) \rangle$$

$$(18)$$

since the ensemble average is independent of the time origin. From (17) we have

 $\dot{\rho}_{\vec{\kappa}}(t) = i\kappa \sum_{i} e^{i\kappa X_{i}(t)} v_{ix}(t)$ (19)

where the direction of \vec{k} has been chosen along the X-axis. v_{ix} denotes the velocity of the ith particle in the X-direction. Using (18) and (19) in (16), we have

$$\frac{\overline{\omega}_{coh}^{2}}{\overline{\omega}_{coh}^{0}} = \frac{1}{NS(\kappa)} \kappa^{2} \sum_{ij} \langle e^{i\kappa(X_{i} - X_{j})} v_{ix} v_{ij} \rangle$$

$$= \frac{1}{NS(\kappa)} \kappa^{2} \sum_{ij} \langle e^{i\kappa(X_{i} - X_{j})} \rangle \langle v_{ix} v_{ij} \rangle$$

$$= \frac{1}{S(\kappa)} \kappa^{2} \langle v_{ix}^{2} \rangle$$

$$= \frac{1}{S(\kappa)} \kappa^{2} \frac{k_{B}T}{M}$$
(20)

The second step follows from the fact that the velocity and position are uncorrelated in a classical system. The third step follows from the fact that only terms with i = j contribute.

Proceeding in a similar manner we can show that

$$\frac{\widetilde{\omega}_{coh}^4}{\widetilde{\omega}_{coh}^0} = \frac{1}{NS(\kappa)} \left\langle \ddot{\rho}_{\overrightarrow{\kappa}}(0) \ddot{\rho}_{\overrightarrow{\kappa}}(t) \right\rangle_{t=0}$$
(21)

where

$$\ddot{\rho}_{\vec{\kappa}}(t) = (i\kappa)^2 \sum_{i} e^{i\kappa X_i(t)} v_{ix}^2(t) + i\kappa \sum_{i} e^{i\kappa X_i(t)} \dot{v}_{ix}(t)$$
(22)

Substituting (22) into (21), we have for the right-hand side of (21)

$$\kappa^{4} \sum_{ij} \langle \mathbf{v}_{i\mathbf{x}}^{2} \mathbf{v}_{j\mathbf{x}}^{2} \mathbf{e}^{i\kappa\mathbf{X}_{ij}} \rangle + \frac{i\kappa^{3}}{M} \sum_{ij} \langle \left(\mathbf{v}_{j\mathbf{x}}^{2} \frac{\partial U}{\partial \mathbf{X}_{i}} - \mathbf{v}_{i\mathbf{x}}^{2} \frac{\partial U}{\partial \mathbf{X}_{j}} \right) \mathbf{e}^{i\kappa\mathbf{X}_{ij}} \rangle$$
$$+ \frac{\kappa^{2}}{M^{2}} \sum_{ij} \langle \frac{\partial U}{\partial \mathbf{X}_{i}} \frac{\partial U}{\partial \mathbf{X}_{j}} \mathbf{e}^{i\kappa\mathbf{X}_{ij}} \rangle$$
(23)

where we have put

$$\dot{v}_{ix} = -\frac{\partial U}{\partial X_i} \frac{1}{M}$$

U is the potential energy of the system; it is a function of all the coordinates of the particles. Using the well known result

$$\langle \mathbf{F} \frac{\partial \mathbf{U}}{\partial \mathbf{X}_{i}} = \mathbf{k}_{B} \mathbf{T} \langle \frac{\partial \mathbf{F}}{\partial \mathbf{X}_{i}} \rangle$$
 (24)

in (23), where $F(R_1 \ldots R_n)$ is any regular function of R, we have

•

$$\frac{\omega_{coh}^{2}}{\omega_{coh}^{0}} = \frac{1}{S(\kappa)} \left[3\kappa^{4} \left(\frac{k_{B}T}{M} \right)^{2} + \kappa^{2} \frac{k_{B}T}{M^{2}} \frac{1}{N} \sum_{ij} \left\langle \frac{\partial^{2}U}{\partial X_{i} \partial X_{j}} e^{i\kappa X_{ij}} \right\rangle \right]$$
(25)

Similarly, one can show that

$$\frac{\widetilde{\omega_{\text{inc}}^4}}{\widetilde{\omega_{\text{inc}}^0}} = 3\kappa^4 \left(\frac{\mathbf{k_B T}}{M}\right)^2 + \frac{\kappa^2 \mathbf{k_B T}}{M^2} < \frac{\partial^2 U}{\partial X_i^2} >$$
(26)

Since

$$U = \sum_{i < j} V(\vec{R}_{ij})$$

$$\langle \frac{\partial^2 U}{\partial X_i^2} \rangle = \int g(\vec{R}) \frac{\partial^2 V}{\partial X^2} d\vec{R}$$
 (27)

Using (27) in (25) and (26) we have

$$\frac{\vec{\mu}_{coh}}{\vec{\omega}_{coh}^{0}} = \frac{\kappa^{4} k_{B} T}{M^{2} S(\kappa)} \left[3k_{B} T + \int g(\vec{R}) \left(\frac{1 - \cos \kappa X}{\kappa^{2}} \right) \left(\frac{\partial^{2} V}{\partial X^{2}} \right) d\vec{R} \right]$$
(28)

and

$$\overline{\omega_{\text{inc}}^4} = \frac{\kappa^4 \mathbf{k}_B T}{M^2} \left[3 \mathbf{k}_B T + \int g(\mathbf{R}) \frac{1}{\kappa^2} \left(\frac{\partial^2 V}{\partial X^2} \right) d\vec{\mathbf{R}} \right]$$
(29)

Defining a frequency Ω_0 by

$$M\Omega_0^2 = \int d\vec{R} g(R) \frac{\partial^2 V(R)}{\partial X^2}$$
(30)

Eq. (29) can be written as

$$\overline{\omega_{\text{inc}}^4} = 3(\overline{\omega_{\text{inc}}^2})^2 + \overline{\omega_{\text{inc}}^2} \ \Omega_0^2$$
(31)

For very large values of $\vec{\kappa}$ the second term in (31) is negligible

compared to the first and in that case $\overline{\omega_{inc}^4} = 3\overline{\omega_{inc}^2}$, which implies that $S_{inc}(\vec{\kappa}, \omega)$ is a Gaussian function of ω . For a perfect gas model neglecting recoil we have

$$S_{inc}^{gas}(\vec{\kappa},\omega) = \frac{1}{\kappa} \left(\frac{M}{2\pi k_{B}T}\right)^{\frac{1}{2}} e^{-\frac{M\omega^{2}}{2\kappa_{2}k_{B}T}}$$
(32)

which leads to (31) with no second term. Thus, for very large values of \vec{k} , the gas model is a good approximation. On the other hand, for small values of \vec{k} the fourth moment given by (31) is much greater than that for a Gaussian model, thereby implying that the actual $S_{inc}(\vec{k},\omega)$ has large wings as for a Lorentzian distribution. For the coherent case we have

$$\frac{\overline{\omega_{coh}^{4}}}{\overline{\omega_{coh}^{2}}} = 3S(\kappa) + \frac{S(\kappa)}{\kappa_{B}T} \int g(R) \left(\frac{1 - \cos\kappa X}{\kappa^{2}}\right) \frac{\partial^{2} V}{\partial X^{2}} d\vec{R}$$
(33)

which in the limit of large $\vec{\kappa}$ reduces to

$$\overline{\omega_{\rm coh}^4} = 3(\overline{\omega_{\rm coh}^2})^2$$

again implying that in this limit the gas model is good. For intermediate values of $\vec{\kappa}$ this ratio shows strong fluctuations as a function of $\vec{\kappa}$. It has the largest value for that $\vec{\kappa}$ for which $S(\kappa)$ is maximum. This means that for such $\vec{\kappa}$ values the distribution $S_{coh}(\vec{\kappa}, \omega)$ becomes narrow in the centre and broad in the wings. Such a narrowing effect in quasi-elastic scattering was first predicted by De Gennes [4] and was later observed experimentally by Brockhouse and Pope [5]. This result as deduced from sum-rule arguments is quite general and does not depend on any specific model. Any model must fulfill these sum-rule requirements.

Remembering the definition of the bracket $\langle \dots \rangle$, Eq. (10a) can be written as

$$S_{coh}(\vec{k}, \omega) = \frac{1}{2\pi} \int e^{-i\omega t} dt \frac{1}{N} \sum_{ij} \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} \times \langle m \mid e^{i\vec{k}\cdot\vec{R}_j(0)} \mid n \rangle \langle n \mid e^{iHt/\hbar} e^{i\vec{k}\cdot\vec{R}_i(0)} e^{-iHt/\hbar} \mid m \rangle$$

where Z is the partition function, $\beta = 1/k_BT$, and $|m\rangle$ and $|n\rangle$ denote, respectively, the initial and final exact eigenstates of the system corresponding to the energies E_m and E_n . Furthermore, we have

$$N S_{coh}(\vec{\kappa}, \omega) = \frac{1}{2\pi} \int e^{-it(\omega - \omega_{nm})} dt \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} |(\rho_{\vec{\kappa}}^{\dagger})_{nm}|^2$$

where

$$\omega_{nm} = \frac{1}{\hbar} (E_n - E_m) \text{ and } \rho_{\vec{k}} = \sum_{i} e^{i\vec{k} \cdot \vec{R}_i(0)}$$

or

$$N S_{coh}(\vec{\kappa}, \omega) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_{m}} |(\rho_{\vec{\kappa}}^{\dagger})_{nm}|^{2} \delta(\omega - \omega_{nm})$$
(34)

Interchanging the indices in (34), we have

$$N S_{coh}(\vec{\kappa}, \omega) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_n} |(\rho_{\vec{\kappa}}^{\dagger})_{mn}|^2 \delta(\omega + \omega_{nm})$$
$$= \frac{1}{Z} \sum_{m,n} e^{-\beta (E_n - E_m)} e^{-\beta E_m} |(\rho_{\vec{\kappa}}^{\dagger})_{nm}|^2 \delta(\omega + \omega_{nm})$$
$$= N e^{\hbar \omega \beta} S_{coh}(\vec{\kappa}, -\omega)$$

where we have used the fact that $|(\rho_{\vec{k}}^{\dagger})_{mn}|^2 = |(\rho_{\vec{k}}^{\dagger})_{nm}|^2$ which follows from time-reversal invariance. We have thus proved the following important result:

$$S_{coh}(\vec{\kappa}, -\omega) = e^{-\beta\hbar\omega} S_{coh}(\vec{\kappa}, \omega)$$
(35)

The above result is a sophisticated statement of the principle of detailed balance.

Relation between $S_{coh}(\vec{k}, \omega)$ and the density-density response function $\chi(\vec{k}, \omega)$:

The function $\chi(\vec{\kappa}, \omega)$ is defined by the relation

$$X(\vec{\kappa},\omega) = \frac{\langle \rho(\vec{\kappa},\omega) \rangle}{\phi(\kappa,\omega)}$$
(36)

where $\langle \rho(\vec{k}, \omega) \rangle$ is the Fourier transform of the average density fluctuation and $\phi(\vec{k}, \omega)$ is the Fourier transform of an externally applied weak scalar potential. Using Kubo's linear response theory one can derive an expression [6] for $\chi(\vec{k}, \omega)$. It is given by

$$\chi(\vec{\kappa},\omega) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} \left| (\rho_{\vec{\kappa}}^{\dagger})_{nm} \right|^2 \left\{ \frac{1}{\omega - \omega_{nm} + i\eta} - \frac{1}{\omega + \omega_{nm} + i\eta} \right\}$$
(37)

where $\eta \rightarrow +0$. Let

$$\chi(\vec{\kappa}, \omega) = \chi'(\vec{\kappa}, \omega) + i\chi''(\vec{\kappa}, \omega)$$

where χ^1 and χ^{11} are, respectively, the real and imaginary part of $\chi.$ Using the identity

$$\frac{1}{\mathbf{x} \pm \mathrm{i}\eta} = \mathrm{P}\left(\frac{1}{\mathbf{x}}\right) \mp \mathrm{i}\pi \ \delta(\mathbf{x})$$

we can write for the imaginary part of $\chi(\vec{\kappa}, \omega)$

$$\chi^{\prime\prime}(\vec{\kappa},\omega) = -\frac{\pi}{Z} \sum_{m,n} e^{-\beta E_m} |(\rho_{\vec{\kappa}}^{\dagger})_{nm}|^2 \left\{ \delta(\omega - \omega_{nm}) - \delta(\omega + \omega_{nm}) \right\}$$
(38)

Using (38) we can write (37) as

$$\chi(\vec{\kappa},\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega' \frac{\chi''(\vec{\kappa},\omega')}{\omega' - \omega - i\eta}$$
(39)

 $\chi^{\mu}(\vec{k},\omega)$ thus serves as the spectral density for $\chi(\vec{k},\omega)$. Using (34) and (35) $\chi^{\mu}(\vec{k},\omega)$ can be written as

$$\chi^{\prime\prime}(\vec{\kappa},\omega) = -\pi N \left\{ S_{\rm coh}(\vec{\kappa},\omega) - S_{\rm coh}(\vec{\kappa},-\omega) \right\}$$

= $-\pi N (1 - e^{-\beta \hbar \omega}) S_{\rm coh}(\vec{\kappa},\omega)$ (40)

The above equation relates the imaginary part of the response function to $S(\vec{k}, \omega)$ which is the Fourier transform of the density fluctuation. It is called the fluctuation-dissipation theorem. Defining a symmetrized $\tilde{S}(\vec{k}, \omega)$ through

$$\widetilde{S}(\vec{k},\omega) = (S_{coh}(\vec{k},\omega) + S_{coh}(\vec{k},-\omega))/2$$

$$= \frac{S_{coh}(\vec{k},\omega)}{2} [1 + e^{-\beta\hbar\omega}]$$
(41)

we can write

$$\widetilde{S}(\vec{\kappa},\omega) = -\frac{1}{2\pi N} \chi^{\prime\prime}(\vec{\kappa},\omega) \operatorname{coth}\left(\frac{\beta \hbar \omega}{2}\right)$$
(42)

Integrating both sides with respect to ω , we have

$$NS(\kappa) = -\int_{-\infty}^{+\infty} \frac{d\omega}{a\pi} \chi^{(\dagger}(\vec{\kappa}, \omega) \coth\left(\frac{\beta\hbar\omega}{2}\right)$$
(43)

where N is the number of particles per unit volume.

It can be shown that [6]

$$\lim_{\vec{\kappa} \to 0} \chi(\vec{\kappa}, 0) = -N^2 \kappa_{iso}$$
$$= -\frac{N}{Ms_{iso}^2}$$
(44)

where κ_{iso} is the isothermal compressibility and s_{iso} is the isothermal sound velocity. From (39). (40) and (44) it then follows that

$$\lim_{\vec{k}\to 0} \left[2N \int_{-\infty}^{+\infty} \frac{S(\vec{k},\omega)}{\omega} d\omega \right] = \lim_{\vec{k}\to 0} \left[-\frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega \frac{\chi^{\prime\prime}(\vec{k},\omega)}{\omega} \right] = \frac{N}{Ms_{iso}^2}$$
(45)

4. INCOHERENT SCATTERING

A good discussion of various models for the self motion of an atom in a liquid has been given in the review article by Sjölander [1]. We shall, therefore, not go into this discussion but rather concentrate on more basic considerations. It has been shown by Rahman et al. [3] that the intermediate scattering function $F_{e}(\vec{k}, t)$ can be written as

$$F_{s}(\vec{\kappa},t) = e^{-\kappa^{2}\gamma_{1}(t) + O(\kappa^{4})}$$
(46a)

where

$$\gamma_{1}(t) = -\frac{it\hbar}{2M} + \frac{1}{3}\int_{0}^{t} (t-u)\langle \vec{v}(0) \cdot \vec{v}(u) \rangle du \qquad (46b)$$

ATOMIC MOTIONS

 $\langle \vec{v}(0) \cdot \vec{v}(u) \rangle$ is the velocity autocorrelation function. In Eq. (46) terms of order κ^4 involve higher velocity correlations which can symbolically be written as

$$\langle 1234 \rangle$$
 - $\langle 12 \rangle$ $\langle 34 \rangle$ - $\langle 13 \rangle$ $\langle 24 \rangle$ - $\langle 14 \rangle$ $\langle 23 \rangle$

If we neglect these and higher-order correlations we have for F_s $(\vec{\kappa},t)$ a very simple expression

$$F_{c}(\vec{\kappa}, t) = e^{-\kappa^{2}\gamma_{1}(t)}$$
(47)

which is valid <u>only</u> under the above assumption. This approximation is called the Gaussian approximation since it leads to a Gaussian form for $G_s(\vec{r}, t)$. From very general considerations it follows that $G_s(\vec{r}, t)$ for a liquid is Gaussian both for very small and very large times. It is only in the intermediate time region that it is non-Gaussian. There are indications that the non-Gaussian corrections are small. Thus (47) is a reasonably good approximation. $\gamma_1(t)$ is the time-dependent width of the distribution and, as is seen from (47), it is complex. For a harmonic solid (47) is exact.

From the definition (9b) of $F_s(\vec{\kappa}, t)$ it is easy to show that [7]

$$\int_{-\infty}^{+\infty} e^{-i\omega t} \operatorname{Im} F_{s}(\vec{\kappa}, t) dt = -i \tanh\left(\frac{\beta \hbar \omega}{2}\right) \int_{-\infty}^{+\infty} e^{-i\omega t} \operatorname{Re} F_{s}(\vec{\kappa}, t) dt \qquad (48)$$

Equation (48) implies the following relation:

Im
$$F_s(\vec{\kappa}, t) = -\tan\left(\frac{\beta\hbar}{2}\frac{d}{dt}\right)$$
 Re $F_s(\vec{\kappa}, t)$ (49)

Let us define a new function $H_{\epsilon}(\vec{\kappa}, t)$ through

$$H_{s}(\vec{\kappa}, t) = F_{s}\left(\vec{\kappa}, t + \frac{i\hbar\beta}{2}\right) \qquad (50)$$

 \mathbf{or}

$$H_{s}(\vec{\kappa}, t) = e^{\frac{i\hbar\beta}{2}\frac{d}{dt}} F_{s}(\vec{\kappa}, t)$$
$$= \sec\left(\frac{\hbar\beta}{2}\frac{d}{dt}\right) \operatorname{Re} F_{s}(\vec{\kappa}, t)$$
(51)

using (49). $H_s(\vec{k}, t)$ is therefore real and an even function of time (since Re $F_s(\vec{k}, t)$ is an even function). One can also show that

$$H_{s}(\vec{\kappa}, t) = e^{-\kappa^{2}\rho(t)}$$
(52)

where

$$\rho(t) = \frac{\hbar^2}{8 M k_B T} + \frac{1}{3} \int_0^t (t-u) \langle \vec{v}(0) \cdot \vec{v}(u) \rangle_{cl_x}$$
(53)

And

$$S_{inc} (\vec{\kappa}, \omega) = e^{\hbar \omega / 2k_B T} \int_{-\infty}^{+\infty} e^{-i\omega t} H_s(\vec{\kappa}, t) dt$$
 (54)

Thus, for a classical liquid the problem of calculating the incoherent scattering cross-section is reduced to that of calculating the classical velocity autocorrelation function.

5. FREQUENCY SPECTRUM

 $S_{inc}(\vec{k},\omega)$ is related to the frequency spectrum of the velocity autocorrelation function (see Eq. (63)). A measurement of the former can, in principle, determine the latter. Let us define [3] two frequency spectra related to the real and imaginary parts of the velocity autocorrelation function

$$\operatorname{Im}\left\langle \vec{v}(0) \cdot \vec{v}(t) \right\rangle = \frac{3\hbar}{2M} \int_{0}^{\infty} \omega f(\omega) \sin(\omega t) d\omega$$
 (55)

and

$$\operatorname{Re}\left\langle \vec{v}(0) \cdot \vec{v}(t) \right\rangle = \frac{3k_{B}T}{M} \int g(\omega) \cos(\omega t) \, d\omega$$
(56)

Using the fluctuation-dissipation theorem (48) it follows that

$$g(\omega) = \left(\frac{\hbar\omega\beta}{2}\right) \operatorname{coth}\left(\frac{\hbar\beta\omega}{2}\right) f(\omega)$$
(57)

Integrating (55) with respect to t, one can show that [3]

$$\int_{0}^{\infty} f(\omega) d\omega = 1$$
 (58)

 $f(\omega)$ is, therefore, normalized.

Taking the inverse Fourier transform of (56), we have

$$g(\omega) = \frac{2M}{3\pi k_{B}T} \int_{0}^{\infty} \operatorname{Re}\left\langle \vec{v}(0) \cdot \vec{v}(t) \right\rangle \cos(\omega t) dt$$

which on using (57) becomes

$$f(\omega) = \frac{4M}{3\pi\hbar} \tanh\left(\frac{\hbar\beta\omega}{2}\right) \frac{1}{\omega} \int_{0}^{\infty} \operatorname{Re}\left\langle \vec{v}(0) \cdot \vec{v}(t) \right\rangle \cos\left(\omega t\right) dt$$
(59)

This relation is exact. In the classical case the above equation reduces to

$$f(\omega) = \frac{2M}{3\pi k_B T} \int_0^{\infty} \langle \vec{v}(0) \cdot \vec{v}(t) \rangle_{cl} \cos(\omega t) dt$$
(60)

The diffusion coefficient D is given by

$$D = \frac{1}{3} \int_{0}^{\infty} \langle \vec{v}(0) \cdot \vec{v}(t) \rangle_{cl} dt$$
(61)

It follows that

$$f(0) = \frac{2MD}{\pi k_{p}T}$$
(62)

Also one can easily show that

$$\lim_{\kappa \to 0} \frac{\omega^2}{\kappa^2} S_{inc}(\vec{\kappa}, \omega) = \frac{\hbar}{4M} \omega f(\omega) \left[1 + \coth\left(\frac{\hbar\omega}{2k_BT}\right) \right]$$
(63)

The above relation is exact. In principle, using (63) one can determine $f(\omega)$ if one knows $S_{inc}(\vec{\kappa}, \omega)$ for very small values of $\vec{\kappa}$. In practice, this procedure has not proved very successful.

If we assume that the motion of an atom in a liquid is governed by the Langevin equation, then the velocity autocorrelation function is an exponential. This leads to a frequency spectrum which is Lorentzian. From the available experimental data, although not very reliable, it is certain that $f(\omega)$ does not have a Lorentzian shape. Computer experiments of Rahman [8] for liquid argon have given detailed information about the behaviour of $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ and hence of $f(\omega)$. The former (open circles) is shown in Fig. 1. From an inspection of Fig. 1 it is clear that $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ is far from being an exponential function. Its characteristic feature is that it drops sharply to zero in a time of the order of 3×10^{-13} sec and then remains negative until it finally goes to zero. There does not seem to be an indication of damped oscillations in this function for the case of liquid argon, but oscillations might very well exist for liquid metals. The frequency spectrum (dashed curve) obtained from this velocity autocorrelation function is shown in Fig. 2 and has a broad peak.

The behaviour of $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle$, suggests that the motion of an atom in a liquid consists of a diffusive component and a vibratory component. Models which take into account these two kinds of motions have been proposed. Certain parameters are introduced in these models in a rather ad hoc manner and cannot, therefore, easily be related to microscopic quantities.

6. MEMORY FUNCTION

Let us define a normalized velocity autocorrelation function $\phi(t)$ by

$$\phi(\mathbf{t}) = \langle \vec{\mathbf{v}}(0) \cdot \vec{\mathbf{v}}(\mathbf{t}) \rangle / \langle \mathbf{v}^2 \rangle \tag{64}$$



FIG. 1. Velocity autocorrelation in liquid argon at 85.5 °K. Curve A: $(\omega_{av}^{3} = 50 \times 10^{24} \text{ sec}^{-2}, D = 1.88 \times 10^{-5} \text{ cm}^{3} \text{ sec}^{-1}$. Curve B: $(\omega_{av}^{2} = 45 \times 10^{24} \text{ sec}^{-2}, D = 1.88 \times 10^{-5} \text{ cm} \text{ sec}^{-1}$. The circles are from B.R. A. Nijboer and A. Rahman, (Physica 32 (1966) 415).



FIG. 2. Calculated frequency spectrum of velocity autocorrelation in liquid argon at 85.5°K. Curves A and B: data as in Fig. 1. Curve C: $(\omega^2)_{av} = 50 \times 10^{24} \sec^{-2}$, $D = 2.07 \times 10^{-5} \text{ cm}^2 \sec^{-1}$. The broken curve is from A. Rahman, \mathcal{J} . chem. Phys. <u>45</u> (1966) 2585).

Equation (60) can then be written as

$$f(\omega) = \frac{2}{\pi} \int_{0}^{\infty} \phi(t) \cos(\omega t) dt$$

the inverse transform of which is

$$\phi(t) = \int_{0}^{\infty} f(\omega) \cos(\omega t) d\omega$$
 (65)

ATOMIC MOTIONS

Making a Taylor's series expansion of $\phi(t)$ and remembering that it is an even function of t, we have

$$\phi(t) = \sum_{n=0}^{\infty} \left(\frac{d^{2n} \phi(t)}{dt^{2n}} \right)_{t=0} \frac{t^{2n}}{(2n)!}$$

$$\phi(t) = \sum_{n=0}^{\infty} (-1)^n \frac{\overline{\omega^{2n}}}{(2n)!} t^{2n}$$
(66)

or

where use has been made of (65) and $\overline{\omega^{2n}}$ is defined by

$$\overline{\frac{\omega^{2n}}{\omega^{2n}}} = \int_{0}^{\infty} \omega^{2n} f(\omega) d\omega$$
 (67)

Differentiating (66) once, we have

$$\frac{d\phi(t)}{dt} = \sum_{n=1}^{\infty} (-1)^n \frac{\overline{\omega^{2n}}}{(2n-1)!} t^{2n-1}$$
(68)

Let us write

$$\overline{\omega^{2n}} = \sum_{k=1}^{n} (-1)^{k} \overline{\omega^{2(n-k)}} \alpha^{(2k-2)}$$
(69)

which expresses the 2nth moment as a linear combination of all the lower moments. $\alpha^{(2k-2)}$ are arbitrary numbers. Using the identity

$$\int_{0}^{1} \mathbf{x}^{\beta} (1-\mathbf{x})^{\gamma} d\mathbf{x} = \frac{\beta ! \gamma !}{(\beta + \gamma + 1)!}$$
(70)

it can be shown that (68) can be written as an integro-differential equation

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} - \int_{0}^{t} \Gamma(\tau) \phi(t-\tau) \,\mathrm{d}\tau = 0 \tag{71}$$

In Eq. (69) $\alpha^{(2k)}$ is the 2kth moment of the Fourier transform of $\Gamma(\tau)$. Equation (69) can also be written as

$$\overline{\omega^{2n}} = \sum_{k=1}^{n} (-1)^{k} \overline{\omega^{2(n-k)}} \left(\frac{d^{2k-2}}{dt^{2k-2}} \Gamma(t) \right)_{t=0}$$
(72)

Equations (66) and (71), therefore, provide two equivalent formulations of the problem which are connected by the relationship (69). The advantage

of using Eq. (71) is that it enables one to guess a reasonable functional form for the kernel $\Gamma(t)$ which has the physical meaning of a memory function. The foregoing discussion is due to Singwi and Tosi [9]. A more formal derivation of (71) from statistical-mechanics considerations was given earlier by Zwanzig and Mori and later used by Berne et al.[10] to discuss the velocity autocorrelation function.

The frequency spectrum $f(\omega)$ can also be evaluated directly from the Laplace transform of the kernel $\Gamma(t)$ for imaginary argument. Indeed, by multiplying both sides of Eq. (71) by $\exp(\pm i\omega t)$ and integrating over time we find

$$f(\omega) = -\frac{1}{\pi} \left[\frac{1}{\widehat{\Gamma}(i\omega) + i\omega} + \frac{1}{\widehat{\Gamma}(-i\omega) - i\omega} \right]$$
(73)

where

$$\hat{\Gamma}(\pm i\omega) = \int_{0}^{\infty} \Gamma(t) e^{\pm i\omega t} dt$$
(74)

In particular, one has

$$f(0) = -\frac{2}{\pi} \left[\int_{0}^{\infty} \Gamma(t) dt \right]^{-1}$$
 (75a)

On using (62), (75a) becomes

$$\frac{2\mathrm{MD}}{\pi k_{\mathrm{B}}\mathrm{T}} = -\frac{2}{\pi} \left[\int_{0}^{\infty} \Gamma(t) \, \mathrm{d}t \right]^{-1}$$
(75b)

One sees immediately from Eq. (71) that when $\Gamma(t)$ is a delta function $\phi(t)$ is an exponentially decaying function corresponding to the motion of a particle governed by the Langevin equation. On the other hand, if $\Gamma(t)$ is a constant, $\phi(t)$ is an oscillatory function corresponding to the case of an Einstein oscillator. Thus, the two limiting cases are contained in Eq. (71) for an appropriate choice of the memory function. A simple and reasonable choice for the memory function in a liquid will be a Gaussian form

$$\Gamma(t) = -Ae^{-Bt^2}$$
(76)

We note that the choice of an exponentially decaying memory function is not consistent with the relationship (69), since only the zeroth moment of its Fourier transform exists. However, this form of the kernel may be alright for very large times but then these times do not play any significant role for our present discussion.

For a Gaussian kernel, the frequency spectrum $f(\omega)$ tends to zero at high frequencies as $\omega^2 \exp(-\omega^2/4B)$. On the other hand, for small frequencies it has the form

$$f(\omega) = f(0) \left\{ 1 + \frac{\dot{\omega}^2}{4B} \left[1 - \frac{16}{\pi} \left(\frac{B}{A} - \frac{1}{2} \right)^2 \right] \right\}$$
(77)

 $f(\omega)$ will, therefore, have a positive slope in this limit if the parameters satisfy the condition (see Ref. [9]):

$$0.057 \leq B/A \leq 0.943$$

The parameters A and B can be fixed from experimental data by means of Eq. (69) for n = 1, and from Eq. (75). These give

$$A = \overline{\omega^2}$$
(78)

and

$$\frac{B^2}{A} = \frac{1}{4} \pi^{\frac{3}{2}} f(0)$$
(79)

Now

$$\overline{\omega^2} = \frac{1}{3M} \int g(\vec{\mathbf{r}}) \nabla^2 \phi(\vec{\mathbf{r}}) d\vec{\mathbf{r}}$$
(80)

where g(r) is the pair distribution function, $\phi(r)$ is the interatomic potential, and M is the atomic mass.

7. THEORY OF SELF MOTION

In Fig. 3 the dashed curve shows the memory function $\Gamma(t)$ (rather $\Gamma(t)/\Gamma(0)$) as obtained by Rahman [11] from a numerical solution of Eq. (71) using his computer data for $\phi(t)$ for liquid argon. One notices that $\Gamma(t)$ has two important characteristic features: (a) it drops very sharply from its value at time t = 0 to a value which is smaller by an order of magnitude in a time range of 3×10^{-13} sec, and (b) it has a fairly long tail with a much smaller time dependence. The theory that I am going to outline has been recently worked out by Singwi and Sjölander [12]. This theory is capable of explaining these two characteristic features of $\Gamma(t)$ in terms of g(r) and $\phi(r)$. In this sense, it is what may be called a first-principle theory. Since the theory is somewhat involved, I will only attempt to sketch its outlines without going into too many mathematical details. The interested reader should refer to the original paper.

The basic physical idea underlying the theory can be briefly summarized as follows: we focus our attention on an atom marked "blue" and having a velocity $\vec{v}_0(t)$ and ask how the surroundings will respond to the motion of this marked atom. The change in the density of the surroundings arising from the motion of the "blue" atom is calculated from a simplified Liouville equation. Knowing the change in the density enables us to calculate the force on the "blue" atom from the surroundings and hence enables us to write its equation of motion. From this equation of motion we finally obtain an integro-differential equation of the type (71) for the velocity autocorrelation function.

The one-particle distribution function $f_1(\vec{x}, \vec{p}, t)$ of the surrounding medium is governed by the equation

$$\frac{\partial f_1(1)}{\partial t} + \vec{v} \cdot \vec{\nabla}_x f_1(1) - \vec{\nabla} V(\vec{x} - \vec{x}_0(t)) \cdot \vec{\nabla}_p f(1) - \int \vec{\nabla} V(\vec{x}, \vec{x}') \cdot \vec{\nabla} f_2(1, 1') d(1') = 0 \quad (81)$$



FIG. 3. Ratio $\exp(t/\tau) \Gamma_0(t)/\Gamma_0(0)$ versus time and versus the parameter $\zeta = a(t)/\Delta_0$. The solid curve represents the calculations of Singwi and Sjölander for $\tau = \infty$, and the corresponding dotted curve is for $\tau = 1.0 \times 10^{-12}$ sec. The dashed curve represents Rahman's machine computations of the memory function for liquid argon at T = 85.9 °K.

where "1" is here an abbreviated notation for (\vec{x}, \vec{p}, t) and $\vec{\nabla}_x$ and $\vec{\nabla}_p$ stand for gradients with respect to \vec{x} and \vec{p} , respectively. $\vec{x}_0(t)$ denotes the position of the "blue" atom. $V(\vec{x})$ is the interaction potential between the atoms. The third term in the above equation is due to the influence of the "blue" atom. The last term takes into account all interactions between the surrounding atoms and contains the two-particle distribution function $f_2(1, 1')$. Writing

$$f_1(1) = f_1^0(1) + \overline{f_1}(1)$$
 (82)

and

$$f_2(1, 1') = f_2^0(1, 1') + \overline{f}_2(1, 1')$$
(83)

where $f_1^0(1)$ and $f_2^0(1, 1')$ are the equilibrium distribution functions around the "blue" particle at $\vec{x}_0(t)$. $\vec{f}_1(1)$ and $\vec{f}_2(1, 1')$ refer to corresponding deviations from equilibrium. $f_1^0(1)$ is further given by

$$f_{1}^{0}(1) = f_{1}^{0}(\vec{p}) g(\vec{x} - \vec{x}_{0}(t))$$
 (84)

where

$$f^{0}(\vec{p}) = \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{\beta p^{2}}{2m}}$$

 $\beta = 1/k_B T$; $g(\vec{x} - \vec{x}_0(t))$ is the static equilibrium pair distribution function around the marked atom. Note that the function g depends here on time.

Substituting (82) and (83) into (81) and remembering the equilibrium equation, we have

$$\frac{\partial \bar{f}_{1}(1)}{\partial t} + \vec{v} \cdot \vec{\nabla}_{x} \bar{f}_{1}(1) - \vec{\nabla}_{x} V(\vec{x}, \vec{x}_{0}(t)) \cdot \vec{\nabla}_{p} \bar{f}_{1}(1) - \int \vec{\nabla}_{x} V(\vec{x} - \vec{x}') \cdot \vec{\nabla}_{p} \bar{f}_{2}(1, 1') d(1) = -\frac{\partial f_{1}^{0}(1)}{\partial t}$$
(85a)

where

$$\frac{\partial f_1^0(1)}{\partial t} = -f^0(\vec{p}) \vec{\nabla} g(\vec{x} - \vec{x}_0(t)) \cdot \vec{v}_0(t)$$
(85b)

Here the major complication arises from the last term on the left-hand side of Eq. (85a). It is responsible for the following physical effects:

- (i) The bare interaction between the particles will be normalized to some effective interaction.
- (ii) The free-particle flow term represented by the second term in (85a) will be modified so as to take into account the erratic Brownian type of motion.
- (iii) The surroundings will have a tendency to reach thermal equilibrium around the "blue" atom.

In order to illustrate the point of view we are going to adopt in our discussion, we shall consider the following special case of Eq. (85a):

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla}_{x} + \frac{1}{\tau}\right) \vec{f}_{1}(1) = f^{0}(p) \vec{\nabla}g(\vec{x} - \vec{x}_{0}(t)) \cdot \vec{v}_{0}(t)$$
(86)

where τ is some appropriate relaxation time for the medium. In this way, we have incorporated the effects mentioned under (iii), but have disregarded (i) and (ii). The above linear equation can easily be solved by going over to the Fourier transforms. The solution is

$$\overline{f}_{1}(\vec{x},\vec{p},t) = \int_{0}^{t} dt' \int d\vec{x}' \left\{ \int \frac{d\vec{q}}{(2\pi)^{3}} e^{iq \cdot (\vec{x} \cdot \vec{x}') - i\vec{v} \cdot \vec{q}(t \cdot t')} \right\}$$

$$\times e^{\frac{t \cdot t'}{\tau}} f^{0}(p) \ \nabla g(\vec{x}' - \vec{x}_{0}(t')) \cdot \vec{v}_{0}(t')$$
(87)

The change in density is obtained by integrating (87) over the momenta. We thus obtain

$$\overline{\rho}_{1}(\vec{x},t) = \int_{0}^{t} dt^{1} \int d\vec{x}^{1} e^{\frac{t-t^{2}}{\tau}} G_{s}^{0}(\vec{x}-\vec{x}^{1}, t-t^{1}) \nabla g(\vec{x}'-\vec{x}_{0}(t^{1})) \cdot \vec{v}_{0}(t^{1})$$
(88)

where

$$G_{s}^{0}(\vec{x},t) = (\pi a(t))^{-\frac{3}{2}} e^{-\frac{x^{2}}{a(t)}}$$
 (89)

and

$$a(t) = \left(\frac{2k_B T}{m}\right) t^2$$

 $G_s^0(\vec{x}, t)$ is the classical form of the Van Hove self-correlation function for a freely moving particle. In a real physical situation the particle does not move as a free particle but performs a complicated Browniantype motion. One should, therefore, in Eq. (88) replace the free particle "propagator" G_s^0 by the appropriate "propagator" $G_s(\vec{x}t, \vec{x}'t' | \vec{x}_0(t))$. This function gives the probability of finding an atom at \vec{x} at time t, if it was located at \vec{x}' at time t' with due consideration of the presence of the "blue" atom. In this respect, it differs from the proper Van Hove selfcorrelation form. We, therefore, instead of Eq. (88) write

$$\bar{\rho}_{1}(\vec{x},t) = \int_{0}^{t} dt^{\dagger} \int d\vec{x}^{\dagger} e^{-\frac{t-t^{\prime}}{\tau}} G_{s}(\vec{x}t, \vec{x}^{\dagger}t^{\dagger} \mid \vec{x}_{0}) \vec{\nabla}g(\vec{x}^{\dagger} - \vec{x}_{0}(t^{\dagger})) \cdot \vec{v}_{0}(t^{\dagger})$$
(90)

In this way, we have taken care in an approximate way of all the effects mentioned under (i), (ii) and (iii). The time τ represents the average time it takes for the surrounding medium to establish complete thermal equilibrium.

The equation of motion for the "blue" atom is then

$$m \frac{d\vec{v}_0(t)}{dt} = -\int d\vec{x} \vec{\nabla} V(\vec{x}_0(t) - \vec{x}) \ \vec{\rho}_1(\vec{x}, t) + a \ fluctuating \ term \qquad (91)$$

In the above equation we have not specified the form of the fluctuating force term. This term arises from fluctuations in the density of the surrounding medium. We shall assume these fluctuations not to depend significantly on the velocity of the "blue" atom. In this case the fluctuating force will be statistically independent of the velocity and, therefore, disappear in the equation for the velocity autocorrelation function. It should be noted that $V(\vec{x}_0(t)-\vec{x})$ in (91) is the bare potential and not any renormalized interaction potential.

Substituting (90) into (91), multiplying both sides by $\vec{v}_0(0)$ and taking the statistical average, we have

$$m \frac{d}{dt} \langle \vec{\mathbf{v}}(t) \cdot \vec{\mathbf{v}}(0) \rangle = -\sum_{\alpha \beta} \int_{0}^{t} dt^{\mathbf{i}} e^{-\frac{t-t^{\mathbf{i}}}{\tau}}$$

$$\times \int d\vec{\mathbf{x}} d\vec{\mathbf{x}} \cdot \langle \nabla_{\alpha} \mathbf{V}(\vec{\mathbf{x}}_{0}(t) - \vec{\mathbf{x}}) \mathbf{G}_{s}(\vec{\mathbf{x}}t, \vec{\mathbf{x}} \cdot t^{\mathbf{i}} \mid \vec{\mathbf{x}}_{0}) \nabla_{\beta} \mathbf{g}(\vec{\mathbf{x}} \cdot - \vec{\mathbf{x}}_{0}(t^{\mathbf{i}})) \mathbf{v}_{\beta}(t^{\mathbf{i}}) \mathbf{v}_{\alpha}(0) \rangle (92)$$

where we have omitted the suffix zero on v. The bracket $\langle \dots \rangle$ denotes the thermal average. α and β each denote the three cartesian components.

 $G_s(\vec{x} t, \vec{x} t' t' | \vec{x}_0)$ depends on the history of $\vec{x}_0(t)$. However, the most dominant effect arising from the presence of the "blue" atom is that a surrounding atom is excluded from a small region around the position $\vec{x}_0(t)$ at time t. We shall average $G_s(\vec{x} t, \vec{x} t' t' | \vec{x}_0)$ over all the paths of the "blue" atom which terminate at $\vec{x}_0(t)$ at time t, and we substitute the so-obtained "propagator" for the one introduced earlier. This averaged "propagator" will be denoted by $\overline{G}_s(\vec{x} t, \vec{x} t' t' | \vec{x}_0(t))$. We further define

an effective potential through the relation

$$\nabla \overline{V}(\vec{x}_{0}(t) - \vec{x}', t - t') = \int \nabla V(\vec{x}_{0}(t) - \vec{x}) \overline{G}_{s}(\vec{x}t, \vec{x}'t' \mid \vec{x}_{0}(t)) d\vec{x}$$
(93)

Using (93) in (92) we have

$$m \frac{d}{dt} \langle \vec{v}(t) \cdot \vec{v}(0) \rangle = -\sum_{\alpha \beta} \int_{0}^{t} dt' e^{\frac{t-t'}{\tau}} \int d\vec{x}' \langle \nabla_{\alpha} \overline{V}(\vec{x}_{0}(t) - \vec{x}', t-t') \rangle$$

$$\times \nabla_{\beta} g(\vec{x}' - \vec{x}_{0}(t')) v_{\beta}(t') v_{\alpha}(0) \rangle$$
(94)

In the Gaussian approximation, as discussed in section 4, it can be shown (Ref. [12]) that Eq. (94) can be written as

$$\frac{d\phi(t)}{dt} + \int_{0}^{t} \Gamma_{0}(t-t^{*}) \phi(t^{*}) + \int_{0}^{t} \Gamma_{1}(t-t^{*}) dt^{*} \int_{t^{*}}^{t} \phi(\tau) d\tau = 0$$
(95)

where

$$\Gamma_{0}(t) = \left[-\frac{1}{3m} \int \vec{\nabla} g(\vec{x}) \cdot \vec{\nabla} \vec{\nabla} (\vec{x} - \vec{x'}, t) G_{s}(\vec{x'}, t) d\vec{x} d\vec{x} \right] e^{-\frac{t}{\tau}}$$
(96)

and

$$\Gamma_{1}(t) = \left[-\frac{1}{3m} \int \vec{\nabla} g(\vec{x}) \cdot \vec{\nabla} \, \vec{\nabla} (\vec{x}, \vec{x}', t)' \frac{\partial}{\partial t} \, G_{s}(\vec{x}', t) \, \right] e^{-\frac{t}{\tau}} \tag{97}$$

 $G_{s}(\vec{x}, t)$ is the Van Hove self-correlation function given by

$$G_{s}(\vec{x}, t) = (\pi a(t))^{-\frac{3}{2}} e^{-\frac{\vec{x}^{2}}{a(t)}}$$
 (98)

and

$$\mathbf{a}(\mathbf{t}) = \frac{4}{3} \int_{0}^{\mathbf{t}} (\mathbf{t} \cdot \mathbf{u}) \langle \vec{\mathbf{v}}(\mathbf{0}) \cdot \vec{\mathbf{v}}(\mathbf{u}) \rangle d\mathbf{u}$$
(99)

Equation (95) is our basic equation. It is clear from an inspection of the above equations that (95) is a very complicated non-linear integral equation and can only be solved numerically. Compare (95) with (71). In general, Eq. (95) cannot be written in the form of Eq. (71) unless the term containing $\Gamma_1(t)$ is negligible. It turns out that this term is small but not insignificant. A detailed numerical integration of Eq. (95) has been undertaken by the Swedish group [13]. An approximate evaluation of $\Gamma_0(t)$ has been made by Singwi and Sjölander [12] on the basis of our earlier knowledge of a(t) and noting the fact that the detailed form of $\phi(t)$ will have a small influence on the integrated value in a(t).

To calculate the memory function $\Gamma_0(t)$ we should have a knowledge of the function $\overline{G}_{\varepsilon}(\vec{x}t, \vec{x}', t'|\vec{x}_0)$. This probability function is obviously zero

for $|\vec{x} \cdot \vec{x}_0| < \sigma, \sigma$ being the radius of the hard core of the interatomic potential. We may write

$$\overline{G}_{s}(\vec{x}+\vec{y},t;\vec{x},0\mid\vec{x}_{0}) = \frac{\alpha(\vec{x}+\vec{y}-\vec{x}_{0}) G_{s}(\vec{y},t)}{\int \alpha(\vec{x}+\vec{y}'\cdot\vec{x}_{0}) G_{s}(y',t) d\vec{y}'}$$
(100)

The normalization condition

$$\int \overline{G}_{s}(\vec{x} + \vec{y}, t; \vec{x}, 0 | \vec{x}_{0}) d\vec{y} = 1$$

is automatically fulfilled. The function $\alpha(\vec{x} \cdot \vec{x}_0)$ is such that it drops sharply to zero for $|\vec{x} \cdot \vec{x}_0| < \sigma$ and is of order of unity for $|\vec{x} \cdot \vec{x}_0| > \sigma$. Its precise form is not known to us. It plays the role of excluding a certain volume corresponding to the hard-core radius around \vec{x}_0 . The interatomic potential V(x) is taken as the 6-12 Lennard-Jones potential. For mathematical reasons and also in order to get a better physical insight, V(x) has been divided into a hard-core part V_c(x) and a soft attractive part V_s(x); the latter is shown in Fig. 4. V_c(x) is given by the difference V(x) - V_s(x); V_s(x) has again been chosen as a Gaussian for mathematical reasons. Contributions of V_c(x) and V_s(x) to Γ_0 (t) have been studied separately.

For t = 0, since $\overline{G}_{s}(\vec{x}t; \vec{x}'0 | \vec{x}_{0}) = \delta(\vec{x} - \vec{x}')$ and $G_{s}(\vec{x}, t) = \delta(\vec{x})$, it follows from (93) that

$$\overline{V}(x) = V(x)$$

and from (96)

$$\Gamma_{0}(0) = -\frac{1}{3m} \int \nabla V(\mathbf{x}) \cdot \nabla g(\mathbf{x}) \, d\vec{\mathbf{x}}$$
(101)

which is the expression for the second moment (Eq.80). Remembering the fact that a(t) appearing in Eq. (97) varies as t^2 for small times, one concludes that $\Gamma_1(0) = 0$.

One can easily convince oneself that the form of the function $\alpha(y)$ is unimportant as far as the contribution of the soft attractive part of the potential to $\Gamma_0(t)$ is concerned. On the other hand, it plays a vital role as far as the contribution of the hard-core part is concerned. What enters into the expressions is the function $V_c^t(y) \alpha(y)$, $V_c^t(y)$ being the derivative of $V_c(y)$. This function has an extremely sharp peak at $y = \sigma_0 \simeq \sigma$ with half width $\sqrt{\Delta}$. We shall choose the following form:

$$V_{c}^{\bullet}(y) \alpha(y) = -c(\pi \Delta)^{-\frac{1}{2}} e^{-\frac{(y-o_{0})^{2}}{\Delta}}$$
 (102)

c denotes the area under the peak. We have two unknowns c and Δ in (102) which are related to $\Gamma_0^c(0)$. $\Gamma_0^c(0)$ is the contribution of the hard core to the second moment (Eq. 101) and which can be calculated if V (x) and g(x) are known. In this theory, therefore, Δ is left undetermined and occurs as a parameter. The other parameter is the relaxation time τ . The quantity of interest which enters into the calculation of the memory function is the function g'(x) which we know and is shown in Fig. 5. The first two



FIG. 4. Lennard-Jones potential (in units of $\epsilon = 120 \text{ k}_{\text{B}}$) and the pair correlation function g(t) (based on Rahman's computations for liquid argon at $T = 85.9^{\circ}\text{K}$) versus distance (in units of $\sigma = 3.817 \text{ Å}$). The dashed curve represents the assumed Gaussian form for the "soft part" of the potential.

peaks of g'(x) one of which is positive and the other negative play an important role. In the present calculations these two peaks have been approximated for mathematical reasons by two Gaussian functions with half widths $\sqrt{\Delta}_0$ and $\sqrt{\Delta}_1$.

In Fig. 3 the solid curve denotes the calculated value of $\exp(t/\tau) / \Gamma_0(t) / \Gamma_0(0)$ for $\Delta/\Delta_0 = 0.5$ and $\tau = \infty$. For $\Delta/\Delta_0 = 0.7$ and $\tau = \infty$, our calculations gave a nearly perfect fit with Rahman's curve (dashed) for $t \leq 10^{-13}$ s, but it gave an appreciable increase over Rahman's value in the height of the tail. On the other hand, for $\Delta/\Delta_0 < 0.5$ the height of the tail becomes less but instead the peak for small times becomes narrower. Now it is unreasonable to expect $\tau = \infty$. For illustration, we have also plotted in the same figure (dotted curve) the results obtained for $\tau = 10^{-12}$ s, which is a reasonable value to assume for the relaxation time. The diffusion coefficient of a liquid in terms of $\Gamma_0(t)$ is given by

$$D = \frac{\frac{k_{B}T}{M}}{\int_{0}^{\infty} \Gamma_{0}(t) dt}$$

which using our calculated $\Gamma_0(t)$ (corresponding to $\Delta/\Delta_0 = 0.5$) for $\tau = 10^{-12}$ s, gave $D = 2.2 \times 10^{-5}$ cm²/s, whereas the value of D obtained from Rahman's $\Gamma_0(t)$ is 2.10×10^{-5} cm²/s. The correction term $\Gamma_1(t)$ was estimated by us to contribute less than 20%.

It is worth noting that in the present theory the width of the rapidly falling part of $\Gamma_0(t)$ is determined by the half width $\sqrt{\Delta}$ of the function $V_c^{\dagger}(x) \alpha(x)$, whereas the width of the tail is essentially governed by the relaxation time τ . The value of $\Gamma_0(0)$ is determined precisely by the static pair correlation function and the interatomic potential. The shape of $\Gamma_0(t)$ depends on the detailed shape of the main peak of g(x). The dependence of $\Gamma_0(t)$ on time is neither an exponential nor a Gaussian but a rather complicated function. The time expansion of $\Gamma_0(t)$ is valid as long as $a(t) < \Delta$, i.e. for $t \le 4 \times 10^{-14}$ s. This smallness of the radius of convergence is responsible for the failure of some of the recent attempts towards time expansion of the velocity autocorrelation function.

The theory which I have briefly outlined makes it possible to understand the main features of the memory function and hence of the velocity autocorrelation function in terms of the static pair correlation function and the interatomic potential. The question of what the predictions of the theory are for liquid metals is now under investigation.



FIG.5. The derivative of g'(r) versus r (in units of $\sigma = 3.817$ Å). The solid curve is based on Rahman's numerical computations for liquid argon at 85.9°K. The dashed curve represents a Gaussian approximation used in the calculations of Singwi and Sjölander.

ATOMIC MOTIONS

Assuming that the hard-core part of the potential is more or less the same in liquid metals as that for liquid argon, one would expect the short-time behaviour of the memory function to be the same in the two cases. In liquid metals, on the other hand, the remaining part of the potential is long-range and has an "oscillatory" character; one should, therefore, expect a different behaviour in the intermediate and long-time region of Γ_0 (t) from that of liquid argon. All this needs to be shown quantitatively. Assuming for the moment that the predictions of the theory are correct, the interatomic potential derived from the use of, say, the Percus-Yevick equation with a previous knowledge of g(x) should also give a right dynamical behaviour.

8. COHERENT SCATTERING

That collective modes corresponding to sound waves (low ω and q values) exist in a liquid has long been known through the Brillouin scattering of light. These long wavelength density fluctuations are governed by the Navier-Stokes equations. In this hydrodynamic limit $S_{coll}(\vec{\kappa}, \omega)$ is given by (see Ref. [14]):

$$S_{coh}(\vec{\kappa},\omega) = \bar{\rho} k_B T \chi_s \frac{1}{\pi} \frac{\Gamma_s^2 C^2 \kappa^4}{(\omega^2 - C^2 \kappa^2)^2 + (\Gamma_s \omega \kappa^2)^2}$$
(103)

where χ_s is the adiabatic compressibility, $C = (M\bar{\rho}\chi_s)^{\frac{1}{2}}$ is the sound velocity and $\Gamma_s = (\zeta + \frac{4}{3}\eta/M\bar{\rho})$, where η and ζ are the coefficients of viscosity. It is evident from (103) that the structure of $S_{coh}(\vec{\kappa}, \omega)$ consists of two Lorentzian peaks centered at $\omega = \pm c\kappa$ with a width determined by the coefficients of viscosity. From (103) we have

$$F(\vec{\kappa}, 0) = \int S_{coh}(\vec{\kappa}, \omega) d\omega$$

= $\bar{\rho} k_{B} T \chi_{s}$, (104)

whereas the exact value of $F(\vec{\kappa}, 0)$ is

$$F(\vec{k}, 0) = 1 + \Gamma(\kappa)$$

= $\bar{\rho}k_{B}T \chi_{T}$ for $\kappa \rightarrow 0$ (105)

where χ_T is the isothermal compressibility. The two results given by (104) and (105) are different. This discrepancy arises from the fact that in writing (103) we have neglected the non-propagating entropy fluctuations which are governed by the equation of heat diffusion. The correct expression for $S_{coh}(\vec{\kappa}, \omega)$ is obtained by adding the following term to Eq. (103):

$$\bar{\rho} \mathbf{k}_{\mathrm{B}} \mathbf{T} \mathbf{\chi}_{\mathrm{s}} \left(\frac{\mathbf{c}_{\mathrm{p}}}{\mathbf{c}_{\mathrm{v}}} - 1 \right) \left\{ \frac{1}{\pi} \frac{\mathbf{D}_{\mathrm{T}} \kappa^{2}}{\omega^{2} + (\kappa^{2} \mathbf{D}_{\mathrm{T}})^{2}} - \frac{1}{\pi} \frac{\mathbf{D}_{\mathrm{T}} \kappa^{2} (\omega^{2} - \mathbf{C}^{2} \kappa^{2})}{(\omega^{2} - \mathbf{C}^{2} \kappa^{2})^{2} + (\mathbf{\Gamma} \omega \kappa^{2})^{2}} \right\}$$

and replacing $\Gamma_{\!\!\!\!c}\,$ by $\Gamma_{\!\!\!\!c}\,$ D $_{\!\!\!\!r}$ is the heat diffusion coefficient

$$\Gamma = D_{T} \left(\frac{c_{p}}{c_{v}} - 1 \right) + \left(\zeta + \frac{4}{3} \eta \right) / M\overline{\rho}$$

The next question that arises is: do collective excitations in the large ω and q region, where hydrodynamic considerations do not apply, exist in a classical liquid? Until a few years ago the answer to this question was negative, but recent neutron scattering experiments which indeed measure in the high ω and q region have indicated that such collective modes probably do exist. Such studies have been made for insulators like liquid argon [15] and liquid metals [16-18] such as Na, Pb, Al, and Sn. These studies have shown a striking similarity between the spectra scattered from the solid and the liquid phase.

As an illustration we have shown in Fig.6 the data of Larsson and Dahlborg (see Ref. [1], Larsson's article) on coherently scattered beryllium-filtered neutrons from polycrystalline Al at 630°C and from liquid Al at 677°C. The striking similarity between the two inelastically scattered spectra is quite evident. The sharp cut-off in the intensity on the low frequency side in the solid is the result of the operation of the usual momentum conservation condition

$$\left|2\pi \vec{\tau} - \vec{q}\right| \leqslant \vec{\kappa} \leqslant \left|2\pi \vec{\tau} + \vec{q}\right|$$

where τ is the reciprocal lattice vector. Also, the peak in intensity at $\omega = 2.5 \times 10^{13}$ rad/s is due to transverse modes. This peak continues to persist in the liquid phase. Reasonably well defined peaks due to longitudinal vibrations have been observed by Egelstaff and his co-workers in liquid metals. These peaks do not change their width by more than a factor of two as one goes from the solid to the liquid phase (near the melting point). Observations like these have prompted many workers, in particular Egelstaff [19] and Singwi [20], to use quasi-harmonic solid-like models with minor modifications to interpret the inelastic coherent scattering in liquids. This kind of approach leads one to propose dispersion relations for "quasi-phonons" in classical liquids. These models have had a reasonable success but their theoretical foundation is very shaky.

There exists another set of very beautiful experiments of Woods [21] on collective excitations in He II and He I. His results are shown in Fig. 7. Incident neutrons of wavelength 4.05 Å (energy 5.0 MeV) were used. The second peak marked with an arrow in the figure represents neutrons scattered from liquid He with the excitation of a phonon. The position of the peak denoted by ϵ gives the energy in °K of the phonon and its width is denoted by $\Delta \epsilon$. All the phonons measured have a momentum corresponding to p/h = 0.38 Å⁻¹. The point to note is that these phonon peaks continue to persist even beyond the λ -point (2.17°K) though they are somewhat broader. Above the λ -point liquid He is a classical liquid, probably with some quantum corrections. One notices the broadening of the peak with the increase of temperature. At 4.2°K, which is near the boiling point, the phonon peak is no longer well defined and has moved to the left considerably on the energy scale. This experiment clearly demonstrates that phonons do exist in He I, which is a classical system. The existence of the phonons, therefore, does not necessarily depend on



FIG.6. Coherently scattered neutron spectra scattered from an aluminium polycrystal at 630° C, and a liquid sample at 677° C. The angle of observation in both cases was 60° , while the ingoing spectrum was the full cold neutron spectrum.

the existence of a superfluid phase. What is the nature of these phonons? Are the phonons observed in He I and those "observed" in other classical liquids the same or different? These are still open questions.

9. CONVOLUTION APPROXIMATION

Equation (9a) for the intermediate scattering function $F(\vec{k}, t)$ can be written as

$$F(\vec{\kappa}, t) = F_{s}(\vec{\kappa}, t) + \frac{1}{N} \sum_{i \neq j} \langle e^{-i\vec{\kappa} \cdot \vec{R}_{j}(0)} \rangle$$

$$\approx F_{s}(\vec{\kappa}, t) (1 + \Gamma(\kappa))$$
(106)

In writing (106) we have assumed that the thermal average in the first line can be written as the product of two thermal averages. This approximation was first introduced by Vineyard [22]. This is equivalent to writing

$$G(\vec{r}, t) = G_{s}(\vec{r}, t) + \int g(r') G_{s}(\vec{r} - \vec{r}', t) d\vec{r}'$$
 (107)



FIG. 7. Distributions of neutrons scattered from liquid helium at $p/f_1 = 0.38$ Å⁻¹ at various temperatures (A.D.B. Woods, see Ref.[21]).

as can easily be verified by taking the Fourier transforms of both sides of the equation. The nature of the convolution approximation consists in assuming that the motion of an atom which is at r' at time t=0 from another atom at the origin at time t=0 is independent of the presence of the atom at the origin. Obviously, this is not a good approximation if the two atoms are close together, but may not be too bad if the atoms in question are widely separated from each other.

There are certain objections to the convolution approximation. The first, and the one which is often cited, is that it violates the second moment relation (20). Instead, it gives

$$\overline{(\omega_{\rm coh}^2)}_{\rm con} = \frac{{\bf k}_{\rm B} {\rm T}}{{\rm M}} \kappa^2$$

The second objection is that in the limit $\vec{k} \rightarrow 0$, it predicts an undisplaced Rayleigh line whose width is determined by the macroscopic self-diffusion coefficient, whereas in actual fact one has three lines — the central Rayleigh line corresponding to entropy fluctuations and the two displaced Brillouin components corresponding to density fluctuations. Also, it does not predict the De Gennes narrowing effect of the quasi-elastic scattering discussed earlier from very general sum-rule arguments. The ATOMIC MOTIONS

predictions of this approximation regarding the inelastic coherent scattering are not borne out by experiments. In spite of all these failures, the convolution approximation has the merit of simplicity and of not involving any adjustable parameters which are invariably present in all models. Attempts to improve upon it [20] have been made during recent years with reasonable success.

Very recently Sköld [23] has proposed that Eq. (106) should be modified to

$$F(\vec{\kappa}, t) = (1 + \Gamma(\kappa)) e^{-\kappa^2 \gamma_1(t)/(1 + \Gamma(\kappa))}$$
(108)

This modification, which is ad hoc, implies replacing every κ^2 in $F_s(\vec{\kappa}, t)$ of the convolution approximation by $\kappa^2/1 + \Gamma(\kappa)$. The physical idea behind this modification is that the coherently scattered intensity is composed of scattering from several atoms, $1 + \Gamma(\kappa)$ being the measure of the effective number of atoms which contribute to the intensity. The recoil energy transferred to the system is $\hbar^2 \kappa^2 / [2M(1 + \Gamma(\kappa))]$, i.e. the same as if the recoiling mass was $M(1 + \Gamma(\kappa))$. With formula (108), Sköld was able to explain his measured width of the quasi-elastic scattering as a function of $\vec{\kappa}$ in liquid argon.

Approximation (108) fulfills the second moment but violates the fourth moment. It is also apparent from the structure of the formula that it will not be able to explain the inelastic scattering.

There is another recipe proposed by Rahman [8] called the delayed convolution approximation. It is based on the results of his machine computations for liquid argon and lacks a theoretical basis. According to this recipe $F_{\varsigma}(\vec{k}, t)$ in Eq. (106) should be replaced by $F_{\varsigma}(\vec{k}, t^{\dagger})$, where

$$t' = t - \tau \left[1 - e^{-t/\tau} - \left(\frac{t}{\tau}\right)^2 e^{-t^2/\tau^2} \right]$$

with the delay time $\tau = 1 \times 10^{-12}$ s. This recipe says that the instantaneous geometrical structure of atoms around a given atom does not dissolve as quickly as given by the convolution approximation. There is a finite time lag determined by τ . It is very likely that τ is a function of \vec{k} .

Equation (107) is an approximation for $G(\vec{r},t)$. The exact expression shoud read

$$G(\vec{r}, t) = G_{s}(\vec{r}, t) + \int g(r') H(\vec{r}, \vec{r}', t) d\vec{r}'$$
 (109)

where $H(\vec{r}, \vec{r}', t)$ is the probability that given an atom A at the origin at time zero, an atom B at \vec{r}' at time zero moves to \vec{r} in time t. In the convolution approximation $H(\vec{r}, \vec{r}', t)$ is replaced by $G_s(\vec{r} - \vec{r}', t)$. Now if the atom A has moved to \vec{r}'' in time t, then the atom B is excluded from a sphere of radius σ around \vec{r}'' at this time, σ being the radius of the hard core. In our discussion of the theory of the self-motion in section 7, we introduced a function $\overline{G}_s(\vec{x} + \vec{y}, t; \vec{x}, 0 | \mathbf{x}_0)$ defined by Eq. (100) which has the property of taking into account the effect of exclusion. The form of the function $\alpha(y)$ is given by Eq. (102). It would be interesting to calculate $G(\vec{r}, t)$ from (109) using for the function H the expression for G_s given by Eq. (100). No such attempt has been made so far.

10. QUASI-CRYSTALLINE MODEL

Since there is no theory for coherent scattering which could even remotely be called basic, one is forced to take recourse to models. These phenomenological models are due to Egelstaff [19] and Singwi [20] and are essentially the same although the one due to the latter is more general.

Egelstaff's suggestion is that the usual one-phonon coherent scattering formula valid for a polycrystalline solid should also be applicable to a liquid with the difference that the distribution of the reciprocal lattice vectors, instead of being discrete as in a solid, is continuous in a liquid; the distribution being given by the structure factor $1 + \Gamma(\kappa)$. The phonon wave vectors thus have their origin in a liquid at any point in the reciprocal space. The formula for a liquid then becomes

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\mathrm{coh}} = \overline{b}^2 \frac{\mathrm{k}}{\mathrm{k}_0} e^{\frac{\hbar\omega}{2\mathrm{k}_\mathrm{B}\mathrm{T}}} e^{-\mathrm{a}\kappa^2} \coth\left(\frac{\hbar\omega}{2\mathrm{k}_\mathrm{B}\mathrm{T}}\right) \frac{\hbar\kappa^2}{4\mathrm{M}\omega} f(\omega) Z \tag{110}$$

where

$$Z = \frac{1}{2\kappa q} \int_{\kappa-q}^{\kappa+q} x(1+\Gamma(x)) P_{J}(x, q, \vec{\kappa}) dx$$
(111)

The polarization factor $P_{I}(x, q, \vec{\kappa})$ is

$$P_{L}(x, q, \vec{\kappa}) = (\vec{\kappa} \cdot \vec{a}_{L})^{2} / \kappa^{2}$$
 for longitudinal phonons

and

$$P_{T}(\mathbf{x},\mathbf{q},\vec{\kappa}) = (\vec{\kappa}\cdot\vec{\alpha}_{T})^{2}/\kappa^{2} \text{ for transverse phonons.}$$

 $\vec{\alpha}_{\rm L}$ and $\vec{\alpha}_{\rm T}$ are unit vectors parallel and at right angles, respectively, to the phonon wave vector \vec{q} . It is assumed that the transverse branches are degenerate. The momentum conservation condition is

$$\vec{\kappa} \pm \vec{q} = 2\pi \vec{\tau} \tag{113}$$

(112)

The symbols in the above equation have their usual meaning.

The adoption of formula (110) for a liquid involves some basic assumptions: (a) that the harmonic approximation is valid for a liquid and (b) that the concept of a reciprocal lattice in a disordered structure like a liquid has a meaning. Both of these are far-reaching assumptions whose validity is very questionable. Nonetheless the formula is capable of explaining the observed features in the scattering.

In the approach adopted by Singwi [20], it is assumed that all terms in the intermediate scattering function that contain position vectors of atoms more than a certain distance \vec{R} apart from each other could be treated according to the convolution approximation. Correlated motion of atoms closer to each other than this distance were treated as if the liquid was a quasi-harmonic solid. In this approach one could derive expressions both for the quasi-elastic and inelastic scattering without

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making any explicit assumption of the existence of reciprocal lattice vectors in a liquid. The structure factor $1 + \Gamma(\kappa)$ enters in the formulation in a natural way but there occurs a parameter R which is a measure of short-range order in a liquid. In the limit $R \rightarrow \infty$, Singwi's formula reduces to that of Egelstaff with due care for the polarization factor. For details the reader is referred to the original papers. Using formula (110) it has been possible to derive dispersion relations (ω versus q) for "quasi-phonons" in liquids like argon, lead and tin. These dispersion relations are very much like those expected in a solid after directional averaging. Such dispersion relations are shown in Figs 8 and 9 for liquid lead. Measurements of Randolph and Singwi [16] have been performed in the first "Brillouin zone".



FIG. 8. Frequency-wave-number plot of the peaks in $S_C(Q, \omega)$ for liquid lead. The full line is calculated using the equation $\omega^2(Q) = (N+1)kTQ^2/MS(Q)$. Broken curve, extrapolation of $\omega = cQ$; thick strokes, Cocking and Egelstaff [17].

In a liquid the translational symmetry of a solid is lost, but it appears that the short-range order still persisting in a liquid is sufficient to preserve the collective nature of the excitations. In physics one often comes across such cases.

11. SCATTERING IN LIQUID HELIUM

The existence of quasi-particles (here phonons and rotons) in liquid He II was predicted many years ago by Landau. It is a remarkable example of his great and penetrating intuition. The nature of the dispersion curve for these excitations was explained theoretically by Feynman [24]. His results can be derived in a simple manner from the following sum-rule arguments:

We have for the zeroth and the first moment the relations

$$\int S(\vec{\kappa},\omega) \, d\omega = S(\vec{\kappa}) \tag{114}$$



FIG. 9. Dispersion curve for liquid lead derived from the experiments of Randolf and Singwi (see Ref. 16) and compared with other measurements.

and

$$\int \omega S(\vec{\kappa}, \omega) \, d\omega = \frac{\vec{n}\vec{\kappa}^2}{2M}$$
(115)

Here $S(\kappa)$ stands for $1+\Gamma(\kappa)$. The principle of detailed balance in inversion symmetric system states

 $S(\vec{\kappa}, -\omega) = e^{-\beta\hbar\omega} S(\vec{\kappa}, \omega)$ (116)

(see Eq. (35)). We write $S(\vec{k}, \omega)$ as a sum of two symmetrically broadened distributions g centered about ω_{κ} and ω_{κ} .

$$S(\vec{k}, \omega) = A_{\kappa} [g(\omega - \omega_{\kappa}) + e^{\delta h \omega} g(\omega + \omega_{\kappa})]$$
(117)

where g is normalized to unity and A_{κ} is some weighting factor. Equation (117) is consistent with (116). A_{κ} can be determined using (114) if the width of g is much less than $\kappa_{\rm B}^{-}$ T. The result is

$$A_{\mu} = S(\kappa) \left[1 + e^{-\beta \hbar \omega} \right]^{-1}$$
(118)

From Eqs (115), (117) and (118) we have

$$\omega_{\kappa} \tanh\left(\frac{\hbar\omega_{\kappa}\beta}{2}\right) = \frac{\hbar\kappa^{2}}{2MS(\kappa)}$$
(119)

if the width of g is less than ω_{κ} .

In the low temperature limit, i.e. $\beta \hbar \omega \gg 1$, Eq. (119) reduces to the well-known relation

$$\omega_{\kappa} = \frac{\hbar \kappa^2}{2 M S(\kappa)}$$
(120)

first derived by Feynman [24]; whereas in the limit $\beta \hbar \omega_{\kappa} \ll 1$ we arrive at

$$\omega_{\kappa} = \left(\frac{\mathbf{k}_{\mathrm{B}} \mathbf{T}}{\mathrm{MS}(\kappa)}\right)^{\frac{1}{2}} \kappa \tag{121}$$

The basic assumption leading to Eqs (120) and (121) consists in writing for $S(\vec{\kappa}, \omega)$ the expression (117). It amounts to saying that at any finite temperature $S(\vec{\kappa}, \omega)$ consists of only two peaks. This certainly is not true for large values of \vec{k} when we have multiple excitations present. For a classical liquid we have further neglected the diffusive part of $S(\vec{k}, \omega)$. It is, therefore, understood that the dispersion relation given by (121) can, if at all, only be approximately correct for a classical liquid. Egelstaff has found that the observed dispersion curve for liquid lead (see Fig. 7) can be fitted with formula (121) with a multiplying factor of nearly two on the right-hand side. The important point to notice in formula (121) is the occurrence of the structure factor $S(\vec{\kappa})$ in the denominator. The minimum in the dispersion curve occurs where $S(\vec{k})$ has its maximum value. In the range of $\vec{\kappa}$ -values over which a fit is obtained. $S(\vec{\kappa})$ varies by as much as a factor of ten. The striking similarity between the dispersion curves in He II and classical liquid lead cannot escape one's notice. There appears to be a very intimate connection between $S(\mathcal{R})$ and the energy of an excitation in a liquid.

12. ZERO SOUND IN LIQUID ⁴HeI

It has been suggested by Pines [25] that the phonons observed by Woods [21] in He I are an analogue of Landau's zero sound for Fermi liquids. They correspond to the collisionless régime for which

$$ω_{_{\rm σ}} \tau \gg 1$$

where ω_q is the phonon energy and τ is a certain mean collision time. Plasmon in an electron liquid is an example of such an excitation. In the long-wavelength limit the plasmon frequency

$$\omega_{\rm p} = \left(\frac{4\pi\,{\rm ne}^2}{{\rm m}}\right)^{\frac{1}{2}}$$

remains unaffected by the transition from the normal to the superconducting state. For such collective modes we know that the restoring force is the

averaged self-consistent field of all the particles acting in concert. For an electron liquid the restoring force responsible for plasma oscillations is the polarization potential ϕ_{nol}^{-} defined by

$$\vec{\phi}_{pol}(\vec{q},\omega) = \frac{4\pi e^2}{q^2} \langle \rho^{-}(\vec{q},\omega) \rangle$$
(122)

where $\langle \rho^{-}(\vec{q}, \omega) \rangle$ is the Fourier transform of the average charge density fluctuation. For a neutral system, we can likewise define a polarization potential

$$\phi_{\text{pol}}(\vec{q}, \omega) = f_0 \langle \rho(\vec{q}, \omega) \rangle$$
(123)

where f_0 is a phenomenological constant. A local relationship of the type (123) between ϕ_{nol} and $\langle \rho \rangle$ will be valid only if

 $qr_0 \ll 1$,

 \mathbf{r}_0 being the interparticle distance. For larger values of q, \mathbf{f}_0 will be q-dependent.

In analogy to the electron liquid one can define two density response functions

$$\langle \rho(\vec{\mathbf{q}},\omega) \rangle = \chi(\vec{\mathbf{q}},\omega) \phi(\vec{\mathbf{q}},\omega)$$
 (124)

and

$$\langle \rho(\vec{\mathbf{q}}, \omega) \rangle = \chi_{sc}(\vec{\mathbf{q}}, \omega) \left\{ \phi(\vec{\mathbf{q}}, \omega) + \phi_{pol}(\vec{\mathbf{q}}, \omega) \right\}$$
 (125)

where $\chi(\vec{q}, \omega)$ measures the density fluctuations induced by an external scaler potential $\phi(\vec{q}, \omega)$ and $\chi_{sc}(\vec{q}, \omega)$ measures the same but induced jointly by ϕ and ϕ_{pol} . From Eqs. (123), (124) and (125) we have

$$\chi(\vec{q}, \omega) = \frac{\chi_{sc}(\vec{q}, \omega)}{1 - f_0 \chi_{sc}(\vec{q}, \omega)}$$
(126)

We now make use of the f-sum rule according to which

$$\lim_{\omega \to \infty} \chi(\vec{q}, \omega) = \lim_{\omega \to \infty} \chi_{sc}(\vec{q}, \omega) = \frac{nq^2}{m\omega^2}$$
(127)

This sum rule follows from Eq. (37). $\chi_{sc}(\mathbf{\bar{q}},\omega)$ will attain its asymptotic value given by (127) as soon as ω is large compared to any of the characteristic frequencies which appear in its spectral representation. We denote such frequencies by ω_{sc} . We therefore have

$$\chi(\vec{q}, \omega) = \frac{nq^2/m}{(\omega + i\eta)^2 - f_0 \frac{nq^2}{m}} \quad \text{for } \omega > \omega_{sc}$$
(128)

where we have introduced $\eta = 0^+$ to allow for the fact that $\chi(\vec{q}, \omega)$ is analytic in the upper half of the complex ω -plane. It follows from (128) that

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 $\chi(\vec{q},\omega)$ has a pole corresponding to a phonon-like collective mode of frequency

$$\omega_{\mathbf{q}} = \mathbf{s}_{\mathbf{0}} \mathbf{q} \tag{129}$$

where

 $s_0 = \left(\frac{nf_0}{m}\right)^{\frac{1}{2}}$ (130)

The existence of a sharp zero sound peak depends on the condition $\omega_{\rm q}>\omega_{\rm sc}$. For a degenerate Fermi liquid we have for the existence of zero sound the condition

 $s_0 > v_{r}$

or

$$\frac{\mathrm{nf}_{0}}{\mathrm{mv}_{\mathrm{F}}^{2}} > 1 \tag{131}$$

The dispersion relation according to (129) is linear in q, but as q increases such that $qr_0 \gtrsim 1$, f_0 will become a function of q. In He II this value of q is nearly 0.6 Å⁻¹ as revealed by Woods' experiments.

As the temperature increases the number of thermally excited quasiparticles increases and there is a broadening of quasiparticle spectrum due to collisions between quasiparticles. Multi-pair excitations start playing an important role. In this circumstance, Landau theory is not applicable. But if f_0 is large enough, high-frequency sound might continue to exist as a reasonably well defined mode even for $k_BT \gtrsim E_F$, E_F being the Fermi energy – the criterion $\omega_q \tau \ge 1$ needs to be satisfied only. In the high-temperature limit there is no difference between ⁴He and ³He since the statistics now does not matter. One might expect that f_0 in ⁴He is of the same order as in ³He. If that be the case, one could reasonably expect the zero sound mode in ⁴HeI, too. On the basis of such arguments one arrives at the conclusion that the zero sound mode will be less broad if Woods' experiment were to be carried out at a higher value of q and, therefore, of ω .

Notice that Eq. (130) will reduce to Eq. (121) for $f_0 = \kappa_B T/nS(\kappa)$. In order to get a reasonable fit with the dispersion curve in liquid lead we need a f_0 which is four times this value.

It might be expected that the high-frequency zero sound is characteristic not only of helium but of classical liquids like argon. In that case the experiments of Ref. [15] could be interpreted as an evidence for the existence of zero sound mode in liquid argon. This mode would, however, be very much damped. An attempt to develop a theory of zero sound in classical liquids is being made at present by the author.

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LIQUID METALS

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Abstract

Physical picture of a liquid metal. 2. Conductivity. 2.1. Accuracy of calculations. 2.2. Effect of the structure factor. 2.3. Plasma and structure resistance. 2.4. Temperature dependence of the resistance.
 The "three electron" electron states. 3.1. Optical properties. 3.2. Hall effect. 3.3. Knight, shift.
 Theoretical calculations of the density of states. 4.1. Perturbation of energy levels. 4.2. E, k relations in a liquid. 4.3. Expansion of the density of states. 4.4. Difficulties with the density of states expansion.
 A state-counting E, k relationship. 4.6. General comments.

I. PHYSICAL PICTURE OF A LIQUID METAL

These lectures are concerned with the electronic properties of the simple metals whilst in the liquid state. By a "simple" metal we mean, technically, a metal for which pseudopotential theory is applicable. Routhly speaking, this means any metal in which the electronic property being studied is unaffected by any "D-bands". Typical of such metals are the alkali metals, Al, etc. On the other hand, a transition metal would not be a simple metal; it has a half-filled D-band at the Fermi surface. The noble metals, which have a filled D-band inter-secting the conduction band below the Fermi surface, will be included for most electronic properties but not for others.

Now, although liquid metals have been studied both theoretically and experimentally for a large number of years, it is only recently that a straightforward physical picture of the simple metals in the liquid state has emerged. We shall start these lectures by stating this "picture". a) The ions in the liquid metal are positioned throughout space in a random close pack distribution. This distribution is similar to that assumed by ball bearings randomly thrown into a box.

The arrangement of the ions in the liquid state is discussed by March in this book. Of the different (static) correlation functions which may be defined in a liquid, only the pair correlation function, g(r) may be measured or approximated theoretically. This function has the typical shape of being zero for small distances (where the atomic cores cannot overlap), unity at large distances and with a number of oscillatory peaks in between these two limits.

The pair correlation function may be deduced from scattering experiments. The intensity of a beam scattered from a liquid depends on the structure factor, a(k). This is defined as

 $a(k) = \left\langle \frac{1}{N} \sum_{\substack{\ell_1, \ell_2}} e^{i\vec{k} \cdot (\vec{\ell}_1 - \vec{\ell}_2)} \right\rangle$ (1.1)

where $\langle \rangle$ denoted the expectation value over the probability distribution for the ion positions \vec{l} . N is the total number of ions.

The structure factor is related to the pair correlation function as follows:

$$a(k) = 1 + \left\langle \frac{1}{N} \sum_{\substack{\vec{l}_1, \vec{l}_2 \\ \vec{l}_1 \neq \vec{l}_2}} e^{i\vec{k} \cdot \vec{l}_1 - \vec{l}_2} \right\rangle$$
(1.2)
$$= 1 + \frac{1}{N} N(N-1) \int e^{i\vec{k} \cdot \vec{r}} P(\vec{r}) d^3 \vec{r}$$
(1.3)

where $P(r)d^3r$ is the probability of finding a second (given) ion in volume element d^3r at a distance \vec{r} from the fixed (given) ion. Hence

$$P(\mathbf{r}) d^{3}\mathbf{r} = \frac{1}{\Omega} g(\mathbf{r}) d^{3}\mathbf{r}$$
(1.4)

where Ω is the volume of the system.

Consequently,

 $\mathbf{a}(\vec{\mathbf{k}}) = 1 + \frac{N}{\Omega} \int e^{\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}} g(\mathbf{r}) d^{3}\mathbf{r} \qquad (1.5)$

This function contains a delta function at k = 0; it is more usual to express this result as

$$a(\vec{k}) = 1 + \frac{N}{\Omega} \int e^{\vec{i}\vec{k}\cdot\vec{r}} [g(r) - 1] d^{3}r$$
(1.6)
for $|\vec{k}| > 0$

The structure factor is then a type of Fourier transform of the pair correlation function. For large values of k it approaches unity; for smaller values of k it has a number of oscillatory peaks. For very small values of k, one is considering very large wave-lengths. At these wave-lengths the ions are not "seen"; the waves will be density oscillations depending only on the compressibility β_L and the absolute temperature, k_BT . In fact one may show

$$\mathbf{a}(\vec{\mathbf{k}}) \Big|_{\vec{\mathbf{k}}=0} = \frac{N}{\Omega} \beta_{\mathrm{L}} \mathbf{k}_{\mathrm{B}} \mathbf{T}$$
(1.7)

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The arrangement of the ions in the liquid state has been described by Bernal as "random close packing". Although the density of the liquid is not greatly different to that in a solid, the structure is in no sense crystalline or microcrystalline. This has an immediate and important simple physical consequence. There will not be any band gaps due to Bragg reflection in the liquid state. Consequently, there will not be any liquid semi-conductors. Indeed all the usual semi-conductors Ge, Si become simple metals on melting.

b) The time dependence of the thermal motion of the ions may, for most problems, be ignored.

In general, the ions just act as a set of stationary, but randomly arranged scattering centres. It is the randomness of the positions of the ions, rather than the time dependence of these positions, which determines most electronic properties. For example, Faber has shown that the time dependence of the arrangement of the ions only alters the conductivity of lithium by a few percent. As lithium is the lightest metal this is where the biggest effect will be seen.

c) In the simple metals the ions act as weak "neutral pseudoatom" scatterers of the electrons.

The screened ion potentials in the simple metals behave "as if" they were very weak. Cohen and Phillips have shown that in these metals the true screened ion potential may be replaced by a screened pseudopotential. It is this fact, together with the fact that the pseudopotential is sufficiently weak to allow perturbation theory to be used, that has led to the progress which has been made in the theory of liquid metals.

The pseudopotentials are often complicated non-local potentials. Throughout these lectures we shall assume that they are ordinary local potentials and denote them by v(r). The total potential of all the ions is then

$$\Gamma(\mathbf{r}) = \sum_{\vec{k}} \mathbf{v}(\vec{r} - \vec{\ell})$$
(1.8)

where \vec{l} is the position of the ions. Also we shall, in general, drop the prefix "pseudo" and just refer to the "potentials".

The Fourier transform of the pseudopotential is usually defined as

$$\mathbf{v}(\mathbf{k}) = \frac{\mathbf{N}}{\Omega} \int d^3 \mathbf{r} \, e^{-i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}} \, \mathbf{v}(\mathbf{r}) \qquad (1.9)$$

i.e. with an additional density factor from the mathematical definition. The approximate shape of this function may be deduced from an argument of Ashcroft's. The screened pseudopotential will be a bare ion pseudopotential $v_{\rm g}(k)$ divided by a dielectric constant $\epsilon(k)$

$$v(k) = \frac{v_{B}(k)}{\epsilon(k)}$$
(1.10)

The dielectric constant will be given for large wave-lengths (small k) by the Thomas-Fermi argument. This gives

$$\epsilon(\mathbf{k}) = 1 + \lambda^2 / \mathbf{k}^2$$
 (1.11)

where the screening parameter λ^2 is $4\pi e^2$ times the density of states at the Fermi surface, i.e.

$$\lambda^{2} = 4\pi e^{2} \frac{k_{F}}{2\pi^{2}}$$
(1.12)

where k_F is the Fermi momentum as given by

$$k_{\rm F}^3/3\pi^2 = \frac{ZN}{\Omega} = n$$
 (1.13)

is the density of electrons.

Now a pseudopotential arises because the orthogonalization of the conduction wave function with the core state wave functions produces an effective potential which cancels the true core potential. If this cancellation was complete then one would have (in real space)

$$v_{B}(r) = \begin{cases} -\frac{Ze^{2}}{r} \text{ for } r > r_{c} \\ 0 \quad \text{for } r < r_{c} \end{cases}$$
(1.14)

where r_c is approximately the radius of the core of the ion. Using expression (1.14) we then have

$$v(k) \approx -\frac{4\pi Z e^2 N/\Omega}{k^2 + \lambda^2} \cos r_c k$$
 (1.15)

as the approximate shape of the screened pseudopotential (in k space).

There are two important general features of this shape. At k = 0 we have

 $v(k) \Big|_{k=0} = -(2/3) \epsilon_{F}$ (1.16)

i.e. it is just the deformation potential and is quite independent of the particular ion being considered. Secondly, the pseudopotential passes through zero at a position corresponding to the core radius of the ion.
d) After the introduction of a screened pseudopotential the electrons may be treated as non-interacting fermion quasiparticles.

The one-particle states of the system are then the solutions of the single-particle Hamiltonian

$$\left[-\frac{\hbar^2}{2M}\nabla^2 + \sum_{k} v(\vec{r} - \vec{\ell})\right]\Psi_k(r) = \epsilon_k \Psi_k(r) \qquad (1.17)$$

Moreover, as the potentials are weak, we shall have

$$\epsilon_{k} \approx \frac{\hbar^{2} k^{2}}{2m} \tag{1.18}$$

i.e. the electrons will be in free electron-like states.

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The occupation numbers of these states will be given by the Fermi distribution function

$$f(\epsilon) = (1 + e^{(\epsilon - \epsilon_F)/k_B T})^{-1}$$
 (1.19)

2. CONDUCTIVITY

From the picture of the liquid given in section 1 we can, following Ziman, easily deduce an expression for the conductivity of a liquid metal. We have a free electron distribution of electrons before switching on the field. The electric field will cause the electrons to accelerate, thereby gaining energy and altering the distribution function. However, the ion potentials will scatter these electrons so that only a finite current results.

These considerations are the basic ingredients of the Boltzmann equation. The standard methods of the Boltzmann equation then predict that the conductivity, σ , is given by

$$\sigma = \frac{ne^2}{m} \tau \tag{2.1}$$

where τ is the relaxation time of the electrons. The relaxation time is also given by the usual result

$$\frac{1}{\tau} = \frac{1}{2\pi} \frac{\mathrm{mk}_{\mathrm{F}}}{\hbar^{3}} \int_{0}^{\pi} (1 - \cos\theta) \Omega \left| \langle \vec{\mathbf{k}} | \Gamma | \vec{\mathbf{k}} \rangle \right|^{2} \sin\theta \, \mathrm{d}\theta$$
(2.2)

where θ is the angle between \vec{k} and $\vec{k'}$; both of which have length k_F . This formula corresponds to the usual interpretation that $\Omega |\langle \vec{k} | \Gamma | \vec{k'} \rangle|^2$ is the Born approximation for scattering around the Fermi surface by an angle θ , and that the factor $(1 - \cos \theta)$ appears because $|\vec{k}|$ $(1 - \cos \theta)$ is the loss of component due to the scattering (Fig. 1).

Fig.1. Scattering around the Fermi surface.

The factor $\Omega\left|\left<\vec{k}\right|\,\Gamma\,\left|\vec{k}'\right>\right|^2$ may be evaluated by forming the components of the potential

$$\Gamma = \sum_{\vec{r}} \mathbf{v} (\vec{r} - \vec{\ell})$$

between box normalized plane wave states.



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$$\Psi_{k}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}}$$
(2.3)

Hence

$$\langle \vec{k} | \Gamma | \vec{k}' \rangle = \frac{1}{\Omega} \int d^{3}r \ e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} \sum_{\vec{\ell}} v(\vec{r} - \vec{\ell})$$
$$= \frac{1}{\Omega} \sum_{\vec{\ell}} e^{-i(\vec{k}-\vec{k}')\cdot\vec{\ell}} \int d^{3}x v(x) \ e^{-i(\vec{k}-\vec{k}')\cdot\vec{x}}$$
$$= \frac{1}{N} \sum_{\vec{\ell}} e^{-i(\vec{k}-\vec{k}')\cdot\vec{\ell}} v(\vec{k}-\vec{k}') \qquad (2.4)$$

Hence

$$\Omega \left| \langle \vec{\mathbf{k}} \mid \Gamma \mid \vec{\mathbf{k}}' \rangle \right|^{2} = \frac{\Omega}{N} \left| \mathbf{v}(\vec{\mathbf{k}} - \vec{\mathbf{k}}') \right|^{2} \frac{1}{N} \left| \sum_{\vec{\mathbf{k}}} e^{-i(\vec{\mathbf{k}} - \vec{\mathbf{k}}') \cdot \vec{\mathbf{k}}} \right|^{2}$$
$$= \frac{\Omega}{N} \left| \mathbf{v}(\vec{\mathbf{k}} - \vec{\mathbf{k}}') \right|^{2} \mathbf{a}(\vec{\mathbf{k}} - \vec{\mathbf{k}}') \qquad (2.5)$$

 $\vec{d} = \vec{k} - \vec{k}$

Therefore,

 $|\vec{q}| = q = |\vec{k} - \vec{k'}|$ $= 2k_F \sin\theta/2 \qquad (2.6)$

$$(1 - \cos \theta) \sin \theta \, \mathrm{d}\theta = \frac{1}{2} \frac{1}{k_F^4} q^3 \mathrm{d}q \qquad (2.7)$$

Hence

$$1/\tau = \frac{1}{4\pi} \frac{m}{(\hbar k_F)^3} \frac{\Omega}{N} \int_{0}^{Zk_F} |v(q)|^2 a(q) q^3 dq \qquad (2.8)$$

This formula for the conductivity of a liquid metal seems to have been put forward, independently, three times; first by Bhatia and Krishnan in 1948, then by Gerstenkorn in 1952 and finally by Ziman in 1961. However, the earlier workers were hampered by the fact that pseudopotential theory was then unknown; the formula is usually called the Ziman formula.

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2.1. Accuracy of calculations

Before discussing the physics involved in this formula, let us obtain some idea of the accuracy of the calculations. Typical modern calculated values and experimental values are shown in Table I.

TABLE I. o(EXPER	RIMENT) AND	ρ (THEORY)	FOR	SOME	METALS
------------------	-------------	------------	-----	------	--------

(μΩ cm)	Li	Na	ĸ	Rb	Cs	Zn	Al	Pb
ρ (Exp)	24.7	9.6	13.0	22.5	37	37	24	95
ρ (Theory)	25	7.9	23.0	10	10	37	27	64



FIG.2. A plot of $|v(q)|^2$ and q^3 a (q).

We see that the overall agreement is quite good; however, individual calculations may be in error by a factor 2 or more while others are almost exact.

The above table then gives us an idea of what we mean by "good agreement with experiment" in the calculation of the conductivity of liquid metals: the figures are a marked improvement on older theories.

As well as obtaining an idea of how well we can agree with experiment we must also obtain an idea of how accurately we can numerically evaluate (2.8): the structure factor is only known to within the accuracy of the experimental measurements and the pseudopotential is not completely accurately known. If we plot the terms in the integration in (2.8), then we obtain the curves shown in Fig.2.

The typical integration limit for a monovalent metal has also been shown. The calculation is then strongly dependent on the accuracy of the measurements of the leading edge of the first peak of the structure factor. However, this region, which involves small momentum transfer, is the most difficult region in which to make experimental measurements.

The lesson from this is that the calculated values of resistance or conductivity are very sensitive to small errors in both the pseudopotential and the structure factor. The errors in the numerical calculations may be quite large.

2.2. Effect of the structure factor

The basic formula for the resistance gives the relaxation time (2.8) as

$$\frac{1}{\tau} \propto \int_{0}^{Zk_{\rm F}} \left| v(q) \right|^2 a(q) q^3 dq \qquad (2.9)$$

The structure factor a(q) appeared in this expression because we considered the scattering by the entire potential

$$\Gamma = \sum_{\vec{l}} \mathbf{v} (\vec{r} - \vec{l})$$
 (2.10)

The factor expresses the fact that there is a phase coherence between scatterings from different ions. If the distribution of the ions in the liquid was purely random in the mathematical sense of absolutely no correlation between the positions of the ions, then no phase coherence between the scatterings will exist and indeed (1, 6) shows that

$$a(k) = 1$$
 (2.11)

Alternatively, if we had treated the scattering from each ion separately as one would from different impurities when calculating the impurity resistance of a solid, then we would also have obtained

$$\frac{1}{\tau} \propto \int_{0}^{Zk_{\rm F}} |v(q)|^2 q^3 dq \qquad (2.12)$$

The importance of the coherence in the phase between different scatterings in determining the order of magnitude of the resistance can be seen in Fig.3. Here we see that the majority of the integral (for monovalent metals) is over a region where $a(q) \approx a(0) = (N/\Omega)\beta_L k_BT$, which is considerably smaller than unity. In fact, if the incorrect formula (2.12) is used to evaluate the resistance of the monovalent metals the result is in error by a factor of about 20.



FIG.3. A plot of $|v(q)|^2$ and a (q).

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The correlation which does exist between the positions of the ions in a liquid has a dramatic effect on the value of the resistance.

2.3. Plasma and structure resistance

If we plot the terms in the formula for the relaxation time (2.8) then schematically we have the curves shown in Fig. 3. Here we show the structure factor, the pseudopotential squared and the limits of integration for 1, 2, 3 electrons for ions.

Now the low q part of this integration corresponds to a scattering of the electrons by thermal density waves with a deformation potential of $(2/3) \epsilon_F$. This contribution is then approximately independent of the particular liquid metal. It corresponds to a contribution to the resistance due to the "plasma" of electrons on neutralizing ions which are a basic constituent of any metal.

For larger values of q the contribution is highly sensitive to just where and how the pseudopotential passes through zero and to the peak in the a(q) curve. Both of these depend on the "structure" of the particular liquid metal and in particular on the core radius of the given ion (see 1.15).

In calculating the resistance we see that where the pseudopotential is large, the structure factor is small and vice-versa. This tends to decrease the resistance; but it makes the numerical calculating very sensitive to the details of the structure factor and pseudopotential.

In the above plot we left out the q^3 term which heavily weights the larger q values in the integral. Because of this term the plasma resistance is negligible in doubly and trivalent liquid metals, although it is a major contribution to the monovalent liquid metals.

2.4. Temperature dependence of the resistance

One of the great triumphs of this theory has been the success with which it has explained the temperature dependence of the resistivity. An older theory of the resistance, due to Mott, equated the resistance to the scattering by independant "Einstein oscillators". These were usually pictured as individual atoms moving about some mean position. However, as we have already pointed out, such independent scatters would have a resistance about 20 times too large. In the light of the above discussion it would be fairer to equate these oscillators with density waves (just as Debye waves should be used in the theory of specific heat) and to say that this theory only involved the plasma resistance.

The important point here is that any picture of scattering by independent oscillators gives a resistance proportional to the absolute temperature. Hence any theory based along these lines predicts

$$\frac{d \ln \rho}{d \ln T} \equiv 1$$
 (2.13)

Experimentally this condition is approximately satisfied by the alkali metals but not by the others. The figures for some typical liquid metals are shown in Table II.

These older theories were then quite unable to explain the results for higher valence liquid metals, particularly the divalent metals, as it is impossible for any oscillator to lose amplitude with increasing temperature.

Metal	Valency	dln p dln T
Na	1	0.85
ĸ	1	0.76
Rb	1	0.70
Cs	1	0.69
Zn	2	-0.24
Cd	2	-0.22
Hg	2	-0.10
Ga	3	0.14
In	3	0.16

TABLE II. dlnp/dln T FOR SOME TYPICAL LIQUID METALS



FIG.4. a(q) versus q for lower and higher temperatures.

In the present theory we see that all the temperature dependence is contained in the a(q) curve. Now what happens to this as the temperature is increased at a constant volume? We can answer this quite generally. The part due to the density wave must increase proportional to T, for this is just an oscillator contribution. The position of the peak must stay in the same position for this is determined by the mean spacing of the ions which will stay constant for constant volume conditions. On the other hand, the peak must become broader and less high for there is greatly increased disorder with increasing temperature.

Hence, schematically, we have the curves shown in Fig.4. We can now see at once the explanation of the experimental results: for the monovalent metals the largest contribution to the resistance is the plasma resistance. The closer $d \ln \rho / d \ln T$ is to unity the greater is the contribution of the plasma resistance. For divalent metals the plasma contribution is negligible (~ 2%) for the q³ factor heavily weights the large q values. The resistance of the divalent metals will then decrease with temperature as the height of the main peak becomes smaller. While for the trivalent metals the resistance should again increase with the increasing temperature. This is exactly what is observed.

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3. THE "FREE ELECTRON" ELECTRON STATES

The theory of conductivity that we have presented relies heavily on our physical picture of the electrons being free and our derived result of a well defined relaxation time for the scattering by the ions. Let us now look at some other physical properties.

3.1. Optical properties

The optical properties of eleven liquid metals are known. By reflecting light from the surface of a liquid metal it is possible to measure the real and imaginary parts of the dielectric constant (or refractive index) as a function of frequency. If the dielectric constant

$$\epsilon = \epsilon_1 - \epsilon_2 \tag{3.1}$$

results from a free electron model in which a single relaxation time τ for scattering exists, then the Drude equations for these quantities are

$$\epsilon_1 = 1 - \frac{e^2}{\pi} \frac{n}{m} \frac{1}{\nu^2 + \gamma^2}$$
 (3.2)

$$\epsilon_2 = \frac{e^2}{\pi} \frac{n}{m} \frac{\gamma}{\nu} \frac{1}{\nu^2 + \gamma^2}$$
(3.3)

where n is the number of electrons per unit volume and

$$\gamma = \frac{1}{2\pi\tau} \tag{3.4}$$

is an inverse relaxation time.

From the experimental results we can ask two questions: can we fit the curves over all the frequency range by adjusting the two parameters n and γ ? If so, has n the same value as given by the number of valence electrons and is

$$\sigma = \frac{n e^2 r}{m}$$
(3.5)

the same as the DC conductivity?

The answer to the first question is yes for all the liquid metals that have been measured except Hg. Here two different observers disagree over whether or not Hg has a Drude fit over all the frequency range.

The answer to the second question is given in Table III for some selected liquid metals.

We see that the results are very close to unity in the liquid, whereas this is not the case at all in the solid (cf. last colume of Table III). This gives strong supporting evidence to our picture of the liquid state. On the other

Metals	Cu	Ag	Ga	Ge	Sn	Pb	Pb (solid)
N _{obs} /N _{val}	0.84	1.13	0.98	1.08	1.05	1.18	0.32
σ _{opt} /σ _{elec}	0.70	0.96	0.97	0.82	0.95	0.94	0.7

TABLE III. N_{obs}/N_{val} AND $\sigma_{opt}/\sigma_{elec}$ FOR SOME SELECTED LIQUID METALS

TABLE IV. n e Robs FOR SOME METALS

Metal	Na	Zn	Cd	Hg	Ge	Sb
n e R _{obs}	0.98	0.9	0.98	0.97	1.06	1.14

hand, the difference from unity are outside the experimental errors for some of the liquids (but this is not so for copper). Hence this data can also be interpreted as experimental evidence for small, but significant, deviations from the free electron picture.

3.2. Hall effect

The transverse voltage resulting from an electric current flowing at right angles to a magnetic field is measured in terms of the Hall coefficient, R. The free electron model provides a particularly simple result for this quantity, namely

$$R = -\frac{1}{n|e|}$$
(3.6)

where n is the number of free electrons per unit volume. In a solid metal the free electron value is expected if (1) the Fermi surface is spherical, (2) the relaxation time is isotropic. In solids the Hall coefficient almost never has the free electron value.

In liquids, however, the free electron value is almost invariably found. The measurements have a large experimental error due to magneto-

hydrodynamic effects causing the ions to move and circulate.

These results again show the experimental validity of our free electron picture of a liquid metal.

3.3. Knight shift

The most damaging evidence to the free electron picture comes from the Knight shift. The Knight shift, K, expresses the fractional difference in the magnetic frequency of a nucleus which is measured in a metal and a non-conducting salt. The theory gives

$$K = \frac{8\pi}{3} X_p M P_F$$
 (3.7)

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where χ_P is the paramagnetic susceptibility per unit mass of the electrons, M the mass of one atom, P_F the average probability density at the nucleus for electrons at the Fermi surface. Since both χ_P and P_F depend on the electron states, any change in electronic states on melting should be reflected in K.

The experimental results are shown in Table V.

TABLE V. KNIGHT SHIFT FOR SOME METAL	TABLE	v.	KNIGHT	SHIFT	FOR	SOME	MET/	1LS
--------------------------------------	-------	----	--------	-------	-----	------	------	-----

Metal	Li	Na	Rb	Vs	Hg	A1	Sn
K (sol)	0.0261	0.114	0.654	1.49	2.45	0.164	0.75
K (liq)	0.0261	0.116	0.662	1.46	2.45	0.164	0.73

These results are disturbing; by the criteria of the Knight shift the electronic band structure would not appear to alter on melting.

The current explanation of the above figures is that they should be taken as evidence of a free electron-like density of states in the <u>solid</u>. The paramagnetic susceptibility of the electrons depends on the density of states, or equivalently on m^*/m . Now specific heat measurements predict m^*/m in a solid to differ by 10% from unity: hence the original workers expected to see at least a 10% change in the Knight shift on melting. However it is now believed that the specific heat is strongly altered by an electron-phonon interaction. Indeed all calculations of band structure in these metals give m^*/m only differing from unity by 1 or 2%.

4. THEORETICAL CALCULATIONS OF THE DENSITY OF STATES

We have presented evidence and derived results by assuming that the energy eigenvalues are given by

$$E_{k} = \frac{\hbar^{2}k^{2}}{2m}$$
 (4.1)

This is equivalent to saying that the density of states, n(E), the number of eigenstates per unit volume per unit energy range, is

n(E) =
$$2 \frac{\sqrt{E}}{4\pi^2}$$
 for E > 0
0 for E < 0 (4.2)

or that the integrated density of states, $\mathscr{N}(E)$ the number of eigenstates per unit volume below energy E, is given by

$$2\frac{(E)^{3/2}}{6\pi^2} \text{ for } E > 0$$

 $\mathcal{N}(E) =$
(4.3)
0 for $E < 0$

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Now even under the assumption of weak pseudopotentials there must be at least some change from this result and one might even expect a large change if something analogous to Bragg reflection occurred. We turn now to the question of how to calculate these quantities for the liquid state.

4.1. Perturbation of energy levels

At first sight one might try to use standard perturbation theory on the energy levels (Eq. (4.1)). In fact, we cannot do this, for the states form a continuum and any perturbation, no matter how weak, is large compared with the distance between energy levels. Let us see what actually happens. If we use the Rayleigh-Schrödinger perturbation scheme we obtain

$$E_{k} = k^{2} + \langle \vec{k} | \Gamma | \vec{k} \rangle + \sum_{k'} \frac{|\langle \vec{k} | \Gamma | \vec{k'} \rangle|^{2}}{k^{2} - k'^{2}}$$
(4.4)

For simplicity we choose the energy zero such that $\langle \vec{k} | \Gamma | \vec{k} \rangle = 0$. Then using (2.5) we have

$$E_{k} = k^{2} + \int \frac{d^{3}q}{(2\pi)^{3}} \frac{\Omega}{N} \frac{|v(q)|^{2} a(q)}{k^{2} - (\vec{k} + \vec{q})^{2}}$$
(4.5)

The immediate difficulty is that we do not know how to handle the pole in the denominator.

4.2. E, \vec{k} relations in a liquid

We see from Eq. (4.5) that we cannot uniquely label the eigenstates in a liquid by the \vec{k} value of the unperturbed free electron state. Nor can we define a Bloch vector \vec{k} in the liquid, for we do not have translational invariance for a given arrangement of the ions. There are, however, three physical ways of defining an E, \vec{k} relation. Each of these reduces to the usual relation in a solid; but three different generalizations result for the liquid.

(i) Time development of a plane wave

If we imagine the existence of a plane wave state in a medium at time $t = \mathbf{0}$

$$\Psi_{k}(\vec{x}, 0) = e^{\vec{i}\vec{k}\cdot\vec{x}}$$

then this will not be an eigenstate. It will then develop in time. The amplitude of the plane wave will then be given by

$$\int e^{-i\vec{k}\cdot\vec{x}} \Psi_{k}(\vec{x},t) d^{3}x$$

which after a long time will have a time dependence of the form

$$\sim e^{-2 E_k t}$$

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This time development will define an energy E_k , and in ϵ solid this will be 'just the energy of the Block function labelled by \vec{k} .

In a liquid, however, this energy will be complex and of the form

$$\mathbf{E}_{\mathbf{k}} = \mathbf{E}_{\mathbf{k}}^{\dagger} - \mathrm{i} \, \boldsymbol{\Gamma}_{\mathbf{k}} \tag{4.6}$$

The imaginary part will give rise to an experimental damping

 $\sim e^{-\Gamma_k t}$

and will define a life time of the state.

Without proof we shall state that this energy is given by (to second order)

$$\mathbf{E}_{\mathbf{k}} = \mathbf{k}^{2} + \int \frac{\mathrm{d}^{3}\mathbf{q}}{(2\pi)^{3}} \frac{\Omega}{\mathrm{N}} \frac{\left|\mathbf{v}(\mathbf{q})\right|^{2} \mathbf{a}(\mathbf{q})}{\vec{\mathbf{k}}^{2} - (\vec{\mathbf{k}} + \vec{\mathbf{q}}) + \mathbf{i}\epsilon}$$
(4.7)

i.e. the pole is interpreted as if it had an infinitesimal imaginary part contained in it.

Using the relation

$$\frac{1}{x+i\epsilon} = \frac{P}{x} - \frac{i}{\pi} \delta(x)$$
(4.8)

we obtain that the imaginary part is given by

$$\Gamma_{k} = \frac{2}{\pi} \int \frac{d^{3}q}{(2\pi)^{3}} \frac{\Omega}{N} |v(q)|^{2} a(q) \delta(k^{2} - (\vec{k} + \vec{q})^{2})$$
(4.9a)

which is the same as the inverse life-time of the conductivity problem, except that it does NOT contain the $(1-\cos\theta)$ factor.

(ii) The refractive index

If we allow a plane (electron) wave to fall onto a surface of a medium then it will change its wave-length on entering the medium. The medium will behave as if it has refractive index. In the medium we shall have a wave proportional to

where $\vec{k}_E = \vec{k}_E^{(1)} + i\vec{k}_E^{(2)}$. For a solid this procedure will again define a real Bloch vector \vec{k} ; but in a liquid we shall obtain a complex part to the \vec{k} vector. This complex part will define a coherence length (rather than a life time) for the wave in the medium.

Without proof we state that we can obtain this vector by solving (4.5) with a real E and a complex k^2 .

(iii) A state counting k

The Bloch vector, \vec{k} , energy, E_k , relationship in a solid (as well as describing how the wave develops through space and time) also describes

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the density of eigenstates. The states are uniformly distributed throughout \vec{k} -space. This property can also be used to define an E, \vec{k} relationship for a liquid. As one might expect, this replaces the pole in (4.5) by a principal part. We shall prove this below.

We see that when we have a disordered system, the different physical properties of the E, \vec{k} relation in a solid generalize in different ways. There is no unique E, \vec{k} relation in a liquid. For this reason one must be very careful about using concepts derived from solid state physics E, \vec{k} relations (and in particular the use of an effective mass) in a liquid.

4.3. Expansion of the density of states

In order to overcome the difficulties concerned with interpreting the pole in (4.5), investigations into this problem, almost without exception, start from an alternative expression which gives the density of states directly and bypasses the construction of eigenstates.

The density of states, n(E), is the number of energy levels per unit energy range per unit volume. Consider a finite energy range, ϵ , and a finite volume so that the energy levels are discrete. Then

$$n(E) = \frac{1}{\Omega} \sum_{n} \begin{cases} 1/\epsilon \text{ for } |E_n - E| < \epsilon/2 \\ 0 \text{ for } |E_n - E| > \epsilon/2 \end{cases}$$

We must finally take the limits $\Omega \to \infty$ and $\epsilon \to 0$: it is clear that we must take the limit $\Omega \to \infty$, so that the levels form a continuum, before we take the limit $\epsilon \to 0$.

For mathematical simplicity we replace the function of height, $1/\epsilon$, and width, ϵ , which appear in the above sum by

$$\frac{1}{\pi} \frac{\epsilon}{\left(\mathbf{E} - \mathbf{E}_{n}\right)^{2} + \epsilon^{2}} = -\frac{\mathrm{Im}}{\pi} \frac{1}{\mathbf{E} - \mathbf{E}_{n} + i\epsilon}$$

In the limit $\varepsilon \rightarrow 0$ both these functions approach delta functions. We then have

$$n(E) = \lim_{\epsilon \to 0} \left\{ \lim_{\Omega \to \infty} \frac{Im}{\pi \Omega} \sum_{n} \frac{1}{E - E_n + i\epsilon} \right\}$$
(4.9b)

Now the sum over eigenstates represents a trace of the operator. The trace may be taken in any representation: it is convenient to state it in a momentum representation. Hence

$$n(E) = \lim_{\epsilon \to 0} \left\{ \lim_{\Omega \to \infty} -\frac{2Im}{\pi\Omega} \sum_{\vec{k}} \langle \vec{k} | \frac{1}{E - \underline{H} + i\epsilon} | \vec{k} \rangle \right\}$$
(4.10)

where the factor 2 is due to spin and in the limit of large volumes

$$\frac{1}{\Omega} \sum_{\mathbf{k}} \longrightarrow \frac{1}{(2\pi)^3} \int d^3 \mathbf{k}$$
 (4.11)

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Eq.(4.10) represents the starting point of most investigations. The limiting procedures are explicit, although we shall not generally write them in the formulae, but just understand that they are present. The function $\langle \vec{k} | (E - \underline{H} + i\epsilon)^{-1} | \vec{k} \rangle$ is the diagonal part of the Green's function or the operator $(\overline{E} - \underline{H} + i\epsilon)^{-1}$. The advantage of this approach is that the $i\epsilon$ eliminates (and in the limit $\epsilon \rightarrow 0$, gives a precise meaning to) any poles which otherwise would appear.

If the Hamiltonian is written as

$$\underline{H} = -\nabla^2 + \Gamma$$
$$= H_0 + \Gamma$$
(4.12)

and we again take the origin of energy such that $\langle \vec{k} | \Gamma | \vec{k} \rangle = 0$, then

$$\frac{1}{\mathbf{E} - \underline{\mathbf{H}} + \mathbf{i}\epsilon} = \frac{1}{\mathbf{E} - \mathbf{H}_0 + \mathbf{i}\epsilon} + \frac{1}{\mathbf{E} - \mathbf{H}_0 + \mathbf{i}\epsilon} \Gamma \frac{1}{\mathbf{E} - \mathbf{H}_0 + \mathbf{i}\epsilon} + \cdots$$

This is usually expressed as

$$G = G_0 + G_0 \Gamma G_0 + G_0 \Gamma G_0 \Gamma G_0 + \dots$$

where G_0 is the free-particle Green's function

$$G_0 = \frac{1}{E - H_0 + i\epsilon}$$

From this general operator expansion of the total Green's function we can immediately form the diagonal part in a momentum representation as

$$\langle \vec{k} | G | \vec{k} \rangle = \frac{1}{E - k^2 + i\epsilon} \quad \frac{1}{E - k^2 + i\epsilon} \langle \vec{k} | \Gamma | \vec{k} \rangle \frac{1}{E - k^2 + i\epsilon}$$

$$+ \sum_{k'} \frac{1}{E - k^2 + i\epsilon} \langle \vec{k} | \Gamma | \vec{k} \rangle \frac{1}{E - k'^2 + i\epsilon} \langle \vec{k'} | \Gamma | \vec{k} \rangle \frac{1}{E - k^2 + i\epsilon}$$

$$+ \dots$$

Putting $\vec{k}' = \vec{k} + \vec{q}$ and using (2.5), and $\langle \vec{k} | \Gamma | \vec{k} \rangle = 0$ gives

$$\langle \vec{\mathbf{k}} | \mathbf{G} | \vec{\mathbf{k}} \rangle = \frac{1}{\mathbf{E} - \mathbf{k}^2 + \mathbf{i}\epsilon} + \frac{1}{(\mathbf{E} - \mathbf{k}^2 + \mathbf{i}\epsilon)^2} \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \frac{\frac{\Omega}{N} |\mathbf{v}(\mathbf{q})|^2 \mathbf{a}(\mathbf{q})}{\mathbf{E} - (\vec{\mathbf{k}} + \vec{\mathbf{q}})^2 + \mathbf{i}\epsilon} + \dots \qquad (4.13)$$

The pole in the second-order term is now completely defined, the reason being that nowhere here have we introduced individual eigenstates.

4.4. Difficulties with the density of states expansion

By transferring our attention to the density of states, instead of on individual eigenstates, we have overcome the difficulty that the expansion of the eigenstate only converges when the perturbation is small compared with the separation between levels. However the expansion of the density of states only converges when the change in the density of states is small compared with the free electron density of states. Equation (4.2) then shows that the expansion can never be valid when E < 0; indeed (4.13) shows that the expansion of $\text{Im} \langle \vec{k} | (E - \underline{H} + i\epsilon)^{-1} | \vec{k} \rangle$ is a series of infinite-simal terms when E < 0.

To overcome this we must form some other type of expansion than a straight Taylor series expansion. This may be done in an infinite number of ways: we cannot justify any particular method on purely mathematical grounds. We must justify the type of expansion we use on physical grounds.

The usual method is to assume that the Green's function will have a form analogous to that corresponding to free electrons in a uniform potential, Σ . In this case one would have

$$\langle \vec{k} | \frac{1}{E - \underline{H} + i\epsilon} | \vec{k} \rangle = \frac{1}{E - k^2 - \Sigma}$$

If we now assume a slight extension of this formula, so that the potential is a function of E and k, then we would have

$$\langle \vec{k} | \frac{1}{E - \underline{H} + i\epsilon} | \vec{k} \rangle = \frac{1}{E - k^2 - \Sigma(E, k)}$$
 (4.14)

If now we expand Σ in powers of the potential as

$$\Sigma(\mathbf{E}, \mathbf{k}) = \lambda \Sigma' + \lambda^2 \Sigma^2 + \cdots \qquad (4.15)$$

and then expand (4.14), we have

$$\langle \vec{\mathbf{k}} | \frac{1}{\mathbf{E} - \underline{\mathbf{H}} + \mathbf{i}\epsilon} | \vec{\mathbf{k}} \rangle = \frac{1}{\mathbf{E} - \mathbf{k}^2} + \frac{1}{(\mathbf{E} - \mathbf{k}^2)^2} \left[\lambda \Sigma' + \lambda^2 \Sigma^2 + \cdots \right] + \frac{1}{(\mathbf{E} - \mathbf{k}^2)^3} \left[\lambda \Sigma' + \cdots \right]^2 + \cdots$$

$$+ \cdots$$

$$(4.16)$$

By writing Γ as $\lambda\Gamma$ in Eq.(4.13) we may equate powers of λ with (4.16) to find Σ' = 0

$$\Sigma^{2}(E, k) = \int \frac{d^{3}q}{(2\pi)^{3}} \frac{\frac{\Omega}{N} |v(q)|^{2} a(q)}{E - (\vec{k} + \vec{q})^{2} + i\epsilon}$$
(4.17)

and the density of states to this order is

$$n(E) = -\frac{2 \operatorname{Im}}{\pi} \frac{1}{(2\pi)^3} \int d^3k \, \frac{1}{E - k^2 - \Sigma^2(E, k)}$$
(4.18)

Let us just restate that the functional form (4.14) cannot be rigorously justified; an infinite number of function forms could have been chosen at this stage.

4.5. A state-counting E, \vec{k} relationship

The method given in the last section is the basis of the methods which have generally been used in the literature. In fact, if it is just left at the simple stage (4.18) there are still difficulties in the neighbourhood of E = 0, so further modifications must be made.

As we have stated, the justification of any step, such as (4.14), must be based on physics rather than mathematics. I believe that in the freeelectron limit the best assumption is that an E_k function exists where the k are uniformly distributed. If, as in a liquid, we have an average spherical symmetry, then we should have that the integrated density of states was just the volume of a sphere of radius k in k space, i.e.

$$\mathcal{N}(\mathbf{E}_{k}) = \frac{2}{(2\pi)^{3}} \int d^{3}k$$
$$= \frac{2}{(2\pi)^{3}} \frac{4\pi}{3} k^{3}$$
$$= \frac{k^{3}}{3\pi^{2}}$$
(4.19)

The ordinary density of states is then

$$n(E_{k}) = \frac{1}{\pi^{2}} \frac{k^{2}}{dE_{k}/dk}$$
(4.20)

The method of finding this E_k is then the same as before. After integrating expansion (4.13) both with respect to the energy (to give the integrated density of states) and the k variable in that expression we can invert the expansion to give E_k . The result is

$$E_{k} = k^{2} + \frac{Re}{4\pi} \int d\Omega_{k} \int \frac{d^{3}q}{(2\pi)^{3}} \frac{\Omega}{N} \frac{|v(q)|^{2} a(q)}{k^{2} - (\vec{k} + \vec{q})^{2} + i\epsilon}$$
(4.21)

to second order in the potential. This expression is then the same as (4.5), but with the pole interpreted as a principal part and spherical average of the directions of the vector \vec{k} taken. We may in fact complete

this latter integral; the result is then

$$\mathbf{E}_{\mathbf{k}} = \mathbf{k}^{2} - \frac{1}{8\pi^{2}\mathbf{k}} \frac{\Omega}{N} \int_{0}^{\infty} q \, dq \, |v(q)|^{2} \, a(q) \, \ln \left|\frac{q+2k}{q-2k}\right|$$
(4.22)

4.6. General comments

By two quite plausible procedures we have obtained two different answers for the density of states, namely (4.18) and (4.21) together with (4.20). The first of these is based on the physical picture of an optical potential, while the second is based on an analogy with the Rayleigh-Schrödinger perturbation series. Both of these ideas appear equally likely (in the weak scattering limit); however when $E \approx 0$ the two expressions lead to quite different results. This again demonstrates the lack of uniqueness in the mathematics. Fortunately the two expressions give similar numerical results when $E \approx E_F$.

Calculations based on these types of expressions tend to confirm the general picture of the electron states in the liquid metal being very "free electron like". In particular, no radical changes in these functions appear when $k = q_M/2$, when q_M is the position of the peak in the structure factor. This is the position where Bragg reflection occurs in a solid. Quite small disorder appears to eliminate these strong reflections.

Finally we like to remind you again that this E_k curve is limited in its applications to state counting. It is wrong, for example, to use it in the Boltzmann equation by replacing the equation

$$\frac{\mathrm{d}f_{\mathrm{T}}}{\mathrm{d}t}\Big|_{\mathrm{g}} = \vec{\xi} \cdot \frac{\mathrm{d}}{\mathrm{d}\vec{k}} f(k^2)$$
(4.23)

by

$$\left. \frac{\mathrm{d}f_{\mathrm{T}}}{\mathrm{d}t} \right|_{\xi} = \vec{\xi} \cdot \frac{\mathrm{d}}{\mathrm{d}\vec{k}} f(\mathbf{E}_{\mathrm{k}}) \tag{4.24}$$

In fact the correct quantum-mechanical Boltzmann equation (correct to order Γ^2) shows that this term should be

$$\frac{\mathrm{d}\mathbf{f}_{\mathrm{T}}}{\mathrm{d}\mathbf{t}} \bigg|_{\mathbf{\xi}} = \mathbf{\vec{\xi}} \cdot \frac{\mathrm{d}}{\mathrm{d}\mathbf{\vec{k}}} \mathbf{f}(\mathbf{E}_{\mathbf{k}})$$
$$- \sum_{\mathbf{\vec{k}'}} \frac{\mathrm{P}}{\mathbf{k}^{2} - \mathbf{k'}^{2}} \left| \langle \mathbf{\vec{k}} | \Gamma | \mathbf{\vec{k}'} \rangle \right|^{2} \frac{\mathrm{P}}{\mathbf{k}^{2} - \mathbf{k'}^{2}} \left[\mathbf{\vec{\xi}} \frac{\mathrm{d}}{\mathrm{d}\mathbf{\vec{k}}} \mathbf{f}(\mathbf{k'}) - \mathbf{\vec{\xi}} \frac{\mathrm{d}}{\mathrm{d}\mathbf{k'}} \mathbf{f}(\mathbf{k''}) \right]$$

where P denotes principal part. This later term subtracts off part of any m^*/m correction due to using (4.24) in place of (4.23). Just because the Bloch vector is uniformly increased with time by an electric field, it does not mean that this property still holds for one of the three generalizations of this quantity that we have formed for a liquid.

LIQUID METALS

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A SIMPLE MODEL FOR MONATOMIC LIQUIDS

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Abstract

A SIMPLE MODEL FOR MONATOMIC LIQUIDS. A revival of an old idea in an improved form gives the opportunity of analysing the relationship between the structure of liquids and that of crystals. It also allows one to give simple, if approximate, expressions for the static and time-dependent pair correlation functions. A comparison with the numerical experiment by Rahman suggests interesting conclusions on the role in the dynamics of the liquid played by what is the equivalent of the "vacancies" in a crystalline structure.

We try here to formulate the elusive relationship between the structure of monatomic liquids and that of crystals. This attempt is akin to a much older one made by Prins and Petersen [1].

It is based on the following assumption. The positions of the atoms in a sample of monatomic liquid at any given instant of time are considered. If we take a number of neighbouring atoms — say, a dozen or even more we should be able to recognize a pattern more or less like a distorted crystal lattice in them. Let us now assume that an ideal lattice of a suitable type is superimposed such that the best correspondence possible between the sites of this lattice and the positions of the atoms is achieved. Since neither the angles nor the distances of the real structure are quite correct, we should not be able to follow very far the correspondence between atoms and lattice sites. However, in a place where the correspondence has got lost, we should still be able to relocate the ideal lattice so as to accommodate the atoms that are in this place in a way which, on the average, should be as good as for the initial atoms themselves.

This ideal lattice which, on the average, agrees with the real distribution of the atoms only over a limited range, will, for convenience, be called the tangent lattice. Its existence is, of course, an assumption.

The site of origin of a tangent lattice is, by definition, the one most closely corresponding to an atom of the liquid. By proper choice of the tangent lattice, it can be made to lie near any atom of the liquid, so that we may speak of the tangent lattice "relative to this atom". However, the tangent lattice has also a kind of "collective" character, because it is determined by a certain number - dozens or perhaps hundreds - of atoms. It is, moreover, a dynamic entity, displacing and rotating little by little, according to the individual motions of the atoms. There will be a correlation between the tangent lattices relative to the same atom considered at times close enough to each other, just as there will be a correlation between the tangent lattices relative to two atoms sufficiently close to one another, at the same time. However, these correlations should vanish for sufficiently large separations in time or space.

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To get from the above some formulae which can be compared with experiment, some further assumptions are made, namely: (a) if we plot the positions occupied by the atoms in the course of time in the frame of reference of the tangent lattice relative to any atom, we assume that they cluster about the lattice sites according to Gaussian distributions; (b) the square widths of these distributions increase linearly with the distance of the site from the origin. Herein lies the similarity with the work by Prins and Petersen who assumed that the radial density $\rho(r)$ could be expanded in a sum of Gaussians centred about the radii R_n of a suitable lattice. More recently, a similar assumption has been made by an MIT group of workers [2] who postulated that $r^2\rho(r)$ could be expanded in a similar manner.

From the above assumptions we obtain an expression for $\rho(\mathbf{r})$ which turns out to be

$$\rho(\mathbf{r}) = \left(\frac{3}{2^5\pi^3}\right)^{\frac{1}{2}} \frac{1}{\mathbf{r}} \sum_{n=1}^{\infty} \frac{g_n}{R_n \sigma_n} \left\{ \exp\left[-\frac{3}{2\sigma_n^2} (\mathbf{r} - R_n)^2\right] - \exp\left[-\frac{3}{2\sigma_n^2} (\mathbf{r} + R_n)^2\right] \right\}$$

Here g_n is the number of sites at a distance R_n from the origin of a suitable lattice, while $\sigma_n^2 = \beta R_n$ with β being an adjustable parameter. (The second term in the square brackets is negligible except for $r \rightarrow 0$).

Similarly, for the scattering function i(s) we find

$$\mathbf{i(s)} = \sum_{n=1}^{\infty} g_n \exp\left(-\frac{1}{6} \sigma_n^2 s^2\right) \frac{\sin R_n s}{R_n s}$$

Comparison with known results (for Ar, Ne, He) shows fair, although not perfect, agreement (assuming hexagonal close-packing). The fact that the calculated density is always higher (15% for Ar is typical) than the experimental one suggests there are vacancies in the quasi-crystalline structure.

The model has also been applied to Rahman's numerical experiment [3]. It is found that the results for the time-dependent pair correlation function $G_d(r,t)$ at various times, can be accounted for by giving suitable values to Δ^2 appearing in

$$G_{d}(\mathbf{r}, t) = \left(\frac{3}{2^{5}\pi^{3}}\right)^{\frac{1}{2}} \frac{1}{\mathbf{r}} \sum_{n=1}^{\infty} \frac{g_{n}}{R_{n}(\sigma_{n}^{2} + \Delta^{2})^{\frac{1}{2}}} \left\{ \exp\left[-\frac{3\left(\mathbf{r} - R_{n}\right)^{2}}{2\left(\sigma_{n}^{2} + \Delta^{2}\right)}\right] - \exp\left[-\frac{3\left(\mathbf{r} + R_{n}\right)^{2}}{2\left(\sigma_{n}^{2} + \Delta^{2}\right)}\right] \right\}$$

a formula which follows from the model. Here $\Delta^2(t)$ is the mean square displacement of the origin of any tangent lattice supposed to obey a diffusion law ($\vec{\delta}$ is the instantaneous displacement):

$$\Lambda(\vec{\delta}, t) = \left(\frac{3}{2\pi}\right)^{\frac{3}{2}} \Delta^{-3} \exp\left(-\frac{3}{2\Delta^2}\right), \ \Delta^2 = \Delta^2(t)$$

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The values found for $\Delta^2(t)$ are consistently lower than the corresponding values found by Rahman for the average square displacement $r^2 = f(t)$ of the atoms. Through a tentative analysis of the atomic motion, which cannot be summarized here, we conclude that the above difference can be accounted for by the "jumping" of the atoms into the structure vacancies. A rate of jumping of $\nu = 1.8 \times 10^{10}$ per atom per second is estimated. It amounts to an average of about one jump per 50 "oscillations" of the atom about its (approximate) position of equilibrium.

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INTERATOMIC FORCES IN SOLIDS

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Abstract

1. Introduction. 1.1. Born's theory: harmonic approximation and adiabatic approximation. 1.2. Relation between force constants and dynamical matrix. 1.3. Illustration with a 3-D lattice and symmetry effect. 1.4. Central and tensor forces. 2. Forces in simple solids. 2.1. Central force and tensor force model for Na. 2.2. Method of Fourier analysis. 2.3. Work of de Launay, Bhatia and Krebs; failure of Cauchy relations. 3. Forces in alkali halides and semiconductors. 3.1. Discussion on Ge. 3.2. Discussion Na I. 4. Forces in free-electron-like metals. 4.1. Pseudopotential approach of Harrison and Sham. 4.2. Harrison's method. 4.3. Work of Sham and others.

1. INTRODUCTION

Many solids occur in crystalline form in nature, i.e. their atoms are arranged in a regular repetitive structure. However, this statement is true only on the average, because at any instant the atoms constituting the solid are vibrating about their equilibrium positions and the term "repetitive structure" applies only to their equilibrium positions. These motions constitute the thermal energy of the solid. Historically, the interest in these motions arose with a view to understanding the thermodynamic properties of solids. However, it is natural to expect that these motions of the atoms will depend upon how the atoms interact with one another. Consequently, the interest in recent years has shifted to learning the detailed information these motions reveal about the nature of interatomic forces. We will see in this paper how experimental information about dispersion relations, obtained through inelastic scattering of neutrons, is used to understand the nature of interatomic forces.

We begin with a quick review of Born's theory of lattice dynamics and the basic assumptions on which it is based [1].

1.1. Born's theory: harmonic approximation and adiabatic approximation

The dynamics of the vibrations of the atoms in a solid is discussed in terms of the harmonic approximation. For small displacements of the atoms from their equilibrium positions, the potential energy ϕ of the solid is expanded as a Taylor's series in the displacements of atoms. The series is broken off at terms of second order in displacements. This is the so called harmonic approximation. The equation of motion is then set up for each atom: these are, in general, coupled differential equations. They are solved by transforming to normal co-ordinates of the system taking advantage of the translational periodicity of the system. These normal coordinates are independent of each other (in the harmonic approximation) and are just as many in number as the total number of degrees of freedom

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for the system. They give the normal modes of vibrations of the system, each with a characteristic frequency. The solution of the equations of motion shows that the motion of atoms can be described by a superposition of quantized elastic waves called the normal modes of vibration of the system.

It turns out that these modes of vibrations are directly related to the interatomic force constants. Thus, a study of these will enable us to derive information on the force constants.

<u>Adiabatic approximation</u>: In many solids the presence of a (mobile) gas of valence electrons necessitates the introduction of another approximation, the so-called adiabatic approximation, according to which the electrons adiabatically adjust to ionic motions. The physical basis of this approximation is that the ions, being much heavier than the electrons, must be moving much more slowly than the electrons. Therefore, from the point of view of electrons every ionic configuration (in the course of vibration) can be assumed as though the ions are frozen in that configuration. A consequence of this approximation is that the energy of the electron gas acts as a potential energy for the motion of the ions. This total potential energy (of ion-ion interaction + that due to electrons) must be treated within the framework of the harmonic approximation. itself, the

1.2. Relation between force constants and dynamical matrix

We now proceed to a study of the relation between dynamics and interatomic force constants in a solid. For this purpose, we consider a solid of n atoms per unit cell. The relationship between the frequencies of normal modes of vibration of the solid and the force constants (this term will be defined below) is best expressed as a matrix equation:

$$\sum_{\mathbf{k}'\mathbf{v}} \left\{ \left(m_{\mathbf{k}'} \omega^2 \delta_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{x}\mathbf{y}} - M_{\mathbf{x}\mathbf{y}}(\mathbf{\vec{q}}, \mathbf{k}\mathbf{k}') \right) \right\} U_{\mathbf{y}}(\mathbf{k}', \mathbf{\vec{q}}) = 0$$

where Σ runs over all k' = 1... n (i.e. atoms in a unit cell) and over the Cartesian components; m_k^t = mass of k'th atom in the unit cell. The δ are Kronecker deltas. $U_y(k', \vec{q})$ is the yth component of the amplitude of the k'th atom, and \vec{q} is the wave vector of the propagating mode. The quantity $M_{xy}(\vec{q}, kk')$ is called the element of the dynamical matrix and is related to the second derivatives of the potential energy function ϕ by:

$$M_{xy}(\vec{q}, k k') = \sum_{\ell'} \phi_{xy}(\ell k, \ell' k') e^{i\vec{q} \cdot (\vec{r}(\ell' k') - \vec{r}(\ell k))}$$

where \vec{r} (*lk*) denotes the equilibrium position of kth atom in *l*th unit cell and

$$\phi_{xy}(\ell k, \ell' k') = \frac{\partial^2 \phi}{\partial r_x(\ell k) \partial r_y(\ell' k')} \bigg|_0$$

where ϕ is defined above and subscript 0 refers to the value of derivative being taken at the equilibrium separation of the relevant atoms. The quantity M_{xy} is independent of ℓ and therefore $\vec{r}(\ell)$ is set equal to zero.

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For a given pair of atoms (lk), (l'k') the quantities- ϕ_{xy} are called force constants and the corresponding 3×3 matrix

$$\begin{pmatrix} -\phi_{xx} & -\phi_{xy} & -\phi_{xz} \\ -\phi_{yx} & -\phi_{yy} & -\phi_{yz} \\ -\phi_{zx} & -\phi_{zy} & -\phi_{zz} \end{pmatrix}$$

is called the force constant matrix. The physical meaning of $-\phi_{\alpha\beta}$ is that $(\phi_{\alpha\beta}\delta)$ is α th component of the force induced on (ℓk) th atom when the atom at $\vec{r}(\ell k)$ is given an infinitesimal displacement δ along the direction β . Since the approximation is harmonic, the force constants are usually called harmonic force constants.

1.3. Illustration with 3-D lattice and effect of symmetry:

So far we have given only a very formal discussion. We illustrate all that we have said by a hypothetical example (since no such crystal is found in nature) of a (3-D) simple cubic crystal in which only the nearest neighbours interact. To demonstrate this example, let us refer to Fig.1. We have taken an atom at the origin and chosen its six nearest neighbours. Choosing the axis as indicated, it is easy to write down the co-ordinates of all the atoms.

Atom label	Co-ordinates
0	(000)
1	(a 0 0)
2	(0 a 0)
3	(-a00)
4	(0-a0)
5	(00a)
6	(0.0-a)

Let us write down the force constant matrix connecting the atoms 0 and 1. Through symmetry arguments it can be shown that the matrix

		$-\phi_{xy}$	$-\phi_{xz}$
$\phi(0, 1) =$	$\left(-\phi_{yx}\right)$	- ф _{уу}	$-\phi_{yz}$
	$\langle -\phi_{zx} \rangle$	$-\phi_{zy}$	$-\phi_{zz}$

gets very much simplified. Now it is clear that since a symmetry operation of the lattice transforms the lattice into itself, the force constant matrix also must transform in a definite way under the symmetry operations, e.g. the operation of a clockwise 90° rotation about the x axis brings atom 5 to the position 2, and so the force constants for the atoms (0-2) and (0-5) must be related by (see Ref. [2]:

$$\phi(0,2) = T \phi(0,5) \tilde{T}$$



FIG. 1. An atom with six nearest neighbours.

The result essentially follows from the transformation law of second-rank tensors. \widetilde{T} is the transpose of T, and T is the matrix representing the 90° rotation about the x axis.

To see how $\phi(0, 1)$ gets simplified, note that a 90° rotation (clockwise) about the x axis leaves the atoms 1 and 0 invariant. And the matrix T representing this rotation is given by

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

since this transformation takes $x \to x$, $y \to z$, $z \to y$. With the arguments given above $\phi(0, 1)$ must satisfy

$$\begin{pmatrix} \phi_{xx} & \phi_{xy} & \phi_{xz} \\ \phi_{yx} & \phi_{yy} & \phi_{yz} \\ \phi_{zx} & \phi_{zy} & \phi_{zz} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} \phi_{xx} & \phi_{xy} & \phi_{xz} \\ \phi_{yx} & \phi_{yy} & \phi_{yz} \\ \phi_{zx} & \phi_{yy} & \phi_{yz} \\ \phi_{zx} & \phi_{zy} & \phi_{zz} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} \phi_{xx} & \phi_{xy} & \phi_{xz} \\ \phi_{xx} & \phi_{xy} & \phi_{zz} \\ \phi_{yx} & \phi_{yy} & \phi_{yz} \\ \phi_{zx} & \phi_{zy} & \phi_{zz} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} \phi_{xx} & \phi_{xz} & -\phi_{xy} \\ \phi_{yx} & \phi_{yz} & -\phi_{yy} \\ \phi_{zx} & \phi_{zz} & -\phi_{zy} \\ \phi_{yx} & \phi_{zz} & -\phi_{zy} \\ \phi_{yx} & \phi_{yz} & -\phi_{yz} \\ \phi_{yx} & \phi_{yz} & \phi_{yz} & \phi_{yz} \end{pmatrix} = \begin{pmatrix} \phi_{xx} & \phi_{xz} & -\phi_{xy} \\ \phi_{yx} & \phi_{zz} & -\phi_{zy} \\ \phi_{yx} & \phi_{zz} & -\phi_{yy} \\ \phi_{yx} & \phi_{yz} & -\phi_{yz} \\ \phi_{yx} & \phi_{yz} & \phi_{yz} \\ \phi_{yx} & \phi_{yz} & \phi_{yz} \\ \phi_{yx} & \phi_{yz} & \phi_{yy} \end{pmatrix}$$

This gives us the following relations

$$\phi_{yy} = \phi_{zz} = -\beta (say) ; \qquad \phi_{xx} = -\alpha (say)$$

$$\phi_{xy} = \phi_{xz} = -\phi_{xy} \text{ consequently } \phi_{xy} = \phi_{xz} = 0$$

$$\phi_{yx} = \phi_{zx} = -\phi_{yx} \text{ therefore } \phi_{yx} = \phi_{zx} = 0$$

$$\phi_{yz} = \phi_{zy} = -\gamma (say)$$

Substituting these values into the definition of ϕ we obtain:

$$\phi(0,1) = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & \gamma \\ 0 & -\gamma & \beta \end{pmatrix}$$

Another symmetry operation is a mirror plane (the xy plane). The transformation matrix has to represent $x \rightarrow x$; $y \rightarrow y$; $z \rightarrow -z$ and therefore is given by:

$$\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}$$

Thus $\phi(0, 1)$ must satisfy (just as before)

$$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & \gamma \\ 0 & -\gamma & \beta \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & \gamma \\ 0 & -\gamma & \beta \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & -\gamma \\ 0 & -\gamma & \beta \end{pmatrix} = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & -\gamma \\ 0 & \gamma & \beta \end{pmatrix}$$

This tells us that $\gamma = -\gamma$ therefore $\gamma = 0$. Hence the symmetry of the lattice requires that $\phi(0, 1)$ have the form:

$$\phi(0,1) = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}$$
(1.1)

To find out $\phi(0, i)$ with i = 2, 3, 4, 5, 6 we note that suitable rotations transform the atom 1 to atoms 2, 3, 4, 5, 6. In this way we can, for example, see that a rotation through 90° (counterclockwise) about z axis takes $x \rightarrow y$ and $y \rightarrow -x$ and $z \rightarrow z$ and takes (0, 1) to (0, 2) and, therefore, $\phi(0, 2) = T \phi(0, 1) \tilde{T}$ where T represents the above symmetry operation.

Going through the algebra as before we get:

$$\phi(0,2) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$$
 (1.2)

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and, similarly,

$$\phi(0,3) = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix} \qquad \phi(0,4) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

(1.3)

$$\phi(0,5) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix} \qquad \phi(0,6) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix}$$

Note that the structure of all these force constant matrices is the same, i.e. there occur two β and one α in diagonal element in all these. It is therefore usual to indicate only the structure of force constant matrices for each type of neighbour. Since our lattice is without basis the formulae are very simple. The dynamical matrix $M_{xv}(\vec{q}, kk)$ is defined as:

$$M_{xy}(\vec{q}, kk) = \sum_{\ell'} \phi_{xy}(0, \ell') e^{i\vec{q}\cdot\vec{r}(\ell')} - \sum_{\ell'} \phi_{xy}(0, \ell')$$
(1.4)

where, as stated earlier in the definition of $M(\vec{q}, kk)$, $\vec{r}(\ell)$ has been set = 0. And also the second term on the right-hand side of Eq.(4) appears because of the definition of the term $\phi_{xy}(0,0)$. The prime on the summation indicates that the 1' = 0 term is to be omitted. Since we have asserted that only nearest-neighbour interactions are important the summations in Eq.(1.4) run only over the atoms labelled by 1, 2, 3, 4, 5, 6 in Fig. 1.

It is a simple matter to use the Eqs (1-4) to get an expression for $M(\vec{q}, kk)$ which we write as $M(\vec{q},)$ for the sake of simplicity.

$$M(q) = \begin{pmatrix} 2\alpha c_x + 2\beta(c_y + c_z) & 0 & 0 \\ 0 & 2\alpha(c_x + c_z) + 2\beta c_y & 0 \\ 0 & 0 & 2\alpha c_z + 2\beta(c_x + c_y) \end{pmatrix}$$

	$2\alpha + 4\beta$	0	0 \
-	0	$2\alpha + 4\beta$	0
	0	0	$2\alpha + 4\beta$

where $c_x = \cos(q_x a)$, $c_y = \cos(q_y a)$, and $c_z = \cos(q_z a)$. Thus

$$M(q) = \begin{pmatrix} 2\alpha(c_x^{-1}) + 2\beta(c_y^{-1} + c_z^{-1}) & 0 & 0 \\ 0 & 2\alpha(c_x^{-1} + c_z^{-1}) + 2\beta(c_y^{-1}) & 0 \\ 0 & 0 & 2\alpha(c_z^{-1}) + 2\beta(c_x^{-1} + c_y^{-1}) \end{pmatrix}$$

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The eigenvalues of the above matrix give the square of frequencies (ω^2). In this way a plot of ω versus \vec{q} for any given direction of \vec{q} can be built up.

The parameters α , β , etc. are usually adjusted so as to either fit the dispersion relations (ω versus \vec{q} plot) measured experimentally or to reproduce the observed elastic constants. The scheme outlined here is very simple. Of course, the assumption of only nearest-neighbour interactions is very drastic. However, the inclusion of the interaction with further neighbours presents only a computational problem. Indeed, in a realistic analysis of the experimentally determined phonon dispersion relations interactions even up to 4th or 5th neighbours are allowed. Only the number of parameters increases. In this way if the ω -versus- \vec{q} plot is known from experiment we can get the force constants.

1.4. Central and tensor forces

Up to now, no assumption about the nature of the forces has been made except in that they are derivable from a potential energy function ϕ . The only thing we have used is the lattice symmetry. The model that we have considered is the so-called tensor-force model (t.f. model). It was developed by Born and his students (see e.g. Ref. [2]. Some other models in which specific assumptions are made about the nature of ϕ have also been used in the calculation of dispersion relations. These models assume that the potential energy function ϕ is a sum of two-body potentials, which are functions of the value of their separation, i.e. $\phi(\vec{r}(\ell k), \vec{r}(\ell' k')) = \phi(|\vec{r}(\ell k))$ - $\vec{r}(\ell' k')|$). If we start with such a potential energy function we shall, in general, get only two types of parameters for a given set of neighbours.¹

$$\frac{1}{r} \frac{d\phi}{dr} \Big|_{0}$$
 and $\frac{d^2\phi}{dr^2} \Big|_{0}$

where r is the separation of the atoms and the subscript 0 indicates that the values have to be computed at the equilibrium separation. The two types of constants mentioned here are called "bond bending" and "bond stretching" force constants. This model has been suggested by Lehman et al. [3]. They called it axially symmetric model and applied it to Cu, Al and $Zr H_2$ including interactions up to three nearest-neighbours, with six adjustable parameters for Cu and four for Al. The fit which they obtain to the experimental measure is not as good as with t.f. model.

There is yet another kind of model in which "bond bending" force constants are altogether dropped. This is a central-force model with a still greater simplification. But the fact that experimental results are almost never satisfactorily fitted with this type of model shows that this is an over simplification of the facts.

To sum up, the experimental information on the phonon dispersion relation can be used to understand the nature and magnitude of the force constants (in the framework of harmonic approximation); usually it turns out that for almost all solids for reasonable agreement with the experiment results tensor forces extending up to 5th or 6th neighbours are required.

¹ The actual number of force constants is (2n-1) because of the equilibrium conditions. Here n is the number of neighbours up to which interactions are assumed to extend.

2. FORCES IN SIMPLE SOLIDS

2.1. Central-force and tensor-force model for Na.

We have seen how symmetry arguments are used to get the force constant matrices. We discovered that, in general, the lattice symmetry reduces the number of force constants. We will now take up a few examples, of simple solids wherein the agreement between theory based on such models and experiment is quite satisfactory. A simple solid that we are going to talk about is sodium.

Sodium has a bcc structure. Its phonon dispersion relations were calculated by Toya [19] from first principles and later on measured by Woods et al. [5] using neutron spectroscopy. For the moment we are not interested in the basic calculations, but will concentrate on the force constant models. We shall return to the basic approach of Toya later on.

Now in sodium it is known that the elastic constants C_{12} and C_{44} satisfy the Cauchy relations (namely $C_{12} = C_{44}$) to about 20%, therefore the possibility of the existence of central forces cannot be excluded. In fact, it turns out that nearly as good fits to the experimental dispersion curves are obtained by tensor-force and central-force models. Now, as was pointed out previously in the case of central forces, there are only 2 parameters for every set of neighbours. But, in addition, the equilibrium condition imposes some relations on the force constant parameters. For a simple structure like bcc there are 2n-1 independent force constant parameters if interaction up to the nth neighbour are included. On the other hand, symmetry alone governs the number of force constant parameters occurring in tensor-force model.

Following the above indicated procedure it can be shown that for the tensor-force model in the case of a bcc lattice the force constants for various neighbours have the following form:

Neighbour position	<u>force-constant</u> <u>matrix</u>			
1st neighbour $\frac{a}{2}(1, 1, 1);$ a is side of cube	$\begin{pmatrix} \alpha_1 \\ \beta_1 \\ \beta_1 \end{pmatrix}$	$\beta_1 \\ \alpha_1 \\ \beta_1$	$ \begin{array}{c} \beta_1 \\ \beta_1 \\ \alpha_1 \end{array} \right) $	
2nd neighbour $\frac{a}{2}$ (2, 0, 0).	$\begin{pmatrix} lpha_2 \\ 0 \\ 0 \end{pmatrix}$	0 β ₂ 0	$\begin{pmatrix} 0 \\ 0 \\ \boldsymbol{\beta}_2 \end{pmatrix}$	

(Note that 2nd neighbours in the bcc lattice are in the same position as the nearest neighbours in simple cubic lattices and, therefore, the structure of the force-constant matrix is of the type indicated earlier.)

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3rd neighbour $\frac{a}{2}$ (2, 2, 0)	$\begin{pmatrix} \alpha_3 \\ \gamma_3 \\ 0 \end{pmatrix}$	γ ₃ α ₃ 0	$\begin{pmatrix} 0 \\ 0 \\ \boldsymbol{\beta_3} \end{pmatrix}$
4th neighbour $\frac{a}{2}$ (3, 1, 1)	$\begin{pmatrix} lpha_4 \\ \delta_4 \\ \delta_4 \end{pmatrix}$	$\delta_4 \ eta_4 \ \gamma_4$	$\left. \begin{array}{c} \delta_4 \\ \gamma_4 \\ \beta_4 \end{array} \right)$
5th neighbour a (1, 1, 1)	$\begin{pmatrix} \alpha_5 \\ \beta_5 \\ \beta_5 \end{pmatrix}$	$eta_5^{lpha_5^{}}$	$ \begin{pmatrix} \beta_5 \\ \beta_5 \\ \alpha_5 \end{pmatrix} $

With the help of these, the dynamical matrix can be set up and for phonons propagating in high-symmetry directions the dynamical matrix itself reduces to the diagonal form. The parameters α , β , γ , δ are now varied so that the experimental data on the dispersion relation is best fitted in the sense of the method of least squares. If these parameters do not show unnecessarily large oscillations when the range of forces is increased, then we consider them to be really meaningful. For sodium Woods [4] carried out this type of analysis using both the central- and tensor-force models. The results are summarized in Table I:

By including interactions up to 5th neighbours the tensor-force and centralforce models give an agreement within experimental errors. By including interactions up to 2nd neighbours we obtain a qualitative fit only. The fair success of the central-force model achieved led to the derivation of an effective interatomic potential from these three-neighbour force constants. The best fit in the form

$$V(r) = Ar^{-n} - Br^{-m}$$

was obtained as

 $\frac{V}{a^2} = 35.7 \left(\frac{r}{a}\right)^7 - 99.8 \left(\frac{r}{a}\right)^{-3.5}$, $a = 4.24 \times 10^{-8}$ cm

It is plotted in Fig. 2.

Assuming that the form of the potential function does not change with temperature, calculations of the temperature dependence of compressibility were made with this potential which had only qualitative success.

Thus, we see that the interatomic forces in solid sodium extend say as far as up to the 4th or the 5th neighbour only. However, the nature of the interatomic forces is not purely central. Thus, the force-constant analysis reveals the fact that for a more basic understanding of the dispersion relations, a mechanism giving rise to long-range forces should be sought.

Force constant	t.f. model	c.f. model		
α ₁	11 78 ± 10	1173 ± 10		
β ₁	1320 ± 10	1319 ± 10		
α2	472 ± 30	431 ± 20		
β ₂	104 ± 30	110 ± 20		
α3	-38 ± 10	-47 ± 10		
β ₃	-4 ± 3 0	20 ± 10		
γ_3	-65 ± 10	$-67 \pm 10 \ (\alpha_3 - \beta_3)$		
α4	52 ± 20	44 ± 1 0		
B ₄	-7 ± 10	0.5 ± 10		
γ ₄	3 ± 10	5 ± 10		
δ ₄	14 ± 1 0	16 ± 10		
α ₅	17 ± 10	17 ± 10		
β	33 ± 10	17 ± 10		

TABLE I.	FORCE C	CONSTANTS	FOR 1	Na AT	90°K	OBTAINED
EXPERIMEI	NTALLY	(in dynes/cr	m)			



FIG. 2. V/a² versus r/a.

2.2. Method of Fourier analysis

The labour involved in making a tensor-force analysis of the experimentally determined phonon dispersion relations is very large. A simpler approach was given by Foreman and Lomer [6] in 1957. To appreciate their idea fully, let us first consider the dynamics of a linear chain of atoms, each of mass m, separated from each other by a distance a
The equation of motion of the atom at origin is then:

$$m \frac{\partial^2 u_0}{\partial t^2} = \sum_{n=0}^{\infty} \left\{ P_{n+1} \left(u_{n+1} + u_{n-1} - 2u_0 \right) \right\}$$
(2.1)

where \mathbf{P}_1 is the force constant for the nearest neighbour; \mathbf{P}_2 that for next nearest neighbour, etc.

Making use of the translational periodicity of the lattice and thus writing the solution of Eq.(2.1) in the form of travelling waves

$$u_n = U e^{i(qna - \omega t)}$$

we obtain

$$-m \omega^{2} = \sum_{n=0}^{\infty} P_{n+1}(e^{iq(na+a)} + e^{-iq(na+a)} - 2)$$
(2.2)

or we write it in Foreman's notation as

$$m\omega^2 = \sum_{n=0}^{\infty} 2 \phi_n (1 - \cos (qna))$$

where $\phi_1 = P_1$, etc. Consequently,

$$q_{max} = \pi/a$$

such that

m
$$\omega^2 = \sum_{n=1}^{\infty} 2 \phi_n (1 - \cos(nq\pi/q_{max}))$$
 (2.3)

Consider now a fcc crystal (e.g. lead or aluminium). Consider a phonon propagating in a symmetry direction, say, e.g. the (100) direction. Recall that the displacement of ℓ th atom here is given by (for a 3-D lattice it is just an extension of 1-D):

$$\vec{u}_{\ell} = \vec{U} e^{i (\vec{q} \cdot \vec{r}(\ell) - \omega t)}$$

with the usual notation. Note that atoms lying in a plane $\mathbf{1}^{\mathsf{r}}$ to the direction of $\mathbf{\vec{q}}$ will all vibrate in phase, since for any two such atoms the vector $(\mathbf{\vec{r}}(\ell') - \mathbf{\vec{r}}(\ell))$ lies in a plane $\mathbf{1}^{\mathsf{r}}$ to $\mathbf{\vec{q}}$ and hence $((\mathbf{\vec{r}}(\ell') - \mathbf{\vec{r}}(\ell)) \cdot \mathbf{\vec{q}})$ is zero. Therefore, for phonons propagating in symmetry directions in the fcc lattice (as the (100)) the planes of atoms $\mathbf{1}^{\mathsf{r}}$ to $\mathbf{\vec{q}}$ vibrate in phase and so dynamically the problem is very similar to a one-dimensional case, if one treats the ϕ_{n} as the interplanar force constants. Let us now Fourier analyse the dispersion relations along such a high-symmetry direction, e.g. (100) in Al. Then by Fourier analysing the transverse and longitudinal branches we can obtain the Fourier coefficients which are precisely the interplanar



FIG. 3. An example of how interplanar force constants are related to interatomic force constants.

force constants. Roughly speaking, this will give some indication about the range of interplanar and, thus, of interatomic forces; in this way, the method provides, at least, a useful estimate of the range of forces.

To see how these interplanar force constants are related to interatomic force constants, we shall refer to the Fig. 3.

In the figure, let plane 1 contain N' atoms one of which we have shown at the origin, and let it be coupled to the atoms in plane 2 by springs with force constants ϕ_{1j}^{uvw} where (u, v, w) are the co-ordinates of the atom in the 2nd plane with reference to the origin atom in plane 1. The interplanar force constants $\Phi_{11}^{(planes \ 1 \ and \ 2)}$ between planes 1 and 2 are then related to interatomic force constants by:

$$\Phi_{11}^{\text{(planes 1 and 2)}} = N' \sum_{v} \sum_{w} \phi_{11}^{uvw} \qquad (2.4)$$

•Φ^(planes 1 and 2) is the force induced on plane 1 along x-axis when plane 2 is moved parallel to x-axis through a unit distance. Now, by Fourier analysing the longitudinal branch in a Fourier series of the type indicated earlier the left-hand side can be obtained. Similarly, the interplanar force constants between plane 1 and other planes \perp^{r} to the (100) direction at distances 2a, 3a, etc. can be found. Now in such a high-symmetry direction the transverse branches are degenerate, and also the longitudinal and transverse modes can be treated independently. Thus, similar results can be obtained by changing the subscripts 11 in Eq. (2.4) to 22 or 33. The left-hand side can again be obtained by Fourier analysing the transverse branches. The problem of actually estimating the force-constant matrix elements from the data on the interplanar force constants can be solved if one has as many linearly independent equations similar to Eq.(2.4) as the number of force constants. Of course, assumptions as to how many neighbours should be included, etc. have to be made.

An analysis of the type indicated here was first performed by Foreman and Lomer on the results obtained for aluminium. They found that although in the (100) and (111) directions the longitudinal and transverse branches could be fitted by assuming only two harmonics in the Fourier series, in the (110) direction (in this case the two transverse branches are nondegenerate), four Fourier components, at least, were necessary to get a reasonable fit. They concluded that within the framework of adiabatic approximation and harmonic approximation the fourth-nearest-neighbour interactions were not quite negligible.

An analysis of similar type has also been performed on many other substances; for lead, it gave some significantly interesting results. The structure of lead is fcc; it is a substance with four conduction electrons per atom. As remarked earlier, the presence of a mobile electron gas in metals is supposed to be responsible for long-range forces. One would therefore expect very-long-range forces in lead and the method described just now could be used to advantage to check this point.

Brockhouse et al. [7] performed this type of analysis for lead and found that to get a fit to the dispersion relations within experimental errors, indeed, interactions up to the 12th neighbour had to be allowed. It was also found that the interatomic potential showed an oscillatory behaviour after a certain number of neighbours. These oscillations are assumed to be due to the presence of a sharp Fermi surface and thus the effective interatomic potential induced by the electrons is supposed to give rise to such an effect.

So in conclusion, we can say that the work of Foreman and Lomer also gives conclusions similar to the Born-von-Kármán tensor-force analysis, that although qualitative agreement between theory and experiment is possible on the basis of short-range interactions, a quantitative agreement is possible only if long-range forces are assumed to exist.

2.3. Work of de-Launay, Bhatia and Krebs; failure of Cauchy relations

Our conclusion that the electron gas plays an important part in determining the lattice vibrational spectrum and the interatomic forces has also been drawn long ago. It was found that in many cubic metals (in fact in many solids) the elastic constants do not obey the Cauchy relations ($C_{12} = C_{44}$). If the forces between atoms were of central character only, this should not have been the case. Thus, there must be forces of other character. Although people have erroneously interpreted this fact as meaning that even in the presence of forces of other types the central part of the forces still obeys Cauchy's relation, we must remove any doubts of this kind. Cauchy relations can be expected to hold only if central forces alone are acting.

The efforts to include the presence of the electron gas in determining the lattice vibration spectrum were initiated by de Launay [8] and Bhatia [9]. In their models, the electron gas is assumed to have a bulk, but not shear modulus, and so the electron gas is assumed to affect only the longitudinal and not transverse vibrations. In this way, the models had two types of success: 1) since we have now some volume-dependent forces, the Cauchy relations need not hold; 2) the dispersion relation could be fitted rather well using only nearest-neighbour and next-nearest-neighbour interaction together with a parameter related to the bulk modulus of the electron gas. It had, however, a great disadvantage in that dispersion relations did not obey some required degeneracies at certain points. This was corrected later on by Krebs [10] whose model was very often used in the interpretation of dispersion relations. But a number of examples were found (e.g. lead) where the model did not work. These were all simple attempts to include

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the effects of the electron gas. But considerable progress has now been made to include the effects of the electron gas in a more fundamental way. We shall return to this problem later on.

3. FORCES IN ALKALI HALIDES AND SEMICONDUCTORS

The subject of interatomic forces in alkali halides and semiconductors presents some very interesting results. We shall confine ourselves to one example from either group, i.e. NaI and Ge.

The reason why we say that they present some interesting results is that naively one would expect that in a covalent solid like germanium the interatomic forces would not extend beyond the first or at best the second neighbour. Similarly, in alkali halides one would expect that the interaction between ions is well known. For example, the ions can be assumed to be point charges for electrostatic interaction and their overlap potential should be well accounted for by Born-Mayer interaction. Indeed, the compressibility of the alkali halides computed on the basis of such a model turns out to be in good agreement with experiment. However, it turns out that the phonon dispersion relations measured by neutron spectroscopy for Ge by Brockhouse and Iyengar [11] cannot be fitted by assuming interactions even up to second-nearest-neighbour and only after extending up to fifthneighbour-interactions the agreement of theory and experiment is somewhat good (Herman [12]). Similarly, in alkali halides a calculation for NaI based on the simple picture indicated here, which usually is called pointion approximation, gives results which are very far from the experimental measurements, In this lecture, we shall direct our attention to the possible explanations that have been put forward to account for these somewhat anomalous observations.

3.1. Discussion on Ge

It is found that the elastic constants of germanium obey rather well an identity obtained by Born

4
$$C_{11} (C_{11} - C_{44}) = (C_{11} + C_{12})^2$$

where the C's are the usual elastic constants. This identity can be shown to follow if only the nearest-neighbour interactions are important. However, the validity of the identity does not imply that only nearest-neighbour interactions are important. Hsieh [13] was the first to make a Born-von-Kármán tensor-force analysis for germanium based on the assumption of nearestneighbour interaction. His calculations involved only two adjustable parameters, which could be found from elastic constant data. However, the phonon dispersion relation measurements later on revealed that the transverse acoustic modes at small wavelengths were as much as 70% off from the measurements. Although the experimental observations of Brockhouse and Iyengar [11] were also interpreted in terms of a general second-nearest-neighbour tensor-force model, the conclusion reached was that simple Born-von-Kármán theory does not seem to hold.

3.2. Discussion on NaI

NaI is a substance with fcc structure and two atoms per unit cell. In a simple picture, the interatomic forces in such a solid are assumed to be due to two contributions:

- (1) Short-range overlap interaction of the ions;
- (2) The long-range Coulomb interaction between ions assumed to be fully ionized, i.e. e^+ on Na and e^- on I.

The calculations of the phonon dispersion relation based on such a simple model can be done exactly by assuming some form for interaction (1) The usual form is b exp $(-r/\rho)$ where b and ρ are parameters, and r is the separation of the two atoms. The contributions to the dynamical matrix from interaction (1) is then easily evaluated. The calculation of the contribution to the dynamical matrix from interaction (2) involves the evaluation of a series like

$$\sum_{\substack{\mathbf{k}^{\mathsf{I}}\\\mathbf{k}^{\mathsf{I}}}} \frac{\partial^2 \phi(\left| \vec{r}(\ell^{\mathsf{I}} \mathbf{k}^{\mathsf{I}}) - \vec{r}(\ell, \mathbf{k}) \right|)}{\partial \mathbf{x} \partial \mathbf{y}} e^{i\vec{q} \cdot (\vec{r}(\ell^{\mathsf{I}} \mathbf{k}^{\mathsf{I}}) - \vec{r}(\ell, \mathbf{k}))}$$

where ϕ varies as 1/r.

Such a series is only conditionally convergent. However, following a method due to Ewald known as θ -function transformation, it is possible to evaluate such a series. The parameters b and ρ entering interaction (1), and thus the corresponding contribution to the dynamical matrix can be found using elastic-constant data. A calculation for the dispersion relations for NaI based on this picture was done by Woods et al. [14]. The results are shown in Fig.4. The dotted line shows the calculations based on the above-described model. The experimental measurements were carried out by Woods et al. The full line is based on the shell model, which will be discussed later on.

The lack of agreement between theory and experiment shows clearly that there must be some other forces not taken account of. It is not very difficult to obtain an answer, for we have assumed ions to be rigid, i.e. non-polarizable. But, in fact, the experimental atoms or measurements on the infrared absorption in germanium, even before the dispersion relation measurements were made, had shown the presence of dipoles in solid germanium. And, similarly, there is no reason to believe that during the vibrations of an ion in an ionic crystal the entire ion should vibrate as a rigid point ion. The structure of an ion will suggest that during vibrations of an ion it is possible that the positive and negative charge centres in the ion may get separated either because of a "mechanical rubbing" of the ion - against its neighbour, or owing to some external field. In short, there is a chance for the ion to get polarized.

Although in a covalent solid like germanium which has strongly "directed bonds" one may find it hard to understand whether such a polarizability is possible or not, it can be shown on the basis of quantum mechanics that the atom can be polarizable.

It turns out that if such dipoles are produced during lattice vibrations they may give rise to long-range forces. Of course, the polarizability of the atoms will suggest that there may be higher multipoles induced in the lattice. In fact, it has been shown by Lax [15] that the symmetry of lattice



FIG. 4. The dispersion curves for the three symmetry directions in Na I at 110°K determined by Woods et al. The curves are calculated a priori and are not fitted to the neutron measurements.

permits quadrupole interactions, but the dipole approximation is much easier to work with (see Ref. [15]).

We have essentially discussed the physical basis of a model that we are going to describe and which is called shell model; it was first introduced by Cochran [16] in lattice dynamics. There have been several extensions of the model suggested by Cochran (see, e.g. Cowley [17]), but we will restrict ourselves to a discussion of the simplest kind of shell model, in which only seven parameters occur. The model has intuitive simplicity and has been quite successful in explaining the dispersion relations of germanium (and Born's identity) and the dispersion relations in NaI.

We shall not give any details as to how the calculations are done, but will give the essential physics of the model. We are mainly interested in learning what light the model sheds on the interatomic forces in semiconductors and halides.

Cochran regards every atom in the solid as consisting of a rigid "core" that comprises the nucleus and the inner electrons and a "shell" of the outer electrons. We shall collectively speak of the "shell" and the "core" as atom or unit. The shell is assumed to be coupled to the core with an isotropic force constant k. It is doubtful whether for germanium this is very true because of the presence of covalent bonds, but it is nevertheless a simplifying assumption which appears to work. Similarly, in ionic crystals the ions are assumed to be made up of a "core" and a "shell of electrons". The core is assumed to be rigid and non-polarizable. The positive ion also is assumed to be non-polarizable, although this restriction



FIG. 5. Cochran's generalized shell model. The interactions F(12) and F(21) are frequently taken to be equal.

has been removed by Cowley to include the polarizability of positive ions as well. We shall discuss the use of this model for Ge, although for alkali halides the discussion is almost parallel.

The entire solid is now assumed to be consisting of such units, i.e. cores and shells. The schematic representation of possible types of short-range interactions between two units is given in Fig. 5. Thus, there can be core-core, core-shell, and shell-shell interactions.

Discussing the lattice dynamics of such a system, Cochran sets up the equations of motion for the entire system treating each of the four quantities in the unit cell, i.e. two cores and two shells as independent. The contribution to the dynamical matrix (which will now be a 12×12 matrix) from the different sources of interaction between the constituents are divided into two parts.

(1) Representing the short-range overlap interaction.

(2) The long-range Coulomb interaction.

The most general tensor forces are allowed for the interaction between neighbouring units for part (1).

The short-range interactions that are allowed are those between nearest neighbours. The contribution (2) due to the Coulomb interaction is evaluated using the method given by Kellermann based on theta-function transformation.

The assumption corresponding to adiabatic approximation is made by assuming the shells to be massless such that the system of equations governing the lattice vibrational frequencies reduces to a system of six equations. Its solution gives the frequencies of normal modes of vibration for the crystal.

Mashkevich and Tolpygo [18] had earlier obtained expressions similar to those of the "shell model" by assuming that the potential energy of the system is made of nuclear displacements and dipole moments of the nuclei². Mathematically speaking, it is, therefore, possible to arrive at all the conclusions stated here without introducing the shell and core picture, but the model has physical appeal.

In all, in Cochran's theory seven parameters occur, three of which represent the ratio of (some short-range) force constants for core-core, core-shell and shell-shell interactions to be denoted by γ_R , γ_T and γ_S . (If the nearest-neighbour interaction alone is taken into account for the overlap interaction, only then seven parameters are obtained.) The other parameters entering the theory are related to the values of bonding co-

 $^{^2}$ Cochran has pointed out that there are differences in the final expressions which are very important in Ge.

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efficients between core-core, core-shell and shell-shell interactions in the limit $q \rightarrow 0$. Another parameter related to the polarizability of the atom is obtained from the dielectric constant. Five of these seven parameters are obtained from elastic constant data and equilibrium conditions, etc. The remaining two parameters related to the bonding coefficients in the limit $q \rightarrow 0$ are obtained by adjusting to the experimentally determined frequencies at some high-symmetry points. The overall agreement between theory and experiment is good except for the LA branch along the (111) direction where the discrepancy was of the order of 14% between theory and experiment. The comparison between the theory and experiment is shown in Fig. 6. Born's identity is also shown to be satisfied by this type of analysis.



FIG. 6. The dispersion curves of germanium at room temperature. The branch assignments TA, LA, etc., were made from the intensities of the neutron groups. The straight lines through the origin have slopes given by the appropriate velocities of sound.

Application to NaI:

The dispersion relations for NaI determined experimentally have also been analysed by Woods et al. [14] in terms of the shell model. The curves shown in Fig. 4 are based on calculations where the polarizability of the positive ions was neglected. Cowley has extended the calculations to include the polarizability of the positive ions also. Though the agreement between theory and experiment does improve, the number of parameters has also to be considerably increased.

In conclusion, we may therefore say that in semiconductors like germanium and in alkali halides like NaI there do exist forces due to the dipole interaction which have considerably long range, and the polarization of atoms due to both short-range forces and long-range electrical fields must be included (at least up to a dipole approximation) in order to get a reasonable description of the actual phenomena.

4. FORCES IN FREE-ELECTRON-LIKE METALS

We have already mentioned that in most metals force-constant analysis shows the existence of long-range forces. We have also stated that this is attributed to the presence of a mobile gas of conduction electrons. In this section we shall briefly survey some attempts made to take account of the presence of electrons in a fundamental way and in this way learn about the role of electrons in determining interatomic forces.

The usual metal model is the following: the valence electrons of free atoms are detached from their parent atoms and spread all over the crystal. The ionic cores (i.e. nuclei + closed shell of electrons) are imbedded in the valence electron gas and carry their charges rigidly with them. Therefore, the model will apply only to simple metals. Our treatment is not applicable to the situation in transition metals, where d-electrons cannot be treated as belonging to parent atoms only or to the entire crystal. Indeed, the problem of transition metals will invoke a lot of interest in the future.³

As stated in section 1, the adiabatic approximation constitutes the basis of all the theories. The different theories differ only in the extent to which the valence electron interactions with the ions and with one another are treated.

The basic problem is to find the total energy of the electron gas which acts as a potential energy for the motion of the ions within the framework of adiabatic approximation or to directly find the self-consistent secondorder change in the energy of the electron gas when the ions are displaced from the equilibrium positions, and from where the contribution to phonon frequencies can be arrived at, directly.

The first fundamental calculation was made by Toya [19] for sodium, by using the Hartree-Fock method. Following Toya, we also treat the potential energy for the motion of ions as coming from three distinct parts:

- (1) The Born-Mayer exchange repulsion interaction between the ionic cores.
- (2) The direct Coulomb interaction between the ionic cores together with a uniform compensating background of electrons to give charge neutrality.
- (3) The potential induced amongst the ions by the response of the electron gas to the ion motion (within the framework of adiabatic approximation). Our task is to find the contribution from each of these terms to the elements of the dynamical matrix. Then to arrive at phonon frequencies we only have to diagonalize the dynamical matrix, i.e. find its eigenvalues.

Since the form of the interaction potential for part (1) is usually taken to be A exp $(-r/\rho)$ with A and ρ being parameters to be found from elastic constant data, it is necessary to include only nearest- or next-nearestneighbour interactions. The corresponding contribution to the dynamical matrix is straightforward to obtain. For part (2) the method of Ewald as extended by Kellermann is used. In evaluating its contribution to the dynamical matrix, a uniform compensating background charge of electrons to neutralize the ionic charge is assumed. This also presents no difficulty.

The problem of finding the contribution due to part (3) is an extremely complicated problem because essentially it is the problem of finding the

³ Recently Sinha [27] has developed a method applicable to transition metals, but no calculations have been made as yet.

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energy changes for a many-body system like electron gas, when the ions are displaced from their equilibrium configuration by the propagation of a normal mode of vibration. One has to resort to one-electron formalism and then add the corrections due to dynamical correlations between electrons in the system. One does not try to arrive at the total energy of the electron gas (which is the problem of finding cohesive energy) but tries to directly evaluate the second order change in energy of the electron gas when the ions are displaced from the equilibrium position.

Now the problem of finding this change in energy is complicated by the fact that electrons strongly interact with one another. Therefore, the exact change in energy has to be found by allowing for the fact that any electron will see a perturbation not only due to the displacement of the ions, but also to the re-adjustment of the other electrons. It is therefore, as if the ions were coupled to one another by springs via the entire electron gas. In order to see the physical basis underlying this ion-ion coupling via the electron gas let us consider an example (Fig. 7).

O Displaced position of ion

lons immersed in valence electron gas

FIG. 7. An example of the ion-ion coupling via the electron gas.

Consider an ion lying at the equilibrium position taken as the origin which is displaced to a position as shown in the figure. The electron cloud at a point \vec{x} shown in the figure will try to re-adjust to such a change in a self-consistent manner, i.e. consistent with the way in which its neighbouring cloud adjusts to this change which, in turn, is determined by the response of this electron. The net result is that the change in the charge density of electrons at \vec{x} can be written as:

 $\delta \rho(\vec{x}) = \int R(\vec{x}, \vec{x}') \delta V_{ie}(\vec{x}') d\vec{x}'$

where $R(\vec{x}, \vec{x'})$ is the response function of the electrons which is independent of the ionic displacements. $\delta V_{ie}(x')$ is the change in the potential at the point $\vec{x'}$ due to a displacement of the ion at origin. This change in the charge density distribution of electrons gives rise to a change in the potential as seen by another ion which also responds to it. In this way, a coupling of the ions is brought about by the electron gas. From this discussion we can see that the response function $R(\vec{x}, \vec{x'})$ and the ion electron interaction potential V_{ie} both will determine the coupling between ions via the conduction electrons.

In the actual theory it is more convenient to work in the reciprocal space rather than the real space and thus the Fourier transform of the response function and of the ion-electron potential enters the calculation. This former quantity is usually called the dielectric matrix of the electron gas. Its off-diagonal components are set equal to zero (or assumed to be very small) in making an explicit calculation. Depending upon how we allow the electrons to interact with one another we get the corresponding dielectric matrix. We shall see what sort of assumptions have been used by various authors.

INTERATOMIC FORCES

The other quantity entering the theory, the Fourier transform of ionelectron potential, is usually taken from the Hartree-Fock potential of the ion either in free state or in a metal. Its validity has been doubted by Vasko et al. [20], but has nevertheless been used very often in literature.

We will now survey the work of several authors. To evaluate contribution (3), Toya assumed that the valence electrons interact with one another in a Hartree-Fock way, but for the exchange term he used simplified Slater picture. Toya also assumed that the unperturbed valence electrons in sodium can be well represented by single plane waves $(1/\sqrt{\Omega}) \exp(i\vec{k}\cdot\vec{r})$ and their energies can be represented by the equation

$$\epsilon_{\overrightarrow{k}} = \epsilon_0 + \frac{\hbar^2 k^2}{2m}$$

He then applied usual second-order perturbation theory to evaluate the second-order change in the energy of the electron gas due to the displacement of ions (second-order in ionic displacements), and the corresponding contribution to the dynamical matrix was written out, in which the Fourier transform of the electron-ion potential was written in the form

$$\left\{-\frac{4\pi Z e^2}{q^2 \Omega_0} + \beta_0\right\} g(q_{r_s})$$

in which r_s is the Wigner-Seitz sphere radius and $g(x) = 3(\sin x - x \cos x)/x^3$. β_0 is a parameter. The other quantity occurring in the theory corresponding to the response function in direct space is the wave-number-dependent dielectric constant of the electron gas which in the Hartree approximation is given by:

$$\epsilon(\vec{q}) = 1 + \frac{4\pi Z e^2}{q^2 \Omega_0} \left\{ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \log \left| \frac{2k_F + q}{2k_F - q} \right| \right\}$$

To take account of correlations between the electrons Toya modified the dielectric constant.

Toya made calculations for four symmetry directions in sodium and they were later on experimentally checked by measurements of Woods et al. Toya's calculations were within 15% of the measurements except in one symmetry direction where the discrepancy in some branches was quite large. Although the calculations cannot be said to give a better agreement than the Born-von-Kármán tensor-force model analysis, the essential correctness of the approach of Toya was nevertheless proved.

Later on, Toya [21] extended his method to copper and lead, but in these calculations the results do not agree as well with the theory as in case of sodium.

4.1. Pseudo potential approach of Harrison and Sham

The very useful concept of a 'pseudo-potential' has recently been borrowed by Harrison [22] from the band structure theory to investigate a series of metal properties. There is a method of orthogonalized plane waves in band structure theory in which one starts with a basic set of functions for the conduction electrons which are plane waves orthogonalized to core states.

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It has been shown by Phillips and Klienmann that the effect of orthogonalization may be looked upon as giving rise to a "Pauli repulsive potential" which the conduction electrons see in addition to the bare ion potential. The repulsive potential acts against the ionic potential to give a sum called the pseudo-potential. Actually this pseudo-potential is a complicated integral operator, but it can be approximated by a local potential and it is this local pseudo-potential which becomes very handy for treating many electron properties.

4.2. Harrison's method

In this method of computing lattice vibration spectrum Harrison evaluates the contribution due to part (2) and neglects part (1). To obtain part (3) he finds the total energy of the electron gas and then separates it into volume-dependent, but structure-independent and volume-independent, but structure-dependent parts. And assuming that during lattice vibrations volume remains constant he drops the volume-dependent term in the total energy of the electron gas.

The rest of the energy terms can then be factorized into a form-factor and a structure-factor part, just as in diffraction theory (in fact Harrison calls this a diffraction model of solid). The structure factor part is then expanded in terms of a series involving the displacements of the ions from which the second-order term is extracted, and the corresponding contribution to the dynamical matrix is then evaluated. Harrison has performed such calculations for aluminium with only moderate success.

On the basis of this picture Harrison has also found the effective interatomic potential in some substances. But a basic calculation of this type involving <u>no</u> parameters has not been very successful.

4.3. Work of Sham

A more satisfactory calculation for the phonon dispersion relation in sodium was made by Sham [23] using two models, one involving the local pseudo-potential and the other one the non-local pseudo-potential.

Sham approaches the problem of finding the vibration spectrum in a way similar to the earlier approach of Toya as far as the contributions from parts (1) and (2) are concerned. To find the contribution due to part (3) Sham assumes a model of independent electrons influencing each other through a self-consistent Hartree potential and a screened exchange potential. In this way, the influence of the electron-electron interaction is expressed in terms of a dielectric matrix. He also evaluated the secondorder term in energy by perturbation theory. The contribution to phonon frequencies from the presence of the electron gas can then be expressed in terms of the dielectric matrix and the Fourier transform of the pseudopotential. Sham evaluates an averaged local pseudo-potential in his model A and then extends it to include non-local effects in his model B. For his calculations he uses a dielectric constant instead of a matrix. His calculations show that both models A and B are quite successful in explaining the lattice vibration spectrum.

Very recently, Animalu and Heine [24] have evaluated model potentials based on spectroscopic term value data for many elements. From this they arrive at model potentials in metals, and the computation of the phonon dispersion relations based on these has been done by Animalu et al. [25] in the spirit of the local pseudo-potential model of Sham on a number of alkali metals and aluminium with considerable success.

What does all this tell us about the interatomic forces in metals? Well, surely the fact that very few basic calculations have been successful in explaining the dispersion relation without parameters is discouraging, but also the fact that such a large number of sweeping assumptions made in the analysis still yield a result in the right direction is satisfactory. From the standpoint of understanding interatomic forces in metals, therefore, considerable amount of understanding with regard to the behaviour of electrons is necessary. As for the present, some parametric approaches confirming the internal consistency of our schemes are bound to help. In this connection it is useful to summarize also the work done by Schneider and Stoll [26]. These authors have used the method of local pseudo-potential to find the pseudo-potential from the measured phonon dispersion relation by leaving a few parameters in a plausible form for the pseudo-potential. These parameters are then obtained by least squares analysis of the measured dispersion relation. From this knowledge of the pseudo-potential they have computed a number of electronic properties, e.g. band structure, Fermi surface distortion, etc. Their calculations yield results which are in moderate agreement with experiment.

To sum up, one cannot as yet very accurately find the interatomic forces due to the presence of the electron gas in metals. Considerable effort has to be made by theoreticians before a quantitative agreement between theory and experiment can be obtained.

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PART IV

ELECTRONIC PROPERTIES

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BAND MAGNETISM

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Abstract

Introduction, 1, Experimental properties of transitional metals. 1.1. Magnetic properties. 1.2. Other properties. 2. The band model. 3. Hartree-Fock Stoner theory. 3.1. Non-magnetic Hartree-Fock solution at T=0. 3.2. Magnetic solutions, 3.3. Applications, 4. Spin waves in the random phase approximation. 5. Susceptibilities – equivalence between the RPA and the time-dependent Hartree-Fock approximation. 5.1. Definition and properties of the susceptibilities. 5.2. Susceptibilities in the RPA. Time-dependent Hartree-Fock approximation. 6. Spin density waves. 6.1. Appearance of spin density waves at T_c . 6.2. Spin density waves below T_c . 6.3. Application to chromium. 7. Influence of correlation. 7.1. The Landau theory of Fermi liquids. 7.2. Approximate treatment of correlation. 7.3. Applications. 8. Nearly ferromagnetic metals. 8.1. Mass enhancement due to phonons. 8.2. Mass enhancement due to paramagnons. 8.3. Applications, Conclusion.

INTRODUCTION [1, 2]

In this contribution I intend to discuss only some topics of the field. I do not aim at completeness, but wish to present some aspects of the subject in a pedagogical manner. Band magnetism is of interest for the transitional metals; I shall not discuss in detail the case of real metals, but focus interest on some simple models (with one band). The emphasis will be on methods rather than on a detailed comparison with the experimental results. A qualitative discussion of more recent theories will be given.

A large part of the modern theory of magnetism is based on the Heisenberg Hamiltonian

$$H = -\sum_{ij} J_{ij} \vec{s}_i \cdot \vec{S}_j$$
(1)

where the \vec{S}_i are localized spins on the sites \vec{R}_i and the exchange integral J_{ij} depends only on $(\vec{R}_i - \vec{R}_j)$. Let us summarize some of the important results which can be derived with the use of expression (1):

a) We can justify the molecular field approximation and derive the high temperature susceptibility

$$\chi = \frac{g^2 \mu_{\rm B}^2 S(S+1)}{3 k \left(T - T_{\rm p} \right)}$$
(2)

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b) In the ordered ferromagnetic state, at low temperatures, we can introduce the elementary excitations of the system, the spin waves, and derive the magnetization M(T):

$$M(T) \simeq M(0) \left[1 - \alpha T^{3/2} \right]$$
(3)

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where M(0) per atom is $g\mu_BS$. The spin-wave spectrum for long wavelength is given by $\hbar\omega = Dq^2$ and the variation of D with temperature (due to spin-wave interactions) is

$$D(T) \simeq D(0) \left[1 - \beta T^{5/2} \right]$$
 (4)

c) In the critical domain (T \simeq T_c), the susceptibility X(T) behaves as (T-T_c)^{-\gamma} where $\gamma \simeq 4/3$.

d) When J_{ij} is negative for first-neighbour distances, antiferromagnetism may occur. If J_{ij} extends over first-neighbour distances, we may have helical or sinusoidal structures.

In the Hamiltonian (1), J is often regarded as a phenomenological parameter. In his original work, Heisenberg introduced J as the direct exchange integral between electrons in different orbitals (at different sites). In fact, it appears that this mechanism is small. In ionic crystals, J is due to super-exchange. In rare earth metals, J is due to an indirect mechanism caused by the conduction electrons.

Let us look now at the experimental results for transitional metals and see if they can be explained within the framework of the Heisenberg theory.

1. EXPERIMENTAL PROPERTIES OF TRANSITIONAL METALS [1]

In transitional metals, the existence of d electrons is the origin of magnetism. We shall first review the properties of magnetic transitional metals which are understood within the Heisenberg picture.

1.1. Magnetic properties

At high temperatures, $\chi \propto (T \text{-} T_p)^{\text{-1}};$ this is well observed for Fe and Co.

At low temperatures, the magnetization in Fe, Co, Ni follows the Bloch law given by Eq.(3). The inelastic neutron scattering gives a dispersion relation $\hbar \omega = Dq^2$; D varies with T as given by Eq.(4).

At $T \simeq T_c$ the susceptibility behaves as $(T - T_c)^{\gamma}$ with $\gamma \simeq 4/3$ ($\gamma = 1.36 \pm 0.04$ for nickel). The scattering cross-section for neutrons $d\sigma/d\Omega \propto 1/(q^2+K^2)$ where $K \simeq (T - T_c)^{\alpha}$, $\alpha \simeq \gamma/2$ as expected.

In Fe and Co the electrical resistivity behaves as shown schematically in Fig.1. This is very similar to the case of rare-earth metals and suggests that the magnetic part of the resistivity has the same origin (spin disorder). In nickel, the resistivity is not linear above T_c and varies similarly to the case of Pd. This suggests that spin disorder plays a different role in Fe (or Co) and Ni.



FIG. 1. Electrical resistivity in Fe and Co; ----- total resistivity; ----- magnetic part of resistivity.

The last remark is that the existence of sinusoidal structures (in chromium, for example) is not by itself in contradiction to the Heisenberg model.

1.2. Other properties

The properties which we shall discuss now are usually properties not only of the magnetic metals, but of all the transitional metals. They indicate that the electronic structure of magnetic metals should be explained in the same framework as the structure of non-magnetic metals.

There are, first of all, some magnetic properties which cannot be understood within the Heisenberg model.

The saturation moments should be $g\mu_BS$, an integral number of Bohr magnetons. For Fe, Co, and Ni we have, respectively, 2.22, 1.7, and 0.60 Bohr magnetons. For chromium, the magnetic moment (obtained from neutron scattering) is 0.6 μ_B at the maximum of the sinusoidal distribution. For the ferromagnetic compound $ZrZn_2$, the magnetic moment is 0.18 μ_B .

The Curie constant in the susceptibility law does not lead to halfinteger values for S, and there is no correlation with the saturation moments. In some cases the Curie law is very badly obeyed.

Inelastic neutron scattering above the critical temperature does not reveal any spin fluctuations in chromium as it should with the Heisenberg model.

The magnetic entropy derived from specific heat experiments should be equal to $k \log(2S+1)$. For Fe, this gives S=1. For Cr, the entropy is very small, much smaller than what is expected from the magnetic moment.

Other properties indicate that outside the conduction band incompletely filled bands exist; this is true for all transitional metals (including the 2nd and 3rd series).

The linear electronic term in the specific heat is 5 to 10 times larger than in normal metals. This indicates that the density of states at the Fermi level is very large.

De Haas-Van Alphen experiments have been made in transitional metals, even in the magnetic case (Ni or Cr). They indicate clearly the existence of a Fermi surface for d electrons and give information on its shape.

Transport properties of transitional metals show that d electrons participate in the conduction mechanism. In particular, the galvanomagnetic properties of Fe, Co, and Ni can only be explained if the magnetic electrons are itinerant.

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The variation of the magnetic moment in alloys, as given by the Pauling-Slater curve, indicates very clearly that d bands exist. For example, when one adds Fe, Co, or Cr to Ni, the average saturation moment \overline{m} varies linearly with the concentration $d\overline{m}/dc = -\mu_B \Delta Z$ where ΔZ is the valence difference between the solute and the matrix. This can be understood easily with the filling of d bands for one spin direction. Similarly, the very different variations of \overline{m} with the addition of Cr or Ti indicate the appearance of d bound states above the Fermi energy [3].

The problem of magnetic transitional metals should thus be understood in the framework of a theory of all transitional metals. In particular, we have to understand why some of them are ferromagnetic (Fe, Co, Ni), antiferromagnetic (Cr, Mn, γ Fe) or non-magnetic (Sc, V, Ti, and the 2nd and 3rd series). We have then to understand why some magnetic properties are very similar to those deduced from the Heisenberg model. Finally, we have to explain why some magnetic materials (Fe, for example) are described better in terms of a localized picture (local moments at high temperature) than in terms of a band picture.

It is clear that we need a description in which the d electrons are itinerant. So we must have d bands with interacting electrons. The fact that we have itinerant electrons does not forbid the formation of local moments (around impurities in non-magnetic materials, for example).

2. THE BAND MODEL [2]

Transitional atoms are characterized by incompletely filled d shells. The filling of the d shell occurs from Sc, Ti... to Ni, Cu. The d orbitals are more compact than the s orbitals (4s for the first series; 5s and 6s for the 2nd and 3rd series). When the atoms are brought together to form a solid, there is a partial overlap of the atomic orbitals. This effect is very large for the valence (conduction) electrons and much smaller for d orbitals. In this case, it is a good approach to build linear combinations of atomic orbitals (LCAO) to describe the band states. A first approximation is to build these LCAO wave functions from the d orbitals only. We have thus two kinds of bands:

The conduction band with a width of the order of 10 eV.

The d bands with a width of the order of a few eV.

Theoretical treatments have often considered conduction and d bands as independent. In fact the s-d admixture should not be neglected and it may be important in parts of the Brillouin zone. It may have important effects and be responsible for a part of the d band width. Nevertheless, we shall neglect it and regard the d bands as being independent of the conduction band.

The band Hamiltonian is thus

$$H_{0} = \sum_{\substack{ij\sigma \\ m,m'}} T_{ij}^{mm'} C_{im\sigma}^{*} C_{im'\sigma}$$
(5)

where m and m' are indices for the orbital degeneracy (5 for d states), and i and j are indices for the atomic positions. The Hamiltonian given in Eq. (5) can always be diagonalized to

$$H_{0} = \sum_{\vec{k}\mu\sigma} \epsilon_{\mu\vec{k}} C_{\vec{k}\mu\sigma}^{*} C_{\vec{k}\mu\sigma}$$
(6)

 μ being a band index and \vec{k} a wave vector in the Brillouin zone. We shall refer to H_0 as the "kinetic" part though the ϵ_{ij} are matrix elements of the kinetic energy plus the periodic one-electron potential $V(\vec{r})$

$$T_{ij}^{mm} = \left\langle \phi_i^{*m}(\vec{r} \cdot \vec{R}_i) \left| \frac{p^2}{2m} + V(\vec{r}) \right| \phi_j^m(\vec{r} \cdot \vec{R}_j) \right\rangle$$

We have now to introduce interactions among the electrons. We shall keep only intra-atomic interactions, which are the most important. The Hartree-Fock Hamiltonian for the atom i is



where

$$U_{mm'} = \iint |\phi_{m}(\vec{r_{1}})|^{2} \frac{e^{2}}{|\vec{r_{1}} - \vec{r_{2}}|} |\phi_{m'}(\vec{r_{2}})| d\vec{r_{1}} d\vec{r_{2}}$$
$$J_{mm'} = \iint \phi_{m}^{*}(\vec{r_{1}}) \phi_{m'}(\vec{r_{2}}) \frac{e^{2}}{|\vec{r_{1}} - \vec{r_{2}}|} \phi_{m'}(\vec{r_{1}}) \phi_{m}^{*}(\vec{r_{2}})$$

 U_{mm^\prime} and J_{mm^\prime} are, respectively, Coulomb and exchange integrals. They should be corrected for intra-atomic correlation. The values of U and J have an order of magnitude of 10 eV and a few eV, respectively.

The total Hamiltonian for the d bands is

$$H = H_0 + \sum_i H_i$$
 (8)

Dealing with 5 d bands, even with the simplified interaction given by Eq.(7), is complicated, so that we shall essentially discuss a simplified model with one band (no orbital degeneracy) in the following sections.

This model with one band and intra-atomic interaction has been widely used. It corresponds to the Hamiltonian derived from expression (8)

$$H = \sum_{ij\sigma} T_{ij} C^*_{i\sigma} C_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$
(9)

Diagonalizing the kinetic energy, we obtain

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} C^*_{\vec{k}\sigma} C_{\vec{k}\sigma} + \frac{U}{N} \sum_{\vec{k},\vec{k'}q} C^*_{\vec{k}q\uparrow} C_{\vec{k}\uparrow} C^*_{\vec{k}\uparrow-\vec{q}\downarrow} C_{\vec{k}\downarrow}$$
(10)

where

$$\epsilon_{k} = \sum_{i} T_{ij} e^{i\vec{k}\cdot\vec{R}_{ij}}; \quad C_{\vec{k}\sigma} = \frac{1}{\sqrt{N}} \sum_{i} C_{i\sigma} e^{i\vec{k}\cdot\vec{R}_{i}} (\vec{R}_{ij} = \vec{R}_{i} - \vec{R}_{j})$$

Even with the simplified Hamiltonian the problem is very difficult. It is a many-body problem, and we shall use various approaches to discuss it - Hartree-Fock, RPA, etc. Note that we do not know the fundamental state of the kinetic energy (10); we do not even know if it is a magnetic state.

3. HARTREE-FOCK STONER THEORY [4]

We shall first make the simplest approximation: the Hartree-Fock approximation. As we are interested in magnetic problems, it will be an "unrestricted" Hartree-Fock approximation. This description of band magnetism was first made by Stoner.

As usual, we keep only the terms involving one number operator in the interaction terms and obtain

$$\underbrace{\frac{U}{N}}_{\vec{k}\vec{k'}} n_{\vec{k}\uparrow} n_{k'\downarrow}$$

We then replace $n_{\vec{k}\uparrow}$, $n_{\vec{k}\downarrow}$ by $(\overline{n}_{\vec{k}\uparrow}, n_{\vec{k}\downarrow} + n_{\vec{k}\uparrow}\overline{n}_{\vec{k}\downarrow})$ where $\overline{n}_{\vec{k}\sigma}$ are average values of $n_{\vec{k}\sigma}$ which will have to be determined in a self-consistent way. The one-electron Hartree-Fock Hamiltonian \tilde{H} is

$$\widetilde{H} = \sum_{\vec{k}} \epsilon_{\vec{k}} C_{\vec{k}\sigma}^* C_{\vec{k}\sigma} + \frac{U}{N} \sum_{\vec{k}\vec{k}'} (\overline{n}_{\vec{k}\uparrow} n_{\vec{k}\downarrow} + n_{\vec{k}\uparrow} \overline{n}_{\vec{k}\downarrow}) = \sum_{\vec{k}\sigma} E_{\vec{k}\sigma} n_{\vec{k}\sigma}$$
(11)

where the one-electron H-F energies $\mathrm{E}_{\vec{k}\sigma}$ are

$$\mathbf{E}_{\vec{k}\sigma} = \epsilon_{\vec{k}} + \frac{U}{N} \sum_{k'} \overline{n}_{\vec{k'}, -\sigma}$$
(12)

Equation (12) can be written

$$\mathbf{E}_{\vec{k} \sigma} = \epsilon_{\vec{k}} + \frac{1}{N} \sum_{\vec{k}' \sigma'} (\mathbf{U} - \mathbf{U} \delta_{\sigma \sigma'}) \overline{\mathbf{n}}_{\vec{k}' \sigma'}$$

where two terms appear: the first term is the Coulomb term, the second one is the exchange term. Note that this Hartree-Fock solution is particularly simple. The one-electron states are the same as for the non-interacting system. Let $n_0 = 1/N \sum \overline{n_{\vec{k}\sigma}}$. $n = n \uparrow + n_{\downarrow}$ is the average number

of electrons per atom, m = nt - nt the magnetization per atom (in Bohr magnetons). Equation (12) becomes

$$E_{k\sigma} = \epsilon_{k} + Un_{-\sigma}$$
(13)

3.1. Non-magnetic Hartree-Fock solution at T = 0

 $= 1 \quad \text{if} \quad \mathbf{E}_{\overrightarrow{k\sigma}} < \mathbf{E}_{\mathbf{F}}$ $= 0 \quad \text{if} \quad \mathbf{E}_{\overrightarrow{k\sigma}} > \mathbf{E}_{\mathbf{F}}$

 E_{F} is determined so as to have the good number n of electrons per atom.

Let us study the stability of this state with respect to ferromagnetism. If we take a shell of thickness δE of down-spin electrons and put them in the spin-up band (Fig. 2), the change in the kinetic energy is

$$\Delta T = \rho(E_F) \delta E^2$$

where $\rho(E)$ is the density of states. The variation of the interaction energy is

$$\Delta \mathbf{E}_{int} = \mathbf{U} \left[\frac{\mathbf{n}}{2} + \rho \delta \mathbf{E} \right] \left[\frac{\mathbf{n}}{2} - \rho \delta \mathbf{E} \right] - \mathbf{U} \frac{\mathbf{n}^2}{4} = -\mathbf{U} \rho^2 (\mathbf{E}_F) \delta \mathbf{E}^2$$

The total change in energy is

$$\Delta \mathbf{E} = \rho(\mathbf{E}_{\mathbf{F}}) \, \delta \mathbf{E}^{2} [1 - \mathbf{U} \, \rho(\mathbf{E}_{\mathbf{F}})]$$

We see that ΔE is quadratic in δE (Hartree-Fock solution) and that the non-magnetic state is a stable state (minimum energy) when $U \rho(E_F) \leq 1$.

The condition for a differential ferromagnetic instability of the non-magnetic state is

$$U\rho(E_{\rm F}) > 1 \tag{14}$$





FIG. 3. Calculation of the susceptibility.

FIG. 2. Density of states for spin up and down.

When the non-magnetic state is stable, we can calculate its susceptibility. With a field $\rm H_0$ in the z direction the Hartree-Fock one-electron energies are

$$E_{\vec{k}\uparrow} = \epsilon_{\vec{k}} + U_n \downarrow - g \frac{\mu_B H_0}{2}$$

$$E_{\vec{k}\downarrow} = \epsilon_{\vec{k}} + U_n \uparrow + g \frac{\mu_B H_0}{2}$$
(15)

The up and down bands are displaced by $\pm\,\delta \mathrm{E}$ (see Fig. 3) where

$$\mathbf{E}_{\overrightarrow{\mathbf{k}}\downarrow} - \mathbf{E}_{\overrightarrow{\mathbf{k}}\uparrow} = 2\delta \mathbf{E} = \mathbf{U}(\mathbf{n}\uparrow - \mathbf{n}\downarrow) + g\mu_{\mathbf{B}}\mathbf{H}_{\mathbf{0}} \quad (\mathbf{n}\downarrow) \text{ with } \mathbf{n}\uparrow - \mathbf{n}\downarrow = 2\rho(\mathbf{E}_{\mathbf{F}})\delta(\mathbf{E})$$

So we get

$$\delta \mathbf{E} = \frac{g\mu_{B}H_{0}}{2[1 - U\rho(\mathbf{E}_{F})]}$$

The change in the total energy is: $\Delta E = \Delta \left(\sum_{\sigma} E_{\vec{k}\sigma} \right) - \Delta E_{int}$ where we

subtract the interaction energy which has been counted twice with the Hartree-Fock Hamiltonian (11). We get for ΔE

$$\Delta \mathbf{E} = -\rho(\mathbf{E}_{F})\delta \mathbf{E}^{2} + \mathbf{U}^{2}\rho^{2}(\mathbf{E}_{F})\delta \mathbf{E}^{2} = -\frac{1}{4} \mathbf{g}^{2}\mu_{B}^{2}H_{0}^{2} \frac{\rho(\mathbf{E}_{F})}{1 - U\rho(\mathbf{E}_{F})}$$

where E is equal to $-\chi H_0^2/2$, we have for the susceptibility

$$\chi = \frac{\chi^0}{1 - U\rho(E_F)} \tag{16}$$

where \boldsymbol{X}^0 is the Pauli susceptibility of the non-interacting electron gas:

$$\chi^0 = \frac{g^2 \mu_B^2}{2} \rho(E_F)$$

The susceptibility has been enhanced by the factor

$$S = \frac{1}{1 - U\rho(E_F)}$$
(17)

X becomes infinite when the instability criterion (14) is fulfilled:

$$U\rho(E_F) = 1$$

3.2. Magnetic solutions

If the non-magnetic state is unstable, we may have either complete ferromagnetism (a) or partial ferromagnetism (b) at T = 0 (see Fig. 4). This depends on the band structure through $\rho(E)$ and on the average number n of electrons per atom. In case (a) we can verify that the wave function of the ferromagnetic state is an exact eigenfunction of the Hamiltonian (10). It is the eigenfunction of the lowest energy for the maximum of S_z but we do not know if it is the ground-state wave function and if it has anything to do with it. In case (b) the Hartree-Fock wave function is not an eigenfunction of the Hamiltonian (10).

In the magnetic case, at finite temperatures and zero field, we have to solve a self-consistent equation for m (it looks very much as in the molecular field theory)

$$m = n \dagger - n \downarrow = \frac{1}{N} \sum_{k} [f(E_{\vec{k} \dagger}) - f(E_{\vec{k} \downarrow})]$$
(18)

where f(E) is the Fermi function $1/\{\exp[(E-E_F)/k_BT)]+1\}$; E_F is determined by $n\uparrow+n\downarrow=n$, and the $E_{k\sigma}^{+}$ are given by Eq.(13). We shall not discuss in detail the solution of Eq.(18), which depends on the band structure. We shall only give some results.

m(T) is given schematically in Fig.5. At low temperatures ¹, the magnetization is given for the complete ferromagnetic case by



FIG. 4. Complete (a) and partial (b) ferromagnetism.

¹ There is also complete magnetism if we have only spin-down holes.



FIG. 5. Magnetization as a function of temperature.

where $\Delta = Un - E_F$ is the energy necessary to excite an electron from the spin-up band to the spin-down band (see Fig.4a). In the case of partial magnetism $\Delta = 0$ (Fig.4b), and m(T) behaves as

$$m(T) = m(0) [1 - \beta T^2]$$

In both cases, we do not find the Bloch law $(T^{3/2})$; this is obviously, since in the H-F approximation only individual excitations are considered.

The Curie temperature $\mathbf{T}_{\mathbf{c}}$ is given by the condition

$$1 = \frac{1}{N} \sum_{\substack{i=1\\j \neq i}} \left[\frac{df(\mathbf{E}_{\vec{k}\uparrow})}{dm} - \frac{df(\mathbf{E}_{\vec{k}\downarrow})}{dm} \right]_{m=0}$$

Using Eq.(13), we obtain

$$1 = -\frac{U}{N} \sum_{\vec{k}} \frac{df(\vec{E}_{\vec{k}})}{d\vec{E}_{\vec{k}}} \bigg|_{m=0}$$

i.e.

$$U\int\rho(E)\,\frac{df}{dE}\,dE=-1$$

This equation determines T_c which goes to 0 when $U\,\rho(E_F)$ = 1 [for T = 0 we have df/dE = -\delta(E-E_F)].

Above T_c it is easy to obtain the susceptibility. In the presence of a magnetic field H_0 , m satisfies Eq.(18) where the $E_{\vec{k}\sigma}$ are given by Eq.(15). For the susceptibility we get

$$\chi = \frac{g\mu_B}{2} \left. \frac{dm}{dH_0} \right|_{H_0 = 0}$$

$$\frac{\mathrm{dm}}{\mathrm{dH}_{0}}\bigg|_{\mathrm{H}_{0}=0} = \frac{1}{N} \sum_{\vec{k}} \left[\frac{\mathrm{df}(\mathrm{E}_{\vec{k}\uparrow})}{\mathrm{dH}_{0}} + \frac{\mathrm{df}(\mathrm{E}_{\vec{k}\uparrow})}{\mathrm{dm}} + \frac{\mathrm{df}(\mathrm{E}_{\vec{k}\downarrow})}{\mathrm{dH}_{0}} - \frac{\mathrm{df}(\mathrm{E}_{\vec{k}})}{\mathrm{dH}_{0}} - \frac{\mathrm{df}(\mathrm{E}_{\vec{k}\downarrow})}{\mathrm{dm}} + \frac{\mathrm{dm}}{\mathrm{dH}_{0}} \right]_{\mathrm{H}_{0}=0}$$

$$= \frac{1}{N} \sum_{\substack{\vec{k} \\ \vec{k}}} \frac{df}{dE} \left[-U \frac{dm}{dH_0} - g\mu_B \right]_{H_0 = 0}$$

It follows that

$$\chi = \frac{g^2 \mu_B^2}{2} \frac{\rho(T)}{1 - U\rho(T)}$$
(19)

where $\rho(T)$ is an effective density of states at the temperature T

$$\rho(T) = \int \rho(E) \frac{df}{dE} dE$$
 (20)

3.3. Applications

The Hartree-Fock theory has been widely used for explaining the properties of ferromagnetic metals and alloys. With intra-atomic interactions the properties of the system depend only on the density of states curve. It is commonly recognized that Ni is a case of complete magnetism (with 0.6 d holes per atom), and that Fe and Co are cases of partial ferromagnetism.

The Hartree-Fock theory provides an explanation of the nonintegral values of Bohr magnetons of the saturated magnetization. It also explains the magnetization of alloys at T = 0: dm/dc = $-\Delta Z \mu_B$ is well understood by the filling of d bands. The peculiarities of the Slater-Pauling curve (Cr or Ti) can be very well understood by a Hartree-Fock treatment where the d electrons on the impurity are submitted to a strong repulsive potential.

It also explains why the susceptibility may be different from a Curie susceptibility. There is no a priori reason why the susceptibility given by (19) should behave as $(T-T_p)^{-1}$ at high temperatures. If this is the case, it is not surprising that the Curie constant does not correspond to a half-integer value for S. Nor is it surprising that there are spin fluctuations above T_c and that the magnetic entropy should be different from what is expected in the Heisenberg model.

Finally, the band model is in accordance with all the experiments which show the existence of d bands (electronic specific heat, transport properties, Fermi surfaces, etc.).

In conclusion, we can say that <u>qualitatively</u> the Hartree-Fock treatment of the band model gives a satisfactory explanation of many properties of transitional metals and alloys. For a better understanding of their properties, we need a precise knowledge of the band structure, but we also have to treat the electron interaction in a less simple way. This will be done in the next sections where we shall discuss the notion of spin waves in the band model and the influence of correlation and spin fluctuations.

4. SPIN WAVES IN THE RANDOM PHASE APPROXIMATION [5]

In the last section with the Hartree-Fock approximation (which is time-independent) we have considered individual excitations only; an excited state lowering the spin by one unit²

$$\psi_{\vec{k}\,\vec{q}} = C^*_{\vec{k}+\vec{q}\downarrow} C_{\vec{k}\uparrow} | \psi_{\text{fund}} \rangle$$

has an excitation energy of $E_{\vec{k}+\vec{q}\downarrow} - E_{\vec{k}\uparrow} \simeq U(n\uparrow -n\downarrow)$ for small q. It is obvious that within this framework we cannot describe collective excitations (spin waves) which should have excitation energies Dq^2 for small q.

The simplest thing to do is to try to build up spin waves as a linear combination of individual excitations:

$$\psi(\vec{q}) = \sum_{\vec{k}} \alpha_{\vec{k}} \psi_{\vec{k} \vec{q}}$$
(21)

Obviously, this is an approximation, because true spin waves should also have terms involving the creation of electron hole pairs of the same spin; for example, for one pair the term would be

$$C^*_{\vec{k}+\vec{q}'\downarrow}C_{\vec{k}\uparrow}C^*_{\vec{k}'+\vec{q}'\sigma}C_{\vec{k}'\sigma}|\psi_{fund}\rangle$$

with $\vec{q}' + \vec{q}'' = \vec{q}$.

To build a wave function of type (21), we shall consider the equation of motion for the operators $B_{\vec{k}\vec{q}}^* = C_{\vec{k}+\vec{q}\downarrow}^* C_{\vec{k}\uparrow}^*$ where H is given by Eq.(10). We have

$$\frac{\mathbf{i} \mathbf{d} \mathbf{B}_{\vec{k}\vec{q}}^{*}}{\mathbf{d}\mathbf{t}} = [\mathbf{H}, \mathbf{B}_{\vec{k}\vec{q}}^{*}]^{=}$$
$$= (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}) \mathbf{B}_{\vec{k}\vec{q}}^{*} - \frac{\mathbf{U}}{\mathbf{N}} \sum_{\vec{k}' \cdot \vec{q}_{\downarrow}} \mathbf{C}_{\vec{k}+\vec{q}_{\downarrow}} \mathbf{C}_{\vec{k}' - \vec{q}'_{\downarrow}} \mathbf{C}_{\vec{k}' - \vec{q}'_{\downarrow}} \mathbf{C}_{\vec{k}' + \vec{q}_{\downarrow}} \mathbf{C}_{\vec{k}' - \vec{q}'_{\downarrow}} \mathbf{C}_{\vec{k}' + \vec{q}_{\downarrow}} \mathbf{C}_{\vec{k}' + \vec{q}_{\vec{k}'}} \mathbf{C}_{\vec{k}' + \vec{q}_{\vec{k}'}} \mathbf{C}_{\vec{k}' + \vec{q}_{\vec{k}'}} \mathbf{C}_{\vec{k}' + \vec{q}} \mathbf{C}_{\vec{k}' + \vec{q}}$$

$$-\frac{U}{N}\sum_{\vec{k},\vec{q},\vec{q}}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}^{*}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}^{*}C_{\vec{k}\uparrow}C_{\vec{k}\downarrow}C_{\vec{k}\uparrow}C_{\vec{k}\downarrow}C_{\vec{k}\uparrow}C_{\vec{k}\downarrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\uparrow}C_{\vec{k}\downarrow}C_{\vec{k}}C_{\vec{k}}C_{\vec{$$

Within the random phase approximation (RPA), we shall keep only the terms in which operator numbers $n_{\vec{k}\sigma}$ appear and shall replace them by their average values $\bar{n}_{\vec{k}\sigma}$ in the fundamental state $|\psi\rangle$ in the last term of (22). This can be extended to the case T $\neq 0$ if we take Hartree-Fock averages at the temperature T (see below). The second term of (22) gives

 $[\]vec{k}$ and \vec{q} are wave vectors within the first Brillouin zone. $\vec{k} + \vec{q}$ may be outside the first Brillouin zone. In this case it may be brought back into the first Brillouin zone with the help of a vector \vec{k} of the reciprocal lattice. $\vec{k} + \vec{q}$ means in fact $\vec{k} + \vec{q} + \vec{K}$ where \vec{K} is such that $\vec{k} + \vec{q} + \vec{K}$ is within the first Brillouin zone. Throughout this paper we shall keep the notation $\vec{k} + \vec{q}$ with this new meaning. It may be particularly important to take into account these "umklapp processes" (see section 6).

$$-\frac{U}{N}\sum_{\vec{k'}} \vec{n}_{\vec{k'}\downarrow} B_{\vec{k}\vec{q}}^* - \frac{U}{N}\sum_{\vec{q'}} \vec{n}_{\vec{k}+\vec{q}\downarrow} C_{\vec{k}-\vec{q'}\uparrow} C_{\vec{k}+\vec{q}-\vec{q'}\downarrow}^*$$
(23)

The third term of (22) gives

$$\frac{U}{N}\sum_{\vec{k'}} \overline{n}_{\vec{k'}\uparrow} B_{\vec{k}\vec{q}}^{\pm} + \frac{U}{N}\sum_{\vec{k'}} \overline{n}_{\vec{k}\uparrow} C_{\vec{k'}\uparrow} C_{\vec{k'}\uparrow}^{\pm} q_{\downarrow}$$
(24)

The first terms of (23) and (24) transform $\varepsilon_{\overrightarrow{k}}$ into the Hartree-Fock one-electron energies $\mathrm{E}_{\overrightarrow{k}\sigma}$ such that we have

$$i \frac{d \mathbb{B}_{kq}^{*}}{dt} = [H, \mathbb{B}_{kq}^{*}] \approx [\mathbb{E}_{\vec{k}+\vec{q}\downarrow} - \mathbb{E}_{\vec{k}\uparrow}] \mathbb{B}_{\vec{k}\vec{q}}^{*} + (\overline{n}_{\vec{k}+\vec{q}\downarrow} - \overline{n}_{\vec{k}\uparrow}) \frac{U}{N} \sum_{\vec{k}} \mathbb{B}_{\vec{k}\uparrow\vec{q}}^{*}$$
(25)

The linearized set of Eqs (25) is easy to solve. We look for an operator B^{\ast} of the form

$$B^{*}(\vec{q}) = \sum_{\vec{k}} \alpha_{\vec{k}} B^{*}_{\vec{k} \vec{q}}$$
(26)

such that

$$[H, B^*(\vec{q})] = E B^*(\vec{q})$$
 (27)

If we apply (27) to $|\psi_{\text{fund}}\rangle$, exact or approximate Hartree-Fock eigenstate of H, then $B(\vec{q})|\psi_{\text{fund}}\rangle$ is an approximate eigenstate of H with energy $E_{\text{fund}} + E$.

Writing Eq.(27) with the help of the relation (25) we get

$$\sum_{\vec{k}} \alpha_{\vec{k}} \left[E - \left(E_{\vec{k} + \vec{q} \downarrow} - E_{\vec{k} \uparrow} \right) \right] B_{\vec{k} \vec{q}}^* = \frac{U}{N} \sum_{\vec{k} \vec{k'}} \left(\overline{n}_{\vec{k} + \vec{q} \downarrow} - \overline{n}_{\vec{k} \uparrow} \right) \alpha_{\vec{k}} B_{\vec{k'} \vec{q}}^*$$
(28)

The independence of the $B_{\overrightarrow{kq}}^{\ast}$ leads to the set of linear equations

$$\alpha_{\vec{k}} \left[E - \left(E_{\vec{k} + \vec{q} \downarrow} - E_{\vec{k} \uparrow} \right) \right] = \frac{U}{N} \sum_{\vec{k}'} \left(\vec{n}_{\vec{k}' + q \downarrow} - \vec{n}_{\vec{k}' \uparrow} \right) \alpha_{\vec{k}'} = A$$
(29)

The second part of this equation is a constant A independent of k so that we can solve for $\alpha_{\overrightarrow{k}}$

$$\alpha_{\vec{k}} = \frac{A}{E - (E_{\vec{k}} \rightarrow q_{\downarrow}} - E_{\vec{k}})}$$
(30)

Putting back (30) into (29) gives the eigenvalue equation

$$\frac{U}{N}\sum_{\vec{k}}\frac{\vec{n}_{\vec{k}+\vec{q}\downarrow}-\vec{n}_{\vec{k}\uparrow}}{E-(E_{\vec{k}+\vec{q}\downarrow}-E_{\vec{k}\uparrow})} = 1$$
(31)

The eigenvalues E can be found by a graphical discussion. Let F(E) be the function of E in the first term of Eq.(31). F(E) is infinite when $E = E_i(q) = E_{\vec{k}+\vec{q}\downarrow} - E_{\vec{k}\uparrow}$, one of the excitation energies of the Hartree-Fock description. The E_i are bounded by $E_{min}(\vec{q})$ and $E_{max}(\vec{q})$. The function F(E) has the behaviour given by Fig.6 and the roots are given by F(E) = 1. We see that if there were, for a given value of \vec{q} , M excitation energies $E_i(\vec{q})$ in the Hartree-Fock description, we now find M - 1 roots which are very close to the old values E_i . These are "individual" excitations. The last one is smaller than $E_{min}(\vec{q})$ and well separated. It is a "collective" excitation, a spin-wave. When the spin-wave energy is well separated from the pseudo-continuum of individual excitations we can replace the sum in Eq.(31) by an integral, letting the system become infinite. The spin wave energy is thus given by

$$\frac{U}{(2\pi)^3} \int \frac{\vec{n}_{\vec{k}+\vec{q}\downarrow} - \vec{n}_{\vec{k}\uparrow}}{E - (E_{\vec{k}+\vec{q}\downarrow} - E_{\vec{k}\uparrow})} d^3 k = 1$$
(32)

When $q \rightarrow 0$, $E \rightarrow 0$, as is easily seen from Eq.(32). This corresponds to the fact that the q=0 mode corresponds to a rotation of the whole magnetization. It is easily seen by a development in powers of q that for small q E behaves as $E \simeq Dq^2$.

Let us take a simple example: a spherical band with an effective mass m^{*}. In the Hartree-Fock ground state, the Fermi surfaces for up or down spins have the radii k_{Ft} and k_{Ft} . Then, for small q



FIG. 6. Graphical discussion of the roots of Eq. (31)

The pseudo-continuum of individual excitations with spin reversal corresponds to the shadowed part of Fig.7. The spin-wave energy for small q turns out to be

$$\mathbf{E} = \frac{\mathbf{q}^2}{2\mathbf{m}^*} \left[\frac{\mathbf{n}}{\mathbf{m}} - \frac{4}{3\mathbf{U}\mathbf{m}^2} \left(\epsilon \dagger \mathbf{n} \dagger - \epsilon \downarrow \mathbf{n} \downarrow \right) \right]$$

where n is the number of electrons per atom, m is the magnetization and ϵ_1 and ϵ_4 are the average kinetic energies of up and down electrons in the Hartree-Fock ground state.

When q increases, at the point q_c the spin-wave energy becomes equal to $E_{\min}(\vec{q})$. For $q > q_c$, the spin waves are no longer exact eigenstates in the RPA; they are damped (see next section). It can be verified that the spin-wave curve of Fig.7 runs tangentially into the boundary of the pseudo-continuum $\nabla_{\vec{q}} E(\vec{q}) = \nabla_{\vec{q}} E_{\min}(\vec{q})$.



FIG. 7. Individual excitations and spin waves,

A spin-wave with vector \vec{q} represents a bound state for the electronhole pair; for low q values the binding energy is approximately $-U(n\uparrow -n\downarrow)$. The spin wave function $\psi(\vec{q})$ is

$$\psi(\vec{q}) = B^{*}(\vec{q}) \left| \psi_{\text{fund}} \right\rangle = \sum_{\vec{k}} \alpha_{\vec{k}} C^{*}_{\vec{k}+\vec{q}\downarrow} C_{\vec{k}\uparrow} \left| \psi_{\text{fund}} \right\rangle$$

where the $\alpha_{\vec{k}}$ are given by expression (30), E being the spin-wave root of Eq.(31). Spin waves may be regarded as bosons: the physical reason is that among the M individual excitations (Fig.6) only one is a collective excitation. We can thus construct a wave function with two spin waves $\psi(\vec{q}, \vec{q}') = B^*(\vec{q}) B^*(\vec{q}') | \psi_{\text{fund}} \rangle$. We shall find the same result for the B^* to the order of 1/M (that is 1/N). This remains true as long as the number of spin waves is not a finite fraction of N. (This can be seen also in calculating the commutators of the various B^* and applying the result on $|\psi_{\text{fund}} \rangle$.) Having introduced spin waves, we again find, using Bose statistics, that the magnetization for small T (small number of spin waves) behaves as

$$m(T) = m(0) [1 - \alpha T^{3/2}]$$

At finite temperatures we can also define approximate spin waves if we use for $\overline{n_k}$ in (31) the average values of $n_{\vec{v}}$ corresponding to the

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temperature T. We can use, for example, the Hartree-Fock values and get an approximate renormalization of the spin-wave energies. The best method would be to use the average values $\overline{n_k}$ taking into account the individual and collective excitations: this is difficult because, at finite temperature, the number of excited spin waves is a finite fraction of the number of excitations; they can no longer be regarded exactly as bosons and their existence diminishes the number of degrees of freedom among individual excitations by a finite amount. In fact, the problem has only been treated in the limit $T \rightarrow 0$.

<u>Remarks</u>: One can also define spin waves for a non-magnetic state in the presence of a magnetic field H_0 . The result is the same as in expressions (31) and (32), but with Hartree-Fock one-electron energies $E_{k\sigma}$ given by Eqs (15). For $q \rightarrow 0$ the one-electron excitation energies tend to

$$\mathbf{E}_{\vec{k}\downarrow} - \mathbf{E}_{\vec{k}\uparrow} = \mathbf{U}(n\uparrow - n\downarrow) + g\mu_{\mathbf{B}}\mathbf{H}_{\mathbf{0}}$$

which gives, at T = 0 (see the reasoning of Eq.(15)),

$$\mathbf{E}_{\vec{k}\downarrow} - \mathbf{E}_{\vec{k}\uparrow} = \frac{g\mu_{B} H_{0}}{1 - U\rho(\mathbf{E}_{F})} = \mathrm{S} g \mu_{B} H_{0}$$

S being the enhancement factor (17). Inserting this into Eq.(32) for q = 0 easily gives the energy E(0) of the spin-wave mode

$$E(0) = g \mu_B H_0 \tag{33}$$

This result is exactly the energy which is associated with the frequency of free spins in a magnetic field H_0 . The individual and spin-wave excitations are given schematically for any q in Fig.8 for this case. The spin waves merge into the pseudo-continuum for a critical value q_c . The exact result (33) remains true in Landau's theory of Fermi liquids (see section 7). Observations of such spin waves in non-magnetic metals (and normal metals) have been made by transmission of electromagnetic waves. The shape of E(q) for low q gives information on the interactions [6].

5. SUSCEPTIBILITIES – EQUIVALENCE BETWEEN THE RPA AND THE TIME-DEPENDENT HARTREE-FOCK APPROXIMATION

5.1. Definition and properties of the susceptibilities [7,8]

According to the theory of linear response, one can introduce wavevector and frequency-dependent susceptibilities $\chi(\vec{q},\omega)$. In an isotropic medium, for a small field $h(\vec{R}_i,t)$ in the z direction the magnetization is

$$m(\vec{R}_{i}, t) = \sum_{j} \int dt' X(\vec{R}_{i} - \vec{R}_{j}, t - t') h(\vec{R}_{j}, t')$$
(34)



FIG. 8. Individual and spin wave excitations in a normal non-magnetic metal with a magnetic field H_0 .

 $X(R_i, t)$ is the response to a field

$$h(\dot{R}_i, t) = h \delta_{\vec{R}_i} \delta(t)$$

Taking the Fourier transform of Eq. (34) we have

$$m(\vec{q}, \omega) = \chi(\vec{q}, \omega) h(\vec{q}, \omega)$$
(35)

where ω has a small imaginary part $i\eta$; $\chi(\vec{q}, \omega)$ characterizes the response of the system to a magnetic field $h(\vec{R}_i, t) = h(\vec{q}, \omega) \exp[-i(\omega t - \vec{q} \cdot \vec{R}_i)]$. For a real field $h(q, \omega)\cos(\omega t - \vec{q} \cdot \vec{R}_i)$ the real magnetization is evidently

$$m(\vec{R}_{i}, t) = h(\vec{q}, \omega) \operatorname{Re}[\chi(\vec{q}, \omega) e^{-i(\omega t - \vec{q} \cdot \vec{R}_{i})}]$$
(36)

where Re means "real part".

When the system is anisotropic, having a privileged z axis (this happens, for example, in the ferromagnetic case) we can define longitudinal and transverse susceptibilities.

The longitudinal susceptibility $\chi_L(\vec{q}, \omega)$ is the response to a magnetic field along the z axis $h_z(\vec{q}, \omega) \exp[-i(\omega t - \vec{q} \cdot \vec{R}_i)]$ so that $\chi_L(\vec{q}, \omega) = \chi_{zz}(\vec{q}, \omega)$. The perturbing Hamiltonian is

$$H_{L}^{P} = -\frac{g\mu_{B}h}{2} e^{-i\omega t} \sum_{i} e^{i\vec{q}\cdot\vec{R}_{i}} (C_{i\uparrow}^{*}C_{i\uparrow} - C_{i\downarrow}^{*}C_{i\downarrow})$$

Introducing the operators $\mathbf{C}_{\mathbf{k}}$ which diagonalize the kinetic energy and the q component of the magnetization

$$\sigma_{\mathbf{q}}^{\mathbf{z}} = \frac{1}{2N} \sum_{\mathbf{k}} \left(C_{\vec{k}+\vec{q}\uparrow}^{\mathbf{x}} C_{\vec{k}\uparrow} - C_{\vec{k}+\vec{q}\downarrow}^{\mathbf{x}} C_{\vec{k}\downarrow} \right)$$
(37)

we have for H

$$H_{L}^{P} = -Ng\mu_{B}h(\vec{q},\omega)e^{-i\omega t}\sigma_{-q}^{Z}$$
(38)

In the Heisenberg representation (taking into account $H^p_L)\,\sigma^z_q$ varies with time and the Fourier transform of the magnetization per atom is

$$m_{L}(\vec{q},\omega) = \chi_{L}(\vec{q},\omega) h = g \mu_{B} \sigma_{q}^{Z}(t) e^{-i\omega t}$$
(39)

For the transverse case, we can proceed as follows. Let us consider a magnetic field in the x-y plane having components h exp[-i($\omega t - \vec{q} \cdot \vec{R}_i$)] and i h exp[-i($\omega t - \vec{q} \cdot \vec{R}_i$)] along the x and y axis, respectively. The corresponding real field has components: h cos($\omega t - \vec{q} \cdot \vec{R}_i$) and h sin($\omega t - \vec{q} \cdot \vec{R}_i$). This field on a given \vec{R}_i rotates in the positive direction with time. At a given time, the field is constant in the planes $\vec{q} \cdot \vec{R}_i$ = const. and rotates in the negative direction from plane to plane when $\vec{q} \cdot \vec{R}_i$ increases. With such a field, the perturbing Hamiltonian is

$$H^{P} = -g \mu_{B} h e^{-i\omega t} \sum_{i} e^{i\vec{q}\cdot\vec{R}_{i}} C^{*}_{i\uparrow} C_{i\downarrow}$$
$$= -Ng \mu_{B} h (q, \omega) e^{-i\omega t} \sigma^{+}_{-q}$$
(40)

(41)

where

The response is given by

$$\mathbf{m}_{\mathbf{x}}(\vec{\mathbf{q}},\omega) = \mathbf{m}_{\mathbf{x}}(\vec{\mathbf{q}},\omega) - i\mathbf{m}_{\mathbf{y}}(\vec{\mathbf{q}},\omega) = g\mu_{\mathsf{B}}\sigma_{\rho}^{-}(t)e^{i\omega t}$$

where

$$\sigma_{\mathbf{q}}^{-} = \frac{1}{N} \sum_{\vec{k}} C^{*}_{\vec{k}+\vec{q}\downarrow} C_{\vec{k}\uparrow}$$

 $\sigma_{q}^{+} = \frac{1}{N} \sum_{\vec{x}} C_{\vec{k}+\vec{q}\uparrow}^{*} C_{\vec{k}\downarrow}$

By definition we shall write:

$$\mathbf{m}_{(\vec{q},\omega)} = \chi_{+}(\vec{q},\omega) h(\vec{q},\omega)$$
(42)

Now, we obviously have

$$m_{+}(\vec{q}, \omega) = m_{x}(\vec{q}, \omega) + i m_{y}(\vec{q}, \omega) = 0$$

so that

$$m_x(\vec{q},\omega) = \frac{1}{2}\chi_{+}(\vec{q},\omega)h(\vec{q},\omega)$$

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And we have for the transverse susceptibility $\chi_{T} = \chi_{xx} = \chi_{yy}$

$$\chi_{\rm T}(\vec{\rm q},\omega) = \frac{1}{2} \chi_{-+}(\vec{\rm q},\omega) \tag{43}$$

One could as well have introduced a field rotating in the opposite direction and defined $\chi_{+}(q, \omega)$. Evidently $\chi_{+} = \chi_{-+} \rightarrow \chi_{L}(\vec{q}, \omega)$ and $\chi_{T}(\vec{q}, \omega)$ (susceptibilities per atom) satisfy the Kubo formulae

$$X_{L}(q,\omega) = i g^{2} \mu_{B}^{2} \int_{0}^{\infty} e^{i\omega t} \overline{\left[\sigma_{\vec{q}}^{Z}(t), \sigma_{-\vec{q}}^{Z}(0)\right]} dt$$
(44)

$$X_{T}(\vec{q},\omega) = \frac{1}{2} X_{-+}(\vec{q},\omega) = \frac{1}{2} g^{2} \mu_{B}^{2} \int_{0}^{\infty} e^{i\omega t} \overline{[\sigma_{\vec{q}}(t), \sigma_{-\vec{q}}^{+}(0)]} dt$$

In Eqs (44) the operators at time t are Heisenberg operators varying in time under the influence of the Hamiltonian H (without H^P) and thus the Kubo formulae are relations between the susceptibilities and the spin fluctuations of the system without magnetic field.

In the following we shall be interested in the transverse susceptibility. Above T_c , we have $X_T = X_L$.

5.2. Susceptibilities in the RPA. Time-dependent Hartree-Fock approximation

Let us calculate the transverse susceptibility for the Hamiltonian (10). We have to calculate the commutators $[H+H^P, B^*_{kq}]$. Making the RPA in $[H, B^*_{kq}]$, we get from (25)

$$i \frac{d B_{\vec{k}\vec{q}}^{*}}{dt} = [H + H_{-}^{P}, B_{\vec{k}\vec{q}}^{*}] \simeq [E_{\vec{k}+\vec{q}\downarrow} - E_{\vec{k}\uparrow}] B_{\vec{k}\vec{q}}^{*}$$
$$+ (\overline{n}_{\vec{k}+\vec{q}\downarrow} - \overline{n}_{\vec{k}\uparrow}) \frac{U}{N} \sum_{\vec{k}\uparrow} B_{\vec{k}\uparrow\vec{q}}^{*} + (n_{\vec{k}+\vec{q}\downarrow} - n_{\vec{k}\uparrow}) g \mu_{B} h e^{-i\omega t}$$
(45)

Taking the average, we obtain

$$i \frac{d \mathbf{B}_{\vec{k}\vec{q}}^{*}}{dt} = [\mathbf{E}_{\vec{k}+\vec{q}\downarrow} - \mathbf{E}_{\vec{k}\uparrow}] \overline{\mathbf{B}_{\vec{k}\vec{q}}^{*}} + (\overline{n}_{\vec{k}+\vec{q}\downarrow} - \overline{n}_{\vec{k}\uparrow})$$
$$\times \left[\frac{U}{N} \sum_{\vec{k}} \overline{\mathbf{B}_{\vec{k}\cdot\vec{q}}^{*}} + g \mu_{B} h e^{-i\omega t} \right]$$

We want the Fourier component of $\overline{\mathbf{B}^*}$ at the frequency ω : it is

$$\overline{\mathbf{B}}_{\vec{q}\,\omega}^{*} = \frac{\overline{\mathbf{n}}_{\vec{k}+\vec{q}\downarrow} - \overline{\mathbf{n}}_{\vec{k}\uparrow}}{\omega + i\eta - (\mathbf{E}_{\vec{k}+\vec{q}\downarrow} - \mathbf{E}_{\vec{k}\uparrow})} \left[\frac{\mathbf{U}}{\mathbf{N}} \sum_{\vec{k}'} \overline{\mathbf{B}}_{\vec{k}'\vec{q}}^{*} + g \ \mu_{B}h \ e^{-i\omega t} \right]$$

We can then have for $\overline{\sigma_q} = \sum_{\vec{k}} \overline{B_{\vec{k}q}^*}$:

$$\overline{\sigma_{\vec{q}}} = g \ \mu_{B}h \ e^{-i\omega t} \frac{\chi_{T}^{0}(\vec{q},\omega)}{1 - U\chi_{T}^{0}(\vec{q},\omega)}$$

where

$$\chi_{\rm T}^{0}(\vec{q},\omega) = \frac{1}{N} \sum_{\vec{k}} \frac{\overline{n}_{\vec{k}+\vec{q}\downarrow} - \overline{n}_{\vec{k}\uparrow}}{\omega + i\eta - (E_{\vec{k}+\vec{q}\downarrow} - E_{\vec{k}\uparrow})}$$
(46)

 $(g^2 \mu_B^2 \chi_T^0)/2$ is the susceptibility of a gas of independent electrons with energies $E_{k\sigma}^{\rightarrow}$.

For the RPA susceptibility we obtain

$$\chi_{\rm T}(\vec{q},\omega) = \frac{g^2 \mu_{\rm B}^2}{2} \frac{\chi_{\rm T}^0(\vec{q},\omega)}{1 - U \chi_{\rm T}^0(\vec{q},\omega)}$$
(47)

The RPA result (47) is the same as if we had neglected the second term on the right-hand side of (45) and replaced h $e^{-i\omega t}$ by

h e^{-i\omegat} +
$$\frac{U}{g\mu_B}\overline{\sigma_{\vec{q}}}$$
 = h e^{-i\omegat} $\left[1 + \frac{2U}{g^2\mu_B^2}\chi_T(\vec{q},\omega)\right]$ (48)

We can obtain the same result with a time-dependent Hartree-Fock approximation. In the presence of the magnetic field $h(q, \omega)$ we have a time-dependent Hamiltonian. The interaction term $h_{int} = U \sum n_{i\uparrow} n_{i\downarrow}$ can be written

 $H_{int} = -UN \sum_{\vec{q}} \sigma^+_{\vec{q}}, \sigma^-_{\vec{q}}$ (49)

In the time-dependent Hartree-Fock approximation we make averages at time t. There are only two terms which are different from $0: \vec{q}' = \vec{q}$ which gives $-NU \ \vec{\sigma_q}$ and, in the ferromagnetic case, $\vec{q}' \approx 0$ which gives $U \sum_{\vec{k}} (n_{\vec{k}\uparrow} n_{\vec{l}} + n_{\vec{k}\downarrow} n_{\vec{l}})$. The Hartree-Fock Hamiltonian is then
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$$\widetilde{H} = \sum_{\vec{k}\sigma} E_{\vec{k}\sigma} n_{\vec{k}\sigma} - N \left[g \mu_{B} h(\vec{q}, \omega) e^{-i\omega t} + \overline{\sigma_{\vec{q}}} \right] \sigma_{\vec{q}}^{+}$$
(50)

where the $E_{k\sigma}^{\rightarrow}$ are the Hartree-Fock one-electron energies. Equation(50) clearly exhibits the result given by Eq.(48).

In conclusion, we can say that there is a strict equivalence between the RPA and the time-dependent Hartree-Fock approximation. This is simply a generalization of the concept of the molecular field [9], as can be seen from (47), (48) or (50): the molecular field is in this case $h_{mol} = \lambda m$ with $\lambda = 2U/g^2 \mu_B^2$.

Let us look at some applications.

a) In the non-magnetic ordered state (T>T_c or non-magnetic metal)

$$X_{T} = X_{L} \text{ and } X^{0}(\vec{q}, \omega) = \frac{1}{N} \sum_{\vec{k}} \frac{\overline{n}_{\vec{k}+\vec{q}} - \overline{n}_{\vec{k}}}{\omega + i\eta - (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})}$$
(51)

For free electrons, expression (51) is the well-known Lindhard function [10]. If we look at the static susceptibility ($\omega = 0$) and let $\vec{q} \rightarrow 0$ then $\chi^0(0,0) = -\int \rho(E) (df/dE) dE$, and we find the result of section 3 for the susceptibility $\chi(0,0)$. For non-magnetic metals at T = 0, $\chi^0(0,0) = \rho(E_F)$, and we get the enhanced Stoner susceptibility

$$\chi(0,0) = \frac{g^2 \mu_B^2}{2} \frac{\rho(E_F)}{1 - U\rho(E_F)}$$

The case of $\vec{q} \neq 0$ will be discussed in section 6.

b) In the ferromagnetic case, $\boldsymbol{\chi}_{_{T}}(\vec{q},\omega)$ is infinite when

$$\mathrm{UX}_{T}^{0}(\vec{\mathbf{q}},\omega) = 1 \tag{52}$$

If we write $\chi_T^0 = \chi_T^{*0} + i \chi_T^{*0}$, we must have

$$U\chi'_{T}^{0} = 1$$
 and $\chi''_{T}^{0} = 0$

The real poles $\omega = E(\vec{q})$ of χ_T represent the spin wave energies; Equation (52) is then equivalent to Eq.(32) and this corresponds to $q < q_c$ of Fig.7.

When $q > q_c$, $X_T^{"0} \neq 0$. Suppose that it is a small quantity and let $\omega = E(\vec{q})$ be the root of $UX_T^0 = 1$. $X_T^0(\vec{q}, \omega)$ can be written for ω near $E(\vec{q})$ (Fig.9):

$$X_{T}^{0}(\vec{q}, \omega) \simeq \frac{1}{U} + \frac{\partial X_{T}^{0}}{\partial \omega} [\omega - E(\vec{q})]$$



FIG. 9. Real and itamginary parts of χ_T^0 for $\omega \simeq E(q)$

Then

$$X_{\mathrm{T}}(\vec{\mathrm{q}},\omega)\simeq \frac{\alpha}{\omega-\mathrm{E}(\vec{\mathrm{q}})+\mathrm{i}\,\Delta}$$

where

$$\Delta = \frac{\chi_{T}^{"0}(\vec{q},\omega)}{\frac{\partial \chi_{T}^{"0}(\vec{q},\omega)}{\partial \omega}} \bigg|_{\omega = E(\vec{q})}$$
(53)

and α a constant near $\omega = E(\vec{q})$. $\chi_T(\vec{q}, \omega)$ has a pole for $\omega = E(\vec{q}) - i\Delta$. The spin wave energy has an imaginary part $-i\Delta$ and thus a lifetime of $\tau = \hbar/\Delta$.

6. SPIN DENSITY WAVES [11]

6.1. Appearance of spin density waves at $\ensuremath{T_{\mathrm{c}}}$

Let us look for the static susceptibility in the non-magnetic case. $\chi(\vec{q}, 0)$ is given by Eq.(47) where we have

$$\chi^{0}(\vec{q}, 0) = \frac{1}{N} \sum_{\vec{k}} \frac{\vec{n}_{\vec{k}+\vec{q}} - \vec{n}_{\vec{k}}}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}}$$
(54)

 $\chi(\vec{q}, 0)$ for a given \vec{q} may be infinite at a temperature $T_c(\vec{q})$ such that

$$UX^{0}(\vec{q}, 0) = 1$$
 (55)

If this never happens for any value of \vec{q} , the system is non-magnetic.³ If Eq.(55) is valid for \vec{q} in a domain of the 1st Brillouin zone, then the non-magnetic system will become unstable at the maximum value of

³ In his first papers, Overhauser (see Ref. [11]) emphasized the fact that instability should occur for any small value of the interaction and in the limit of vanishing interaction for $q_0 = 2k_F$. These conclusions are only valid for special cases: one-dimensional problems or in three dimensions with an unscreened Coulomb interaction.





FIG. 10. Sinusoidal (a) and spiral (b) spin density waves

 $T_c(\vec{q})$. Let T_c be this value and \vec{q}_0 the corresponding value of \vec{q} . Obviously, we have $T_c(\vec{q}) = T_c(-\vec{q})$.

If $\vec{q}_0 = 0$, we have ferromagnetic instability; if $\vec{q}_0 = \pi/a$, we have antiferromagnetic instability. But \vec{q}_0 may have any value in the first Brillouin zone. What kind of instability does this represent? By analogy with the discussion of section 5.1. we see that we may have instabilities of two kinds. Let the z axis be taken arbitrary. We may have (Fig.10):

a) Sinusoidal spin density waves

They correspond to the magnetization

$$m_{z}(\vec{R}_{i}) = m\cos \vec{q}_{0} \cdot \vec{R}_{i}$$
(56)

b) Spiral (or helical) spin density waves

The corresponding magnetization is

$$m_{\mathbf{x}}(\vec{\mathbf{R}}_{i}) = m\cos \vec{\mathbf{q}}_{0} \cdot \vec{\mathbf{R}}_{i}$$

$$m_{\mathbf{y}}(\vec{\mathbf{R}}_{i}) = \pm m\sin \vec{\mathbf{q}}_{0} \cdot \vec{\mathbf{R}}_{i}$$
(57)

The choice of \pm corresponds to the positive and negative rotation of the magnetization when $\vec{q}_0 \cdot \vec{R}_i$ increases. From the three spin density waves we can construct spin density waves with any polarization.

At T_c one of these spin density waves builds up with an infinitely small amplitude. Its nature (sinusoidal or spiral) and its polarization cannot be determined by these considerations.

When do helical or spiral structures occur at T_c ? From Eq.(54) we see that \vec{q}_0 will be determined by the maximum of $\chi^0(\vec{q}, 0)$. At a given temperature $\chi^0(\vec{q}, 0)$ will be large if we have a large number of values of \vec{k} for which $\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}$ is small. This will occur if two parts of the Fermi surface nearly coincide over an important area by a transBLANDIN



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FIG. 11. Fermi surface considerations

lation of vector \vec{q} (see Fig.11). It is easy to see that in case (a) there will be a large contribution of those regions of \vec{k} space which will add for \vec{k} inside and outside the Fermi surface. On the contrary, in case (b) they will subtract and give ≈ 0 . (If in case (a) the two parts could match exactly over a finite area, then $\chi^0(\vec{q}, 0)$ would be infinite.) If such a situation exists, then $\vec{q}_0 \approx \vec{q}$.⁴ In all cases a detailed calculation of χ^0_T has to be done in order to determine \vec{q}_0 .

Before ending this section let us remark again that if $\vec{k} + \vec{q}$ is outside the first Brillouin zone, we have umklapp processes and $\vec{k} + \vec{q}$ means in fact $\vec{k} + \vec{q} + \vec{K}$, \vec{K} being the reciprocal lattice vector which brings it back in the first Brillouin zone.

6.2. Spin density waves below T_c

Below $T_{\rm c}$ we have to find static Hartree-Fock solutions corresponding to the cases (a) and (b).

a) Sinusoidal spin density waves

The interaction part of our Hamiltonian (10) can be written

$$H_{int} = U \sum_{i} n_{i\uparrow} n_{i\downarrow} = -\frac{1}{2} U \sum_{i} (n_{i\uparrow} - n_{i\downarrow})^2 + \frac{U}{2} \sum_{i} (n_{i\uparrow} + n_{i\downarrow})$$
$$= 2 N U \sum_{\vec{q}} \sigma_{\vec{q}}^2 \sigma_{\vec{q}}^2 + \frac{n N U}{2}$$

The Hartree-Fock factorization gives for a sinusoidal wave with vector \vec{q} :

$$\widetilde{H}_{\text{int}} = -2 \text{ N U} \left(\sigma_{\overrightarrow{q}}^2 \sigma_{\overrightarrow{q}}^2 + \sigma_{\overrightarrow{q}}^2 \sigma_{\overrightarrow{q}}^2 \right) + \frac{n \text{ N U}}{2}$$

For a wave of maximum amplitude m we have for the total Hartree-Fock Hamiltonian

$$\widetilde{H} = H_0 + \widetilde{H}_{int} = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} - m U \sum_{\vec{k}\sigma} (C^{\dagger}_{\vec{k}+\vec{q}\sigma} C_{\vec{k}\sigma} + C^{\dagger}_{\vec{k}-\vec{q}\sigma} C_{\vec{k}\sigma}) + \frac{n N U}{2}$$
(58)

 $^{^4\,}$ The case of nearly complete coincidence by a translation $\,q\,$ is more likely to appear with two (or more) bands.

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For a given \vec{q} , Eq.(58) has to be solved so as to find the one-electron energies and then determine m self-consistently. Then we have to find the value of \vec{q} minimizing the total energy. This should be done as a function of T. The problem is, in principle, always soluble, but it involves long numerical calculations.

b) Helical spin density waves

The factorization of H_{int} as written in Eq.(49) gives

$$\widetilde{H}_{int} = -N U \left(\sigma_{\overrightarrow{q}}^{+} \overline{\sigma_{\overrightarrow{q}}^{+}} + \overline{\sigma_{\overrightarrow{q}}^{+}} \sigma_{\overrightarrow{q}}^{-} \right)$$

For a spiral wave of amplitude m, $\overline{\sigma_{\vec{q}}} = \overline{\sigma_{\vec{q}}^+} = m$; this gives

$$\widetilde{H} = H_0 + \widetilde{H}_{int} = \sum_{\vec{k},\sigma} \epsilon_{\vec{k}} n_{\vec{k},\sigma} - U m \sum_{\vec{k}} (C_{\vec{k},\vec{q}\uparrow}^{\dagger} C_{\vec{k}\downarrow} + C_{\vec{k},\vec{q}\downarrow}^{\dagger} C_{\vec{k}\uparrow})$$
(59)

For a given \vec{q} we have to solve the one-electron problem, determine m and then calculate \vec{q} . In this case, the problem is simpler because the one-electron Hamiltonian is easy to solve (59). It is evident that only the matrix elements $\langle \vec{k}+\vec{q}\downarrow | H_{int} | \vec{k} \uparrow \rangle$ are different from zero. So that states $\vec{k}\uparrow$ with $\vec{k}+\vec{q}\downarrow$ are only coupled to one another and not to the other states. The eigenvalue equation is

$$\begin{bmatrix} E - \epsilon_{\vec{k}} & g \\ g & E - \epsilon_{\vec{k} + \vec{q}} \end{bmatrix} = 0 \quad \text{where} \quad g = U m$$
 (60)

This gives $E^2 - E(\epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}}) + \epsilon_{\vec{k}} \epsilon_{\vec{k}+\vec{q}} - g^2 = 0$. If $x = (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})/2$ the solutions are

$$E^{\pm} = \frac{\vec{\epsilon} \cdot \vec{k} + \vec{\epsilon} \cdot \vec{k} + \vec{q}}{2} \neq \text{sign } x \sqrt{x^2 + g^2}$$
(61)

and the wave functions

$$\psi_{\vec{k}}^{+} = -\cos\frac{\theta_{\vec{k}}}{2} \varphi_{\vec{k}\uparrow} + \sin\frac{\theta_{\vec{k}}}{2} \varphi_{\vec{k}+\vec{q}\downarrow}$$

$$\psi_{\vec{k}+\vec{q}} = -\sin\frac{\theta_{\vec{k}}}{2}\phi_{\vec{k}\uparrow} + \cos\frac{\theta_{\vec{k}}}{2}\phi_{\vec{k}+\vec{q}\downarrow}$$

where tg $\theta_{\vec{k}}/2 = (\epsilon_{\vec{k}} - E_{\vec{k}}^{+})/g$. With these definitions $\psi_{\vec{k}}^{+}$, which is a mixture of states with wave vectors \vec{k} , and $\vec{k} + \vec{q}$ has a "dominant" wave vector



FIG, 12. One-electron energies as functions of the dominant wave vector



FIG. 13. Fermi surfaces for a spin density wave: \vec{q} in the x-direction

 \vec{k} [11]. $\psi_{\vec{k}+\vec{q}}^{-}$ has a dominant wave vector $\vec{k}+\vec{q}$. The E⁺ are given in Fig.12 as functions of these dominant wave vectors. The states + are dominantly up spin, the states - are dominantly down spin. The energy eigenvalues E⁺ have discontinuities of magnitude 2g

The energy eigenvalues E^+ have discontinuities of magnitude 2g when $\epsilon_{\vec{k}+\vec{q}} = \epsilon_{\vec{k}}$. In a free-electron spectrum, the discontinuity occurs at planes which bisect the vectors $-\vec{q}$ and $+\vec{q}$, respectively, (or $-\vec{q}+\vec{k}$ and $\vec{q}+\vec{k}$, to take into account umklapp processes, if necessary). For more general cases, we shall have discontinuity surfaces on which $\theta_{\vec{k}} = \pm (\pi/2)$. Near these discontinuities the wave function $\psi_{\vec{k}}^+$ and $\psi_{\vec{k}+\vec{q}}^$ are half spin up with wave vector \vec{k} and down with wave vector $\vec{k}+\vec{q}$. If the Fermi level appears to be in the gap, the Fermi surfaces look as shown in Fig.13, as functions of the dominant wave vector.

When the one-electron states are known, we can calculate the total energy and minimize with respect to g. The self-consistent equation is, at finite temperature,

$$\frac{1}{U} = \frac{1}{2N} \sum_{i=1}^{+} \frac{f(E^{i})}{\sqrt{g^{2} + x^{2}}} + \frac{1}{2N} \sum_{i=1}^{-} \frac{f(E^{i})}{\sqrt{g^{2} + x^{2}}}$$

where $\sum_{i=1}^{t}$ means summation with $E^{t} \leq E_{F}$. This equation can be written

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$$\frac{U}{N}\sum_{n}^{+}\frac{f(E^{+})}{\sqrt{g^{2}+x^{2}}} = 1$$
(62)

which is a generalization of Eq.(55). Equation (62) gives $m(\vec{q}, T)$.

Minimizing the total energy with respect to \vec{q} we obtain the value of \vec{q}_0 as a function of T. The determination of $q_0(T)$ and m(T) can only be done by numerical calculations; it involves a good knowledge of the band structure and of the interaction. In fact, such calculations have only been done for very special cases [11].

The value of \vec{q}_0 should be such that the Fermi energy is in the gap of Fig.12 for a large region of \vec{k} directions. This means that the Fermi surface should have a large area of contact with the discontinuity surface (Fig.13). This situation is the most favourable for a decrease of energy. We also understand, with the same argument, why sinusoidal waves are more likely to appear than spiral waves. In the sinusoidal case the discontinuity surfaces are doubled; the state $|\vec{k}\sigma\rangle$ has matrix elements with $|\vec{k} \pm \vec{q}\sigma\rangle$.

The polarization is not determined in the simple band model. To know it, one would have to take into account the anisotropy field.

6.3. Application to chromium

The case of chromium has been particularly studied. Cr (BCC structure) exhibits sinusoidal spin density wave below $T_c = 310^{\circ}$ K. The wave vector is in the [100] direction and $q_0 \simeq 0.96 \ 2\pi/a$ where a is the length of the unit cell. It is very near antiferromagnetism $(q = 2\pi/a)$. The polarization is longitudinal ($||\vec{q}|$ for T < 115°K and transversal ($|\vec{q}|$) for T > 115°K. The maximum value of the magnetization in the wave at low temperatures is 0.59 $\mu_{\rm R}$.

This situation can be qualitatively understood with the above discussion. Detailed comparison, in relation to the Fermi surface of Cr, has been fairly successful [11,12].

The antiferromagnetism of α and γ Mn and γ Fe can be qualitatively understood along the same lines. In all these cases it is not surprising that the properties are different from the Heisenberg picture (specific heat and entropy, susceptibility neutron scattering above T_c).

7. INFLUENCE OF CORRELATION

In the preceding sections we have always used Hartree-Fock theory or generalizations of this theory. It would be necessary to go beyond Hartree-Fock theory and know the effect of correlation on the magnetic properties of the system. A phenomenological way is to use Landau's Fermi liquid theory. Then a second step is to try to determine the parameters of the Landau theory taking into account correlation by some approximate methods.

7.1. The Landau theory of Fermi liquids

We shall not explain here the Landau theory (see Ref.[13], for example), but only recall the results which we need. For weak changes,

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 $\delta n_{\vec{k}}$ in the occupation distribution of quasiparticle states with vector \vec{k} near the Fermi surface, we may write the change of the total energy $\delta \epsilon$:

$$\delta \epsilon = \sum_{\vec{k}\sigma} E_{\vec{k}\sigma} \delta n_{\vec{k}\sigma} + \frac{1}{2N} \sum_{\vec{k}\sigma\vec{k}\sigma'} f(\vec{k}\sigma; \vec{k}'\sigma') \delta n_{\vec{k}\sigma} \delta n_{\vec{k}\sigma'}$$
(63)

where the $E_{\vec{k}\sigma}$ are the quasiparticle energies; $f(\vec{k}\sigma; \vec{k}'\sigma')$ the quasiparticle interaction; N is the number of atoms in the system. In the presence of a magnetic field H_0 , we have to add the term

$$\frac{-g\,\mu_{\rm B}H_0}{2}\sum_{\vec{k}}\left(\delta n_{\vec{k}\uparrow} - \delta n_{\vec{k}\downarrow}\right) \tag{64}$$

The calculation of the susceptibility proceeds as in the case of Hartree-Fock. A difficulty arises if $f(\vec{k}, \sigma, \vec{k}' \vec{\sigma}')$ depends on \vec{k} and \vec{k}' [14]. Thus, we shall suppose spherical symmetry: f is a function of $\cos \theta$ only, θ being the angle between \vec{k} and \vec{k}' and of σ and σ' : $f(\sigma\sigma', \cos\theta)$. The calculation is the same in section 3.1. and one easily obtains for the non-magnetic state ($E_{\vec{k}\uparrow} = E_{\vec{k}\uparrow}$)

$$\chi = \frac{g^2 \mu_B^2}{2} \frac{\rho^L (E_F^L)}{1 - \rho^L (E_F^L) [\overline{f}_{\uparrow\uparrow} - \overline{f}_{\uparrow\downarrow}]}$$
(65)

where $\rho^{L}(E_{F}^{L})$ is the density of states for the quasiparticles. $\chi(\vec{q},\omega)$ can also be calculated, but it is rigorous only in the limit of small \vec{q} and small ω . When \vec{q} or ω is finite the calculations involve quasi-particles above or below the Fermi level by a finite amount of energy. The quasiparticles have a finite life-time and the Landau approach becomes an approximate method. The same results hold for the transverse susceptibility in the presence of a small magnetic field H_0 . The results for the spin-wave spectrum (derived in the remark of section 4) can be rigorously extended to small \vec{q} (and ω). They are approximate for finite values of \vec{q} .

For a ferromagnetic ground state, the longitudinal properties (X_L) of the system can be derived rigorously for small \vec{q} and ω in terms of the quasiparticle energies E and interactions f. We note that these parameters are different from those used in the non-magnetic case. On the contrary, the results for the transverse properties $(X_T$ and the spinwave spectrum) are only approximate even for small q or ω . The reason is the following. The calculation of transverse properties, even for $\vec{q} = 0$, involves the use of states far from the Fermi level and with a finite lifetime. For example, if $E_{\vec{k}\uparrow} \simeq E_F$, $E_{\vec{k}\downarrow}$ is larger than E_F by a finite amount.

The Hartree-Fock approximation used in the preceding sections is an approximation of the Landau theory with the following assumptions:

In the non-magnetic case $\stackrel{k'}{=} \epsilon_{\vec{k}} + \frac{Un}{2}$, where the $\epsilon_{\vec{k}}$ are the one-

electron energies of the band without interaction, and $f(\vec{k}\uparrow, \vec{k}^{\dagger}\uparrow) = 0$, $f(\vec{k}\uparrow\vec{k}^{\dagger}\downarrow) = U$.

In the ferromagnetic case, $E_{\vec{k}\sigma}=\epsilon_{\vec{k}}+Un_{-\sigma}$ and the same interaction function.

We thus see the limit of the Hartree-Fock theory. Firstly, it has the same limitations as the Landau theory. Secondly, it approximates the quasi-particle energies and interactions in a very crude way. In the next section, we shall try to get better values for these parameters by taking into account correlation effects.

7.2. Approximate treatment of correlation [14]

We shall study mainly the non-magnetic state.

Taking correlation into account we shall, first, obtain quasi-particle energies $E_{k\sigma} \neq \epsilon_k + Un_{-\sigma}$. The band shape will be changed, giving a density of states $\rho^L(E)$. From other similar studies (hard-sphere gas) we expect that $\rho^L(E_F^L) > \rho(E_F)$ and a new band width W_{eff} smaller than the original band width W will occur.

Secondly, the interaction functions f will be different from U. We may define an average value U_{eff} :

$$U_{eff} = \overline{f(\vec{k}\uparrow,\vec{k}\downarrow)} - \overline{f(\vec{k}\uparrow,\vec{k}\downarrow)}$$
(66)

 U_{eff} should be smaller than W even when U is very large. The physical reason is that it is always possible to prevent two electrons (or holes) from ever coming on the same atom by increasing the one-electron energy. The maximum value of this energy is of the order of W.

The condition for ferromagnetic instability should thus be (see Eq. (65))

$$U_{eff} \rho^{L}(E_{F}^{L}) > 1 \tag{67}$$

Different methods have been used to study correlation effects [14]. We shall describe here the method due to Kanamori which is similar to the nuclear theory developed by Brueckner. This method is simple, and we know exactly the limit of its validity: it is the short-range potential and the low-density limit, that is, a small number of electrons or holes in the band (n << 1).

In the t-matrix approach used by Kanamori, we keep all the ladder diagrams of Fig.14 for the scattering operator t. The total energy is written as a Hartree-Fock energy with the bare interaction U replaced by the sum of the ladder diagrams (Fig.15).

The t-matrix satisfies the integral equation represented by Fig. 14:

$$(\vec{k} + \vec{q} \uparrow, \vec{k}' - \vec{q}' \downarrow | t | \vec{k} \uparrow \vec{k}' \downarrow) = U$$

$$+ \frac{1}{N} \sum_{\vec{q}'} \frac{(1 - \vec{n}_{\vec{k} + \vec{q} \uparrow})(1 - \vec{n}_{\vec{k} - \vec{q}' \downarrow})}{E_{\vec{k} \uparrow} + E_{\vec{k} \downarrow} - E_{\vec{k} + \vec{q}' \uparrow} - E_{\vec{k} - \vec{q}\downarrow}} U(\vec{k} + \vec{q}' \uparrow, \vec{k}' - \vec{q}\downarrow | t | \vec{k} \uparrow, \vec{k'} \downarrow)$$



FIG. 14. Ladder diagrams for the t matrix



FIG. 15. Diagrams in the energy; (a) Hartree-Fock; (b) t-matrix

The second term does not depend upon \vec{q} so that the matrix elements of t are independent of \vec{q} . We immediately get

$$(\vec{k} + \vec{q}\uparrow, \vec{k}' - \vec{q}\downarrow |t| \vec{k}, \vec{k}'\downarrow) = \frac{U}{1 + Ug(\vec{k}, \vec{k}')}$$
(68)

where

$$g(\vec{k}, \vec{k}') = \frac{1}{N} \sum_{\vec{q}} \frac{(1 - \bar{n}_{\vec{k} + \vec{q} \uparrow})(1 - \bar{n}_{\vec{k} - \vec{q} \downarrow})}{E_{\vec{k} + \vec{q} \uparrow} + E_{\vec{k} - \vec{q} \downarrow} - E_{\vec{k} \uparrow} - E_{\vec{k} \downarrow}}$$
(69)

From t we get the total energy and the quasi-particle energies

$$\mathbf{E}_{\vec{k}\sigma} = \epsilon_{\vec{k}} + \sum_{\vec{k},\vec{\sigma'}} \left[(\vec{k}\sigma \vec{k}'\sigma' \mid t \mid \vec{k}\sigma \vec{k}'\sigma') - (\vec{k}\sigma \vec{k}'\sigma' \mid t \mid \vec{k}'\sigma' \vec{k}\sigma) \right] \mathbf{\bar{n}}_{\vec{k'}\sigma'}$$

Here, with the help of Eq.(68), the last terms are zero, and we have

$$E_{\vec{k}\sigma} = \epsilon_{\vec{k}} + \sum_{\vec{k'}} (\vec{k}\sigma \ \vec{k'} - \sigma \ |t| \ \vec{k}\sigma \ \vec{k'} - \sigma) \delta \overline{n}_{\vec{k}-\sigma}$$
(70)

so that the interaction between quasi-particles is given by

$$f(\vec{k}\dagger\vec{k}^{\dagger}\dagger) = 0 \qquad f(\vec{k}\dagger\vec{k}^{\dagger}\downarrow) = (\vec{k}\dagger\vec{k}^{\dagger}\downarrow|t|\vec{k}\dagger\vec{k}^{\dagger}\downarrow)$$
(71)

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In the Brueckner theory, Eqs (68) and (70) have to be solved selfconsistently. In the denominators in Eq.(69) the quasiparticle energies (70) appear.

Before solving Eqs (68) and (70), let us note that the t matrix is identical with the t matrix for a two-body problem, except for the factors $(1-\overline{n_k})$. This explains physically why the t matrix approximation is good at low densities $(\overline{n_k} \rightarrow 0)$.

7.3. Applications

The solution of Eqs (68) and (70) is difficult, so we shall make the approximation of replacing \vec{k} and \vec{k}' in $g(\vec{k}, \vec{k}')$ by 0. This is not unphysical because we only need to know t for small \vec{k} and \vec{k}' values (inside the Fermi surface). We thus get for a non-magnetic state

$$g \simeq \frac{1}{2} \int \frac{\rho(E) dE}{E}$$

$$E > E_{F}$$
(72)

The matrix elements of t become constant (and equal to U_{eff}) and we get

$$f(\vec{k}\uparrow\vec{k}\downarrow) = U_{eff} = \frac{U}{1+Ug}$$
(73)

With this new approximation the modification of the band structure is completely neglected so that $W_{eff} = W$ and $\rho^L(E) = \rho(E)$. Even within this approximation the values of g and thus of t and U_{eff} would be different in a ferromagnetic state. At this point it is not necessary to refine the theory and we shall take the same value for U_{eff} . We have thus arrived at the situation where the Hartree-Fock approximation becomes approximately valid if we replace U by U_{eff} . For example, the susceptibility of a non-magnetic state is

$$\chi = \frac{g^2 \mu_B^2}{2} \frac{\rho(E_F)}{1 - U_{\text{eff}} \rho(E_F)}$$

 U_{eff} depends on the density of states through g (72), but mainly through the width W. Near the bottom of the band $\rho(E)$ varies as $E^{1/2}$. For a small number of electrons we can write relation (72) as

$$g \approx \frac{1}{2} \int_{E_{F}}^{W} \frac{\rho(E)dE}{E}$$

which is a constant of the order of 1/W. For a spherical band limited at E = W, in order to have one electron, we find $g \simeq 3/2W$. With U = 7 eV, W = 3 eV, this gives $U_{\text{eff}} \simeq 1.5 \text{ eV}$ which is a considerable reduction compared with U.

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Although U_{eff} might be much smaller than U, it seems to be possible to satisfy the ferromagnetic instability condition: $U_{eff} \rho(E_F) > 1$ if the density of states is sufficiently large at low energy (or high energy, for the case of holes).

These considerations have been extended to the case of degenerate d-bands (see Ref.[14]). We shall not discuss here the results, but want to point out one problem which has been widely discussed. Is ferromagnetism due to the Coulomb integral U or to the existence of exchange integrals J? The second alternative would mean that, as in atoms, Hund's rule is obeyed. The answer to this question is not yet very clear. From the values of U_{eff} and J_{eff} obtained in the degenerate case, it appears that ferromagnetism would be possible with J (and J_{eff}) equal to zero. When $J \neq 0$ the corresponding term makes the situation more favourable towards ferromagnetism. It might be essential to satisfy a criterion of the type (67) for the appearance of magnetism although J is a small term. In the case of Ni and Pd, where three bands are involved, this criterion can be written

$$(U_{eff} + 3 J_{eff}) \rho(E_F) > 1$$

where $\rho(E_F)$ is the density of states per band. We can understand the appearance of magnetism in nickel as being due to a larger density of states than in palladium.

In conclusion of these discussions on correlation, we may say that the Hartree-Fock description can be used as a qualitative and semiquantitative theory if, instead of the Coulomb and exchange integrals, one uses effective values for these parameters.

8. NEARLY FERROMAGNETIC METALS [15]

Let us consider a metal very close to the ferromagnetic instability condition. The enhancement factor $S = 1/(1 - U\rho(E_F))$ is large. We may expect large spin fluctuations as in the case of a phase transition slightly above the critical temperature. In fact, the discussion of this section also applies (with some small differences) to magnetic cases for T above and near T_c and to non-magnetic cases and large S. We shall explicitly consider the second case.

Let us look at the susceptibility $\chi(\vec{q},\omega)$ given by Eqs (47) and (51). For $\omega = 0$ and small q,

$$\chi^{0}(\mathbf{q}, 0) \simeq \frac{\rho(\mathbf{E}_{\mathrm{F}})}{1 + \frac{1}{3} \left(\frac{\mathbf{q}}{2\mathbf{k}_{\mathrm{F}}}\right)^{2}}$$

The static susceptibility has the Ornstein-Zernike form

$$\chi(q, 0) = \frac{g^2 \mu_B^2}{2} \frac{12 K_F^2}{K^2 + q^2}$$
(74)

where $K^2 = 12 k_F^2 [1 - U\rho(E_F)]$. In real space the spin-spin correlation function is

$$\chi(\mathbf{r}, 0) = \frac{g^2 \mu_B^2}{2} \frac{3 k_F^2}{\pi} \frac{e^{-kr}}{r}$$
(75)

Formulae (74) or (75) are what is expected near a critical point when spin fluctuations become important.

The frequency dependence of the susceptibility is very typical for large S. When $(q/(2k_F))^2 < 1 - U\rho(E_F)$, X'' has a well pronounced peak for frequency

$$\omega \simeq \frac{q v_F}{S}$$
(76)

The width is of the same order. We can thus qualitatively speak of excitations of the system having a large damping. They behave like phonons, with a phase velocity which goes to zero when the system becomes ferromagnetically unstable. These pseudo-excitations have received the name of "paramagnons". There are three paramagnon modes with values of $S_z m = \pm 1$ or 0.

Paramagnons and phonons have very similar effects. It is therefore interesting to review briefly the effect of phonons on the effective mass of the electrons.

8.1. Mass enhancement due to phonons [16]

Let us consider the Hamiltonian for the electron-phonon interaction

$$H = \sum_{\vec{k}} \epsilon_{\vec{k}} C_{\vec{k}}^{\dagger} C_{\vec{k}}^{\dagger} + \sum_{\vec{q}} \hbar \omega_{\vec{q}} a_{\vec{q}}^{\dagger} a_{\vec{q}}$$
$$+ \sum_{\vec{k} \neq \vec{q}} (M_{\vec{k} \neq \vec{q}} C_{\vec{k} - \vec{q}}^{\dagger} C_{\vec{k}} a_{\vec{q}}^{\dagger} + h.c.)$$
(77)

where a_{d}^{\downarrow} and a_{d}^{\downarrow} are the phonon operators of energy $\hbar \omega_{d}^{\downarrow}$.

In the Green function formalism we have the Dyson equation

$$G(\vec{k},\omega) = G^{0}(\vec{k},\omega) + G^{0}(\vec{k},\omega) \Sigma (\vec{k},\omega)G(\vec{k},\omega)$$
(78)

where G^0 and G are the electron Green functions with and without interactions, respectively, $\Sigma(\vec{k}, \omega)$ is the self-energy.

$$G^{0}(\vec{k},\omega) = \frac{1}{\omega - \epsilon_{\vec{k}} + i\eta \operatorname{sign} \epsilon_{\vec{k}}}$$

where the energies are counted from the Fermi energy. Then (78) gives

$$G(\vec{k},\omega) = \frac{1}{\omega - \epsilon_{\vec{k}} - \Sigma(\vec{k},\omega)}$$
(79)

If $G(\vec{k}, \omega)$ has poles near the real axis, we have

$$E_{\vec{k}} = \epsilon_{\vec{k}} + \operatorname{Re} \Sigma(\vec{k}, E_{\vec{k}} - i \Gamma_{\vec{k}})$$

$$\Gamma_{\vec{k}} = -\operatorname{Im} \Sigma(\vec{k}, E_{\vec{k}} - i \Gamma_{\vec{k}})$$
(80)

 $E_{\vec{k}}$ is the renormalized energy and $\Gamma_{\vec{k}}$ the width of the state which has to go to zero faster than $E_{\vec{k}}$ when $E_{\vec{k}} \rightarrow 0$ in order to have good quasiparticles. Then $G(\vec{k}, \omega)$ can be written

$$G(\vec{k},\omega) = \frac{Z_{\vec{k}}}{\omega - E_{\vec{k}} + i\Gamma_{\vec{k}}} + G_{reg}$$
(81)

where G_{reg} is a regular function near ω = $E_{\overrightarrow{\nu}}$ and

$$Z_{\vec{k}}^{-1} = 1 - \frac{\partial \operatorname{Re} \Sigma(k, \operatorname{E}_{\vec{k}} - \operatorname{i} \Gamma_{\vec{k}})}{\partial \omega}$$
(82)

From there one easily obtains, for the effective mass m^* at the Fermi level,

$$\frac{\mathbf{m}^{*}}{\mathbf{m}} = \frac{1 - \frac{\partial \Sigma (\mathbf{k}_{\mathrm{F}}, \mathbf{0})}{\partial \omega}}{1 + \frac{\mathbf{m}}{\mathbf{k}_{\mathrm{F}}} \frac{\partial \Sigma (\mathbf{k}_{\mathrm{F}}, \mathbf{0})}{\partial \mathbf{k}}}$$
(83)

The second term in the denominator is usually negligible.

The simplest approximation for $\Sigma(\vec{k},\omega)$ is shown in Fig.16. For Eq.(78) this corresponds to the diagram shown in Fig.17. We shall not go any further in this discussion (see Ref. [16] and the references therein) but only comment on the results. The numerator in Eq.(83) is larger than one and we have a mass enhancement which may be important. This may be seen, for example, in the electronic specific heat; at low temperatures $C_e = \gamma T$, where γ is proportional to the density of states and thus to the mass m^{*}.

On the contrary, we have to use this bare mass for the density of states which appear in the susceptibility. The reason is simple: the renormalization produces a hump and a bump in the energy curve (Fig.18). This occurs on a shell of width $\hbar\omega_D$ around about the Fermi energy. It is a phenomenon which is linked to the Fermi surface. When a magnetic field is present, the Fermi level for spin-up moves up, but the hump and the bump move up also. The same happens for spin-down. Then the susceptibility is not affected by the phonon interaction. In calculating enhancement factors S, for example, one should use the

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bare density of states $\rho(E_F)$ (mass m) rather than the density of states deduced from specific heat experiments, which is related to the mass m^{*}. This may be important for all transitional metals where the mass enhancement due to phonons is of importance.

8.2. Mass enhancement due to paramagnons

In analogy to the phonon problem, one can introduce diagrams similar to that of Fig.16 where the phonon line is replaced by a paramagnon line. In the RPA, where the susceptibility is represented by Fig.19, we can replace Fig.16 by Fig.20. The difference in the case of phonons lies in the fact that for the $m = \pm 1$ modes the spin of the electron in the intermediate state is reversed. The paramagnon modes can be represented as in Fig.21.

 $\chi - \bigcirc + \bigcirc + \bigcirc - \cdots$ FIG. 19. Susceptibility in the RPA

The paramagnon contribution to the self-energy $\Sigma(\vec{k},\omega)$ is given by

$$\Sigma(\vec{k},\omega) = -i \frac{U^2}{(2\pi)^4} \iint d^3 \vec{k}' d\omega' G^0(\vec{k}+\vec{k}',\omega+\omega') \chi^{-+}(\vec{k}',\omega')$$
(84)

From Eq.(83) one gets a mass enhancement for a spherical Fermi surface

$$\frac{m^{*}}{m} = 1 + [U\rho(E_{F})]^{2} \int_{0}^{2k_{F}} \frac{\chi(q,\omega) q dq}{g^{2} \mu_{B}^{2} k_{F}^{2}}$$
(85)

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FIG. 20. Paramagnon contribution to the self-energy Σ mode +1



FIG. 21. Paramagnon mode m = +1

Using expression (74) for X(q, 0) we get

$$\frac{m^*}{m} = 1 + 6 \log \frac{S}{3}$$
 (86)

where S is the Stoner enhancement factor.

It has recently been pointed out that also the m = 0 mode should be introduced. Diagrams as shown on Fig.22, where the number of bubbles is odd, should be added to the self-energy diagrams of Fig.20. This includes the contribution of the m = 0 mode and also the contribution of the density fluctuations. The net result gives a factor 3/2 in the mass enhancement[see Eqs (85) and (86)].

This mass enhancement can be observed in the electronic specific heat. It should again be emphasized in this case, as in the case of phonons, that it is the bare mass which enters into the susceptibility.



FIG. 22. Diagram of the m = 0 contributing to the self-energy Σ

8.3. Applications

These results have been applied to the case of palladium, which seems to be nearly ferromagnetic. The simple model which has been discussed here has to be extended in order to make quantitative comparisons. Thus the effects of band structure, non-local interaction, effects of correlation have been included. The enhancement factor for palladium depends crucially on these effects; by including them, one obtains a value for S of the order of 10 and for m^*/m of the order of 2 or 3.

Striking experiments have shown that the mass enhancement really exists. In Ni Rh alloys, ferromagnetism sets in at 63% Ni. The susceptibility increases near the critical concentration, and it has been observed that the γ constant of the specific heat increases considerably.

Finally, if we look for higher temperature terms in the calculation of the electronic specific heat, we find

$$C_{e} = \gamma T + \beta T^{3} \log \frac{T}{T_{s}}$$
(87)

where β is a constant. This T³ log T term seems to have been observed in Ni Rh alloys.

This theory has also been used to explain the properties of 3 He, particularly the specific heat (T 3 Log T term).

CONCLUSION

In this course, we have tried to explain within a simple model the principal methods and ideas in the field of band magnetism. This enables us to understand, at least qualitatively, the properties of itinerant magnetic electrons. It is clear that any quantitative comparison with experiments requires the use of more elaborate models: real band structures, real interactions, influence of the conduction band, etc.

Many difficult problems remain nevertheless unsolved, even with the one-band model with intra-atomic interactions. Let us make a list of some of these problems:

The exact nature of the ground state is not known. Is it ferromagnetic, anti-ferromagnetic, helical or non-magnetic?

In the time-dependent Hartree-Fock theory, individual and collective excitations are not treated at the same level. It would be a great improvement to calculate the magnetization at finite temperatures by taking account of both types of excitations. This has only been done for the low-temperature case.

It will be necessary to clarify the significance of Hund's rule: is magnetism in metals mainly due to Coulomb interaction U or to the exchange interaction J?

A treatment of correlation at finite densities, without too crude approximations, would be appreciated.

The band model in its present state seems to explain particularly well the properties of Ni, Pd, or Cr. On the other hand, Fe, for example, has many properties which are closer to the properties of a Heisenberg ferromagnet. This is true for $T > T_c$ where local moments seem to exist in F_e . How could a band model describe this fact?

This list shows that although the understanding of band magnetism has increased very much, a number of questions still remain unsolved.

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ELECTRON-PHONON AND PHONON-PHONON INTERACTIONS

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Abstract

 Form of crystal Hamiltonian.
 A diabatic approximation and electron-phonon interaction.
 Harmonic approximation and phonon-phonon interaction.
 Electron-phonon interaction in metals.
 Real-time Green functions. Migdal's theorem.
 Renormalization effects in normal state.
 Pair interaction and superconductivity.
 Hydrodynamical limit and transport equation.
 Phonon-phonon interaction in insulators.
 Imaginarytime Green functions and perturbation theory.
 Thermal and elastic properties.
 Phonon renormalization effects.

1. FORM OF CRYSTAL HAMILTONIAN

The exact Hamiltonian of a crystal consists of the kinetic and Coulomb energies of the N nuclei and all the electrons. However, in most crystals part of the electrons are bound to the nuclei forming closed shell ions. The remaining Z electrons per atom occupy the states of the valence band. If at temperature T = 0 this band is not filled the crystal is a metal. If the valence band is filled at T = 0 the crystal is an insulator. It is an ionic crystal or a covalent crystal according to whether the valence electrons are localized at the negative ions (electrostatic cohesion forces) or inbetween ions (covalent cohesion forces). At T > 0 electron-hole pairs are excited; the metal becomes a conductor, the insulator a semiconductor. In a fourth category of crystals the ions and valence electrons form neutral atoms or molecules which keep together in the solid by electric multipole forces. This is the case of the van der Waals crystals. The division into the four categories is of course not sharp.

1.1. Adiabatic approximation and electron-phonon interaction

Because of the small ratio of the electron mass m to the ion mass M (assuming a Bravais lattice), in fact

$$\kappa = \left(\frac{\mathrm{m}}{\mathrm{M}}\right)^{1/4} \leq 0.1 \tag{1.1}$$

the valence electrons establish equilibrium much more rapidly than the ions. As will be discussed in section 1.2 the ratio of their average velocity is

$$\frac{v_{\text{ion}}}{v_{\text{electron}}} \cong \kappa^2$$
 (1.1a)

Therefore the valence electrons screen the Coulomb interaction both between ions and between ions and excited electrons and holes (in ionic crystals the screening is of course not complete). We call the screened potentials U and W, respectively. The effect of screening can of course be treated explicitly, as has been done first by Bardeen (see, e.g. Ref.[1], Chapter 6). Formally it is described by a canonical transformation introduced by Nakajima (see, e.g. Ref. [2]). We skip this problem writing directly the screened form of the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{ion} + \mathcal{H}_{el}$$
 (1.2)

$$\mathcal{H}_{ion} = \sum_{I=1}^{N} \vec{P}_{I}^{2} / 2M + U(R)$$
 (1.3)

$$\mathscr{H}_{el} = \sum_{i=1}^{ZN} \vec{p}_i^2 / 2m + \mathscr{H}_{Coul} + W(r_i, R)$$
(1.4)

where

$$\mathscr{H}_{\text{Coul}}^{\prime} = \frac{1}{2} \sum_{i \neq i'}^{\prime} e^{2/\left|\vec{r}_{i} - \vec{r}_{i'}\right|}$$
(1.4a)

Here R = $(\vec{R}_1 \vec{R}_2 \dots \vec{R}_N)$ are the instantaneous ionic positions, oscillating around the lattice positions $R^0 = (\vec{R}_1^0 \dots \vec{R}_N^0)$,

$$\vec{u}_{I} = \vec{R}_{I} - \vec{R}_{I}^{0}$$
(1.5)

being the displacement, and $r = (\vec{r}_1 \cdot \vec{r}_2 \dots \cdot \vec{r}_{ZN})$ are the electronic positions. The interaction W(r; R) is supposed to depend adiabatically on the ionic positions. The adiabatic approximation of Born and Oppenheimer then consists in writing

$$\mathscr{H}_{el}(\mathbf{R}) | \ell; \mathbf{R} \rangle = \mathbb{E}_{\ell}(\mathbf{R}) | \ell; \mathbf{R} \rangle$$
(1.6)

with

$$\langle \ell^{\bullet}; \mathbf{R} | \ell; \mathbf{R} \rangle = \delta_{\ell^{\bullet}\ell}; \sum_{\ell} | \ell; \mathbf{R} \rangle \langle \ell; \mathbf{R} | = \mathbf{1}$$
 (1.6a)

and where the \vec{R}_{I} enter the electron problem only as parameters. This is justified by Eqs (1.1), (1.1a). Writing in addition

$$\mathcal{H}_{ion} | n > = \Omega_n | n >$$
 (1.7)

with

$$\langle n! | n \rangle = \delta_{n'n}; \sum_{n} | n \rangle \langle n | = 1$$
 (1.7a)

the eigenstates of the total Hamiltonian $\mathscr H$ may be written as linear combinations of the states $|\ell;R\rangle$ and $|n\rangle$,

$$\mathscr{H}\Psi_{\rm s} = \mathscr{E}_{\rm s}\Psi_{\rm s} \tag{1.8}$$

$$\Psi_{s} = \sum_{n\ell} \alpha_{n\ell,s} |\ell; R\rangle |n\rangle \qquad (1.8a)$$

This is the usual form in which the effects of the electrons on the ionic system are discussed (see Ref.[2]). It is, however, complicated by the fact that the ionic kinetic energy acts not only on the states $|n\rangle$ but also on $|\ell; R\rangle$. Indeed

$$\langle \ell^{\dagger}; \mathbf{R} | \mathcal{H} | \ell; \mathbf{R} \rangle = (\mathcal{H}_{\text{ion}} + \mathbf{E}_{\ell}(\mathbf{R})) \,\delta_{\ell^{\dagger}\ell} + \mathbf{A}_{\ell^{\dagger}\ell}(\mathbf{R}) + \mathbf{B}_{\ell^{\dagger}\ell}(\mathbf{R})$$
(1.9)

where

$$A_{\ell'\ell}(\mathbf{R}) \equiv \sum_{\mathbf{I}} \langle \ell' ; \mathbf{R} | \frac{\hbar}{\mathbf{i}} \frac{\partial}{\partial \mathbf{R}_{\mathbf{I}}} | \ell; \mathbf{R} \rangle \vec{\mathbf{P}}_{\mathbf{I}} / \mathbf{M}$$

$$B_{\ell'\ell}(\mathbf{R}) \equiv \sum_{\mathbf{I}} \langle \ell' ; \mathbf{R} | \left(\frac{\hbar}{\mathbf{i}} \frac{\partial}{\partial \mathbf{R}_{\mathbf{I}}} \right)^2 | \ell; \mathbf{R} > 1/2 \mathbf{M}$$
(1.9a)

The trouble is that there are cancellations among $E_{\ell}(R)$, $A_{\ell'\ell}(R)_{+}$ and $B_{\ell'\ell}(R)$. This is seen from a study of the commutator

$$[\mathscr{H}_{\text{ion}}, \mathscr{H}_{\text{el}}] = \left[\sum_{I} \frac{\vec{P}_{I}^{2}}{2M}, W(r; R)\right] = \frac{1}{2} \sum_{I} \left[\frac{\vec{P}_{I}}{M}, \frac{\hbar}{i} \frac{\partial W}{\partial \vec{R}_{I}}\right]_{+} = \frac{1}{2} \sum_{I} \left[\left(\mathscr{H}_{\text{ion}}, \vec{n}_{I}\right] \frac{\partial W}{\partial \vec{R}_{I}}\right]_{+}$$
(1.10)

which measures the mixing of the electronic and ionic states in (1.8a). We get

$$\langle \mathbf{n}^{\mathbf{i}} | \langle \ell^{\mathbf{i}} ; \mathbf{R} | [\mathscr{H}_{ion}, \mathscr{H}_{el}] | \ell; \mathbf{R} \rangle | \mathbf{n} \rangle = \frac{1}{2} \sum_{\mathbf{n}'' \mathbf{I}} \left\{ (\Omega_{\mathbf{n}'} - \Omega_{\mathbf{n}''}) \langle \mathbf{n}^{\mathbf{i}} | \vec{u}_{\mathbf{I}} | \mathbf{n}'' \rangle \right.$$

$$\times \langle \mathbf{n}'' | \langle \ell^{\mathbf{i}} ; \mathbf{R} | \frac{\partial W}{\partial \vec{R}_{\mathbf{I}}} | \ell; \mathbf{R} \rangle | \mathbf{n} \rangle + (\Omega_{\mathbf{n}''} - \Omega_{\mathbf{n}}) \langle \mathbf{n}'' | \vec{u}_{\mathbf{I}} | \mathbf{n} \rangle$$

$$\times \langle \mathbf{n}^{\mathbf{i}} | \langle \ell^{\mathbf{i}} ; \mathbf{R} | \frac{\partial W}{\partial \vec{R}_{\mathbf{I}}} | \ell; \mathbf{R} \rangle | \mathbf{n}'' \rangle \right\}$$

$$(1.10a)$$

To get anywhere an expansion in powers of the \vec{u}_I is necessary. This is certainly allowed at low temperatures, $T < T_D$ (T_D = Debye temperature) where the \vec{u}_I are small, except for <u>quantum crystals</u> for which already the zero-point oscillations are important (see, e.g. Ref. [3]). Then

$$\langle \mathbf{n}^{\mathbf{i}} | \langle \ell^{\mathbf{i}} ; \mathbf{R} | [\mathcal{H}_{\text{ion}}, \mathcal{H}_{el}] | \ell; \mathbf{R} \rangle | \mathbf{n} \rangle = \sum_{\mathbf{I}} (\Omega_{\mathbf{n}}, -\Omega_{\mathbf{n}}) \langle \mathbf{n}^{\mathbf{i}} | \vec{\mathbf{u}}_{\mathbf{I}} | \mathbf{n} \rangle$$

$$\times \langle \ell^{\mathbf{i}} ; \mathbf{R}^{\mathbf{0}} | \left(\frac{\partial \mathbf{W}}{\partial \vec{\mathbf{R}}_{\mathbf{I}}} \right)_{\mathbf{0}} | \ell; \mathbf{R}^{\mathbf{0}} \rangle + \text{higher order terms}$$

$$(1.10b)$$

Deferring further discussion of Eq.(1.10b) to section 1.2 we notice here that the r.h.s. of this equation is closely related to the electron-phonon interaction contained in \mathscr{H}_{el} . Indeed, expanding W in \mathscr{H}_{el} we can write

$$\mathcal{H}_{el} = \sum_{i} \frac{\vec{p}_{i}^{2}}{2m} + W(\mathbf{r}; \mathbf{R}^{0}) + \mathcal{H}_{Coul} + \mathcal{H}_{el-ph}$$
(1.11)

where

$$\mathcal{H}_{el-ph} = \sum_{I} \left(\frac{\partial W}{\partial \vec{R}_{I}} \right)_{0} \cdot \vec{u}_{I} + \text{higher order terms}$$
(1.12)

is the electron-phonon interaction. Here the successive terms describe 1-phonon, 2-phonon, etc. processes. Usually only the 1-phonon term is retained. (The only problem where multi-phonon processes have been considered seriously seems to be the temperature dependence of the mobility of semiconductors, see Ref. [4].) Considerable simplification is achieved by assuming that the electrons interact individually with the ions, which is certainly a good approximation,

W(r; R) =
$$\sum_{i} w(\vec{r}_{i}; R)$$
 (1.13)

Then eliminating the bulk of the Coulomb interaction by a Hartree-Fock treatment we have

$$\mathcal{H}_{el} = \mathcal{H}_{HF} + \mathcal{H}_{el-ph} + \mathcal{H}_{el-el}$$
(1.14)

where

$$\mathcal{H}_{HF} = \sum_{i} \left(\frac{\vec{p}_{i}^{2}}{2m} + V(\vec{r}_{i}) \right)$$
(1.15)

$$\mathcal{H}^{\prime}_{el-el} = \mathcal{H}^{\prime}_{Coul} - \sum_{i} V_{HF}(\vec{r}_{i})$$
 (1.16)

is a residual interaction, and

$$V(\vec{r}) = W(\vec{r}; R^0) + V_{ur}(\vec{r})$$
 (1.17)

is the periodic potential,

$$V(\vec{r} + \vec{R}) = V(\vec{r})$$
 (1.17a)

(Here and in what follows \vec{R} stands for one of the $\vec{R}_{I}^{0},$

Using Bloch states defined by

$$\left(\frac{\vec{p}^{2}}{2m} + V(\vec{r})\right) |k\rangle = \epsilon_{k}^{0} |k\rangle \qquad (1.18)$$

where $\pm k \equiv (\pm \vec{k}, \sigma)$ and $\sigma = \uparrow, \downarrow$ is the electronic spin, the second quantized form of Eqs (1.16), (1.17), (1.13) is

$$\mathcal{H}_{HF} = \sum_{k} \epsilon_{k}^{0} a_{k}^{*} a_{k} \qquad (1.19)$$

$$\mathcal{H}'_{el-ph} = \sum_{kk'} \sum_{I} \langle k' | \left(\frac{\partial w}{\partial \vec{R}_{I}} \right)_{0} | k \rangle \cdot \vec{u}_{I} a_{k'}^{*} a_{k} + \dots \qquad (1.20)$$

$$\mathscr{H}_{el-el} = \frac{1}{2} \sum_{k'kq} \langle k' + q, k - q | \frac{e^2}{r} | k'k \rangle a_{k'+q}^* a_{k'}a_{k-q}^* a_k - \sum_{k'k} \langle k' | V_{HF} | k \rangle a_{k}^* a_k$$
(1.21)

where $k \pm q \equiv (\vec{k} \pm \vec{q}, \sigma)$.

The ground state $|0\rangle$ is characterized by

$$\begin{aligned} \mathbf{a}_{\mathbf{k}} \left| 0 \right\rangle &= 0; \quad \boldsymbol{\epsilon}_{\mathbf{k}}^{0} > 0 \\ \mathbf{a}_{\mathbf{k}}^{*} \left| 0 \right\rangle &= 0; \quad \boldsymbol{\epsilon}_{\mathbf{k}}^{0} < 0 \end{aligned} \tag{1.22}$$

and a Bloch state $\left|k\right>$ describes an excited electron or hole according to whether $\varepsilon_k^{\,0}>0~$ or $\varepsilon_k^{\,0}<0$

$$|\mathbf{k}\rangle = \mathbf{a}_{\mathbf{k}}^{*}|0\rangle; \quad \boldsymbol{\epsilon}_{\mathbf{k}}^{0} > 0$$

$$|\mathbf{k}\rangle = \mathbf{a}_{\mathbf{k}}|0\rangle; \quad \boldsymbol{\epsilon}_{\mathbf{k}}^{0} < 0$$

$$(1.22a)$$

(Note that here $\epsilon^0_{k_F}$ = 0, $\hbar k_F$ being the Fermi momentum)

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Neglecting the residual interaction (1.21) (which would lead us into the Fermi liquid problem) we see that $|R; R^0 \rangle$ are eigenstates of \mathscr{H}_{HF} with fixed number ZN of electrons and characterized by an arbitrary number of excited electron-hole pairs k_j , k'_j ($\epsilon^0_{k_j} > 0$, $\epsilon^0_{k_j} < 0$),

$$|\ell; \mathbf{R}^{0}\rangle = \prod_{j} \mathbf{a}_{\mathbf{k}_{j}}^{*} \mathbf{a}_{\mathbf{k}_{j}}^{*} |0\rangle \qquad (1.23)$$

where $\ell \equiv (k_1 k_1^{\prime} k_2 k_2^{\prime} \dots)$ and

$$\mathbf{E}_{\boldsymbol{\ell}}(\mathbf{R}^{0}) = \mathbf{E}_{0} + \sum_{j} (\boldsymbol{\epsilon}_{k_{j}}^{0} + |\boldsymbol{\epsilon}_{k_{j}}^{0}|) \qquad (1.23a)$$

 $E_0 = \sum_{k \in [0, k]} \epsilon_k^0$ being the ground state energy. Note that Eqs (1.23) are

not all states $|\ell; \mathbb{R}^0 \rangle$, excitations into higher bands being neglected. For semiconductors holes and excited electrons are in different bands (valence and conduction band).

1.2. Harmonic approximation and phonon-phonon interaction

Neglecting the terms (1.9a) in (1.9) the effective ionic potential energy is seen to be

$$\tilde{U}(R) = U(R) + E_0(R)$$
 (1.24)

$$\widetilde{U}(R^{0} + u) = \widetilde{U}(R^{0}) + \sum_{x} U_{x} u_{x} + \frac{1}{2!} \sum_{xx'} U_{xx'} u_{x} u_{x'} + \dots \quad (1.24')$$

Here $\tilde{U}(\mathbb{R}^0)$ is the energy responsible for cohesion and

$$U_{x_1...x_n} \equiv \left(\frac{\partial^n \widetilde{U}}{\partial R_{x_1} \cdots \partial R_{x_n}}\right)_0$$
(1.24")

 $R_{I\nu}$ (ν = 1,2,3) are the Cartesian components of \vec{R}_{I} , etc., and x =(I, ν). In equilibrium at T = 0 without strains, U_x = 0, so that

$$\mathcal{H}_{ion} = \mathcal{H}_{ion} + E_0(R) = \mathcal{H}_{harm} + \mathcal{H}_{anh}$$
 (1.25)

where

$$\mathscr{H}_{harm} = \sum_{\mathbf{x}} \frac{\mathbf{P}_{\mathbf{x}}^2}{2\mathbf{M}} + \frac{1}{2} \sum_{\mathbf{xx'}} \mathbf{U}_{\mathbf{xx'}} \mathbf{u}_{\mathbf{x}} \mathbf{u}_{\mathbf{x}}, \qquad (1.25a)$$

is the harmonic part and

$$\mathcal{Y}_{anh}^{i} = \sum_{n \geq 3} \mathcal{Y}_{n}^{i}$$
 (1.26)

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$$\mathcal{H}_{n}^{\dagger} = \frac{1}{n!} \sum_{x_{1} \dots x_{n}} U_{x_{1} \dots x_{n}} \cdot u_{x_{1}} \dots u_{x_{n}}$$
(1.26a)

the anharmonic interaction. Normal co-ordinates introduced by

$$u_{x} = \sum_{q} \psi_{q}(x) (M\omega_{q}^{0})^{-1/2} Q_{q}$$

$$P_{x} = \sum_{q} \psi_{q}(x) (M\omega_{q}^{0})^{+1/2} P_{q}$$
(1.27)

where

.

$$\psi_{\vec{q}\,\mu}(\mathbf{I}\nu) = \mathrm{Ne}_{\vec{q}\,\mu,\nu}^{-1/2} \mathrm{e}^{i\vec{q}\cdot\vec{R}_{\mathrm{I}}^{0}} \tag{1.27a}$$

and $\pm q \equiv (\pm \vec{q}, \mu)$, transform the Hamiltonian into

$$\mathscr{H}_{ham} = \frac{1}{2} \sum_{q} \omega_{q}^{0} (P_{q} P_{q}^{*} + Q_{q} Q_{q}^{*}) = \sum_{q} \omega_{q}^{0} (b_{q}^{*} b_{q}^{+} + \frac{1}{2})$$
(1.28)

$$\mathscr{H}_{n}^{i} = \frac{1}{n!} \sum_{q_{1} \dots q_{n}} C_{q_{1} \dots q_{n}}^{(n)} Q_{q_{1}} \dots Q_{q_{n}}$$
(1.29)

where

$$Q_{q} = Q_{-q}^{*} = \frac{1}{\sqrt{2}} (b_{q} + b_{-q}^{*})$$

$$P_{-q} = P_{q}^{*} = \frac{1}{i\sqrt{2}} (b_{q} - b_{-q}^{*})$$
(1.30)

and

$$C_{q_{1}}^{(n)} = C_{q_{1}}^{(n)} = M^{-\frac{n}{2}} (\omega_{q_{1}}^{0} \dots \omega_{q_{n}}^{0})^{-1/2} \sum_{x_{1} \dots x_{n}} U_{x_{1} \dots x_{n}} \psi_{q_{1}}^{(x_{1})} \dots \psi_{q_{n}}^{(x_{n})}$$
(1.31)

The polarization vectors $\vec{e}_{\vec{q}\mu}$ and frequencies $\omega_{\vec{q}\mu}^0$ satisfy the eigenvalue equations

$$\sum_{\nu'} (D_{\nu\nu'}(\vec{q}) - \omega_{\vec{q}\mu}^{02} \delta_{\nu\nu'}) e_{\vec{q}\mu,\nu'} = 0; \ \mu = 1, 2, 3$$
(1.32)

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where

$$D_{\nu\nu'}(\vec{q}) = \frac{1}{M} \sum_{\vec{R}} U_{\nu\nu'}(\vec{R}) e^{-i\vec{q}\cdot\vec{R}}$$
(1.32a)

$$\mathbf{U}_{\nu\nu'}(\vec{\mathbf{R}}_{\mathrm{I}}^{0} - \vec{\mathbf{R}}_{\mathrm{I}'}^{0}) \equiv \mathbf{U}_{\mathrm{I}\nu,\mathrm{I}'\nu'}$$

and

$$\vec{e}_{q\mu}^{*}, \vec{e}_{q\mu}^{*} = \delta_{\mu,\mu} \qquad (1.33)$$

From $D \propto M^{-1}$ (\tilde{U} depends slightly on M through screening) follows $\omega_q^0 \propto M^{-1/2}$ and $\vec{u}_I \propto M^{-1/4}$, $\vec{P}_I \propto M^{+1/4}$, $\dot{\vec{u}}_I \propto M^{-3/4}$. Hence with the definition (1.1) and taking the electron mass as unit

$$\mathcal{H}_{harm} \propto \kappa^2; \quad \mathcal{H}_n^{!} \propto \kappa^n$$

$$\mathcal{H}_{HF} \propto \kappa^0; \quad \mathcal{H}_{el-ph}^{!} \propto \kappa$$
(1.34)

This is the justification for treating \mathcal{H}_{el-ph} and \mathcal{H}_{anh} as perturbations. Classically, equipartition implies

$$\frac{\mathrm{m}}{2} \mathrm{v}_{\mathrm{el}}^2 = 3 \mathrm{k}_{\mathrm{B}} \mathrm{T} = \vec{\mathrm{P}}_{\mathrm{I}}^2 / 2 \mathrm{M} \propto \kappa^2$$

Hence $v_{el} \propto \kappa$ and Eq.(1.1a) follows. Quantum-mechanically we have

 $v_{F}^{} q \stackrel{\simeq}{,} \varepsilon_{k+q}^{0} - \varepsilon_{k}^{0} \cong \omega_{q}^{0} \cong v_{Ph}^{} q \propto \kappa^{2}$

Hence

$$v_{\rm Ph} / v_{\rm F} \propto \kappa^2$$
 (1.34a)

Inserting Eq.(1.27) into Eq.(1.20) we find

$$\mathcal{C}'_{el-ph} = \sum_{k'kq} g_{k'kq} a_{k'}^* a_k Q_q + \dots$$
 (1.35)

where

$$g_{\mathbf{k'kq}} = g_{\mathbf{kk'},\mathbf{q}}^* = (\mathbf{N}\mathbf{M}\omega_q^0)^{-1/2} \sum_{\mathbf{l}} \langle \mathbf{k'} | \left(\frac{\partial \mathbf{w}}{\partial \mathbf{\vec{R}}_{\mathbf{l}}}\right)_0 | \mathbf{k} \rangle \cdot \vec{e}_q e^{i\vec{q}\cdot\vec{\mathbf{R}}_{\mathbf{l}}^0} \qquad (1.35a)$$

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In general calculations are made by assuming two-body forces for $\tilde{U}(R)$ and $w(\vec{r}; R)$,

$$\widetilde{U}(\mathbf{R}) = \sum_{\mathbf{I} \neq \mathbf{I}'} \phi(\vec{\mathbf{R}}_{\mathbf{I}}; \vec{\mathbf{R}}_{\mathbf{I}'})$$
(1.36)

$$w(\vec{\mathbf{r}}; \mathbf{R}) = \sum_{\mathbf{I}} \varphi(\vec{\mathbf{r}}; \vec{\mathbf{R}}_{\mathbf{I}}) \qquad (1.37)$$

Equation (1.36) is usually a good approximation except for cubic crystals with inversion centre where three-body forces are sometimes needed (see, e.g. Ref.[5]). $\phi(\vec{R}_I; \vec{R}_{I'})$ is in general restricted to nearest neighbours.

If in addition deformation of the ions is negligible

$$\phi(\vec{R}_{I}; \vec{R}_{I}) = \phi(\vec{R}_{I} - \vec{R}_{I})$$
 (1.36a)

$$\varphi(\vec{r}; \vec{R}_{r}) = \varphi(\vec{r} - \vec{R}_{r})$$
 (1.37a)

Expression (1.36a) is often a poor approximation for the calculation of phonon dispersion curves (see, e.g. Ref.[6]). For us this is not important since neither Eq.(1.36) nor Eq.(1.36a) is very useful for simplifying expression (1.31) for $C_{q_1,\ldots,q_n}^{(n)}$. On the other hand, the rigidion approximation (1.37a) is considered good (see, e.g. Ref.[7]) and it also simplifies the coupling function $g_{k'k_{\sigma}}$, Eq.(1.35a). Writing

$$\frac{\partial \mathbf{w}}{\partial \vec{\mathbf{R}}_{1}} = -\frac{\partial \phi}{\partial \vec{\mathbf{r}}} = -\frac{i}{\hbar} [\vec{p}, \phi]$$

we have

$$<\mathbf{k}^{\mathbf{i}} \left| \left(\frac{\partial \mathbf{w}}{\partial \vec{R}_{I}} \right)_{\mathbf{0}} \right| \mathbf{k} > \cong -\frac{\mathbf{i}}{\hbar} \sum_{\mathbf{k}^{''}} \{ <\mathbf{k}^{\mathbf{i}} \right| \vec{p} \left| \mathbf{k}^{''} > <\mathbf{k}^{''} \right| \phi \left| \mathbf{k} > - <\mathbf{k}^{\mathbf{i}} \right| \phi \left| \mathbf{k}^{''} > <\mathbf{k}^{''} \right| \vec{p} \left| \mathbf{k} > \}$$

This is not rigorous since the valence band states $|k\rangle$ do not form a complete set of states. Approximating the Bloch states by plane waves,

we find (ϕ does not act on the spin variable σ)

$$g_{\mathbf{k}'\mathbf{k}q} \approx \frac{-i}{\sqrt{NM\omega_{q}}} (\vec{\mathbf{k}'} - \vec{\mathbf{k}}) \cdot \vec{\mathbf{e}}_{q} \sum_{\vec{\mathbf{k}}} \langle \vec{\mathbf{k}'} \sigma^{\dagger} | \varphi(\vec{\mathbf{r}} - \vec{\mathbf{k}}) | \vec{\mathbf{k}} \sigma \rangle e^{i\vec{q}\cdot\vec{\mathbf{k}}} \delta_{\sigma^{\dagger}\sigma}$$
(1.35b)

Coming back to Eq.(1.10b) we see that to lowest order in κ we may take the $|n\rangle$ as eigenstates of \mathscr{H}_{harm} . Then the states in $\langle n' | \vec{u}_1 | n \rangle$

differ only by one phonon so that Ω_n . - $\Omega_n = \pm \hbar \omega_q^0$. Hence

$$\langle n^{\dagger} | \langle \ell^{\dagger}; R | [\mathcal{H}_{ion}, \mathcal{H}_{el}] | \ell; R \rangle | n \rangle \propto \kappa^{3}$$
 (1.38)

This shows that in the harmonic approximation the ionic system is decoupled from the electrons and can be treated independently. However, anharmonic effects are of the same order as the mixing effects (1.38). Therefore, for crystals with excited electrons and holes (metals and semiconductors), the anharmonic effects cannot be treated independently of these excitations and one has to go back to the unscreened form of the potentials. For insulators, on the other hand, the electron-hole excitations can be neglected.

Let us now examine the terms of $\langle n' | l'; R | \mathcal{H} | l; R \rangle | n \rangle$. We find from Eqs (1.9), (1.9a)

$$\langle \mathbf{n}^{\mathbf{i}} | \mathbf{E}_{\ell}(\mathbf{R}) | \mathbf{n} \rangle \delta_{\ell^{\mathbf{i}}\ell} = \mathbf{E}_{\ell}(\mathbf{R}^{\mathbf{0}}) \delta_{\mathbf{n}^{\mathbf{i}}\mathbf{n}} \delta_{\ell^{\mathbf{i}}\ell} + \sum_{\mathbf{I}} \left(\frac{\partial \mathbf{E}_{\ell}}{\partial \mathbf{R}_{\mathbf{I}}} \right)_{\mathbf{0}} \langle \mathbf{n}^{\mathbf{i}} | \mathbf{u}_{\mathbf{I}} | \mathbf{n} \rangle \delta_{\ell^{\mathbf{i}}\ell} + \dots (1.39)$$

$$\langle \mathbf{n'} | \mathbf{A}_{\ell'\ell}(\mathbf{R}) | \mathbf{n} \rangle = \sum_{\mathbf{I}} \langle \ell' ; \mathbf{R} | \frac{\partial}{\partial \mathbf{\tilde{R}}_{\mathbf{I}}} | \ell; \mathbf{R} \rangle_{0} (\Omega_{\mathbf{n'}} - \Omega_{\mathbf{n}}) \langle \mathbf{n'} | \mathbf{\tilde{u}}_{\mathbf{I}} | \mathbf{n} \rangle + \dots \quad (1.40)$$

where we have used $\vec{P}_{I} \; / \; M$ = (i/h)[$\mathscr{H}_{ion}, \; \vec{u}_{\; I}]$ and

$$\langle \mathbf{n}^{\dagger} | \mathbf{B}_{\ell'\ell}(\mathbf{R}) | \mathbf{n} \rangle = \sum_{\mathbf{I}} \langle \ell^{\dagger}; \mathbf{R} | \left(\frac{\hbar}{i} \frac{\partial}{\partial \vec{\mathbf{R}}_{\mathbf{I}}} \right)^2 | \ell; \mathbf{R} \rangle_0 \frac{1}{2 \mathrm{M}} + \dots$$
 (1.41)

Now from Eq.(1.6)

$$0 = \langle \ell^{\mathbf{i}}; \mathbf{R} | \frac{\partial}{\partial \vec{\mathbf{R}}_{I}} \{ (\mathscr{U}_{eI}(\mathbf{R}) - \mathbf{E}_{\ell}(\mathbf{R})) | \ell; \mathbf{R} \rangle \}$$
$$= \langle \ell^{\mathbf{i}}; \mathbf{R} | \frac{\partial \mathbf{W}}{\partial \vec{\mathbf{R}}_{I}} | \ell; \mathbf{R} \rangle - \frac{\partial \mathbf{E}_{\ell}}{\partial \vec{\mathbf{R}}_{I}} \delta_{\ell^{\mathbf{i}} \ell} + (\mathbf{E}_{\ell^{\mathbf{i}}}(\mathbf{R}) - \mathbf{E}_{\ell}(\mathbf{R})) \langle \ell^{\mathbf{i}}; \mathbf{R} | \frac{\partial}{\partial \vec{\mathbf{R}}_{I}} | \ell; \mathbf{R} \rangle$$

we find

$$\langle \ell^{\dagger}; \mathbf{R} | \frac{\partial \mathbf{W}}{\partial \vec{\mathbf{R}}_{I}} | \ell; \mathbf{R} \rangle = \frac{\partial \mathbf{E}_{\ell}}{\partial \vec{\mathbf{R}}_{I}} \delta_{\ell^{\dagger}\ell}; \mathbf{E}_{\ell} = \mathbf{E}_{\ell}$$
 (1.42)

$$\langle \ell^{\dagger}; \mathbf{R} | \frac{\partial}{\partial \mathbf{R}_{I}} | \ell; \mathbf{R} \rangle = \frac{\langle \ell^{\dagger}; \mathbf{R} | \frac{\partial \mathbf{W}}{\partial \mathbf{R}_{I}} | \ell; \mathbf{R} \rangle}{\mathbf{E}_{\ell}(\mathbf{R}) - \mathbf{E}_{\ell^{\dagger}}(\mathbf{R})}; \mathbf{E}_{\ell} \neq \mathbf{E}_{\ell}$$
(1.43)

In addition it follows from time reversal invariance of \mathscr{H}_{el} that the states $|\ell; R \rangle$ may be chosen real, so that we find from (1.6')

$$\langle \ell; \mathbf{R} | \frac{\partial}{\partial \mathbf{\tilde{R}}} | \ell; \mathbf{R} \rangle = \frac{1}{2} \frac{\partial}{\partial \mathbf{\tilde{R}}_{\mathrm{I}}} \langle \ell; \mathbf{R} | \ell; \mathbf{R} \rangle = 0$$
 (1.44)

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From Eq.(1.42) we conclude that the second term of Eq.(1.39) is the diagonal part, in the electronic co-ordinates, $\ell^{\dagger} = \ell$, of the electron-phonon interaction (energy is not conserved in this term since it creates or destroys a phonon). From Eq.(1.44) we see that Eq.(1.40) is non-diagonal in the electronic co-ordinates. And Eq.(1.43) shows that its energy-conserving part is identical with the electron-phonon matrix element (see Eq.(1.12)):

$$\langle \mathbf{n}^{\mathbf{i}} | \mathbf{A}_{\boldsymbol{\ell}^{\mathbf{i}}\boldsymbol{\ell}}(\mathbf{R}) | \mathbf{n} \rangle |_{\Omega_{\mathbf{n}^{\mathbf{i}}} + \mathbf{E}_{\boldsymbol{\ell}^{\mathbf{i}}} = \Omega_{\mathbf{n}} + \mathbf{E}_{\boldsymbol{\ell}}} = \sum_{\mathbf{I}} \langle \boldsymbol{\ell}^{\mathbf{i}} ; \mathbf{R}^{\mathbf{0}} | \left(\frac{\partial \mathbf{W}}{\partial \vec{\mathbf{R}}_{\mathbf{I}}} \right)_{\mathbf{0}} | \boldsymbol{\ell}; \mathbf{R}^{\mathbf{0}} \rangle \langle \mathbf{n}^{\mathbf{i}} | \vec{\mathbf{u}}_{\mathbf{I}} | \mathbf{n} \rangle + \dots$$

$$= \langle \mathbf{n}^{\mathbf{i}} | \langle \boldsymbol{\ell}^{\mathbf{i}} ; \mathbf{R}^{\mathbf{0}} | \mathcal{H}_{\mathbf{e}\mathbf{I}-\mathbf{ph}}^{\mathbf{i}} | \boldsymbol{\ell}; \mathbf{R}^{\mathbf{0}} \rangle | \mathbf{n} \rangle + \dots$$

$$(1.45)$$

Physically this means that $\mathscr{H}_{el-ph}^{\bullet}$ also reacts on the ions. The remaining, energy non-conserving, terms of Eq.(1.40) as well as Eq.(1.41) are difficult to estimate (see Ref.[2]). In order to assure the main result Eq.(1.38) they must combine to give terms of order κ^3 at least.

1.3. Crystal momentum conservation

By translation invariance of the whole system both U(R) and W(r;R) in Eqs (1.3), (1.4) depend only on co-ordinate differences. Now the ionic groundstate R = R⁰ is symmetry breaking in the sense that it is invariant only with respect to the translations by lattice vectors $\vec{R} = \vec{R}_{I}^{0}$. Since

$$\frac{1}{N}\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}} = \Delta(\vec{k}) = \sum_{\vec{k}} \delta_{\vec{k},\vec{K}}$$
(1.46)

where \vec{K} are the vectors of the reciprocal lattice defined by $exp(i \vec{K} \cdot \vec{R}) = 1$ we find immediately from Eqs (1.35a) and (1.31) that

$$g_{k'kq} \propto \Delta(\vec{k}' - \vec{k} - \vec{q})$$

$$C_{q_1 \dots q_n}^{(n)} \propto \Delta(\vec{q}_1 + \dots + \vec{q}_n)$$
(1.47)

This means momentum conservation modulo a $\vec{K} \cdot \vec{K} \neq 0$ are umklapp processes. Since \vec{k} and \vec{q} lie within the reduced Brillouin zone umklapp is possible only for processes involving more than two particles. This is the case both for \mathcal{H}'_{el-ph} and \mathcal{H}'_{anh} but not for couplings to external fields which are of the form

$$\sum \alpha_{k'k} a_{k'}^* a_k, \sum \beta_{q'q} b_{q'}^* b_q$$

Writing

$$\mathcal{U}_{el-ph} = \sum_{\vec{k}} \mathcal{U}_{el-ph} (\vec{k})$$
 (1.48)

$$\mathcal{H}_{n}^{\dagger} = \sum_{\vec{k}} \mathcal{H}_{n}^{\dagger}(\vec{k})$$
 (1.49)

where

$$\mathcal{H}_{el-ph}^{\prime}(\vec{K}) = \sum_{k'kq} \delta_{\vec{k}', \vec{k}+\vec{q}} + \vec{K}g_{k'kq} a_{k'}^{*} a_{k}Q_{k} \qquad (1.48a)$$

$$\mathscr{H}_{\mathbf{n}}^{\mathbf{r}}(\vec{\mathbf{K}}) = \frac{1}{n!} \sum_{q_{1}\cdots q_{n}} \vec{\delta}_{q_{1}} + \cdots + \vec{q}_{n}, \vec{\mathbf{K}} C_{q_{1}\cdots q_{n}}^{(n)} Q_{q_{1}} \cdots Q_{q_{n}}$$
(1.49a)

we see that the terms with $\vec{K} = 0$ and $\vec{K} \neq 0$ give rise to <u>normal processes</u> and umklapp processes, respectively. From Eqs (1.35b), (1.46), (1.52) we find for (1.48a) (note that $|k + K\rangle = |k\rangle$)

$$\mathcal{H}_{el-ph}^{\prime}(\vec{K}) \approx -i \sum_{kq} \sqrt{\frac{N}{M\omega_{q}^{0}}} (\vec{q} + \vec{K}) \cdot \vec{e}_{q} \langle \vec{k} + \vec{q}, \sigma | \phi | k, \sigma \rangle \cdot a_{k+q+K}^{*} a_{k} Q_{q} (1.50)$$

which shows that normal processes essentially couple only to the longitudinal phonon mode. In the approximation of the Bloch states $|k\rangle$ by plane waves

$$\langle \vec{\mathbf{k}}^{\dagger} \sigma | \varphi | \vec{\mathbf{k}} \sigma \rangle \cong \frac{1}{V} \widetilde{\varphi} (\vec{\mathbf{k}}^{\dagger} - \vec{\mathbf{k}})$$

where

$$\vec{\varphi}(\vec{q}) = \int_{V} d^{3} \mathbf{r} \varphi(\vec{r}) e^{-i\vec{q}\cdot\vec{r}}$$

is the Fourier transform and V the crystal volume. In this approximation expression (1.50) reduces to

$$\mathscr{H}'_{el-ph}(\vec{K}) \cong \sum_{kq} \gamma_q^0(\vec{K}) a_{k+q+K}^* a_k Q_q$$
 (1.50a)

where

$$\gamma_{q}^{0}(\vec{K}) = -\frac{i}{v_{0}\sqrt{NM\omega_{q}^{0}}} \quad (\vec{q} + \vec{K}) \cdot \vec{e}_{q} \widetilde{\varphi}(\vec{q})$$
(1.50b)

and $v_0 = V/N$ is the volume of the unit cell.

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Formally umklapp is expressed by the fact that the $\vec{K} \neq 0$ terms in Eqs (1.48), (1.49) do not commute with the (Hermitian) crystal momentum operator \vec{J} . As in field theory we define \vec{J} as generator of the translations by lattice vectors \vec{R} ,

$$\mathscr{T}_{\vec{R}} = e^{\vec{i}\vec{J}\cdot\vec{R}}$$
(1.51)

Now the Bloch states have the property

$$\mathcal{F}_{\vec{R}} | k \rangle = e^{i\vec{k}\cdot\vec{R}} | k \rangle$$
 (1.52)

and since $\mathscr{F}_{\overrightarrow{a}}|0\rangle = |0\rangle$ we have from Eqs (1.22), (1.22a)

$$\mathscr{T}_{\vec{R}} a_k^* \mathscr{T}_{\vec{R}}^{\downarrow 1} = e^{+i\vec{k}\cdot\vec{R}} a_k^*$$
 (1.52a)

On the other hand, translation by \vec{R} transforms \vec{u}_I into \vec{u}_I , with \vec{R}_I^0 , = \vec{R}_I^0 + \vec{R}

$$\mathcal{F}_{\vec{R}} \vec{u}_{1} \mathcal{F}_{\vec{R}}^{-1} = \vec{u}_{1} \tag{1.53}$$

With Eqs (1.27), (1.30) we find (see Ref.[8])

$$\mathcal{F}_{\vec{R}} b_q \mathcal{F}_{\vec{R}}^{-1} = e^{+i\vec{q}\cdot\vec{R}} b_q$$
 (1.53a)

Expanding Eqs (1.52a) and (1.53a) in powers of \vec{R} we obtain from the linear terms

$$[\vec{J}, a_k^*] = \vec{k} a_k^*$$

 $[\vec{J}, b_q^*] = \vec{q} \cdot b_q^*$ (1.54)

This has the solution

$$\vec{J} = \vec{J}_{el} + \vec{J}_{ph}$$

$$\vec{J}_{el} = \sum_{k} \vec{k} a_{k}^{*} a_{k}; \quad \vec{J}_{ph} = \sum_{q} \vec{q} b_{q}^{*} b_{q}$$

$$(1.55)$$

Now it is easy to calculate (see Ref.[8], for the phonon case)

$$[\vec{J}_{el}, \mathscr{H}_{el-ph}^{\dagger}(\vec{K})] = \sum_{kq} (\vec{q} + \vec{K}) g_{k+q+K,k,q} a_{k+q+K}^{*} \cdot a_{k} Q_{q}$$
(1.56)

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$$[\vec{J}_{ph}, \mathscr{H}_{el-ph}^{*}(\vec{K})] = \sum_{kq} (-\vec{q}) g_{k+q+K,k,q} a_{k+q+K}^{*} a_{k} Q_{q}$$
(1.57)

$$[\vec{J}_{ph}, \mathcal{H}_{n}^{*}(\vec{K})] = \vec{K} \mathcal{H}_{n}^{*}(\vec{K})$$
(1.58)

Hence for $\vec{K} = 0$,

$$[\vec{J}, \mathcal{H}_{el-ph}^{\prime}(0)] = 0$$

 $[\vec{J}, \mathcal{H}_{anh}^{\prime}(0)] = 0$ (1.59)

The commutator of the umklapp part ($\vec{K} \neq 0$) of the interactions gives rise to external forces exercised by the lattice,

$$i [\mathcal{H}_{el}, \vec{J}] = i \sum_{\vec{K}=0} [\mathcal{H}_{el-ph}(\vec{K}), \vec{J}] \equiv \vec{F}_{el}$$

$$i [\mathcal{H}_{ion}, \vec{J}] = i \sum_{\vec{K}\neq 0} [\mathcal{H}_{anh}(\vec{K}), \vec{J}] \equiv \vec{F}_{ph}$$
(1.60)

Note that the non-vanishing of these force operators \vec{F}_{el} and \vec{F}_{ph} is not in contradiction with the fact that all terms of the Hamiltonian \mathscr{H} are invariant under lattice translations,

$$\mathcal{F}_{R}^{\rightarrow} \mathcal{H} \mathcal{F}_{R}^{-1} = \mathcal{H}$$
(1.61)

This is due to the fact that the latter form a discrete Abelian group. The only examples of such groups in elementary particle physics are parity, time reversal and charge conjugation which are known to give rise to multiplicative conservation laws whereas, according to Noether's theorem, Lie groups give rise to additive conservation laws. Crystal momentum conservation modulo $\vec{K_n}$ therefore is a multiplicative conservation law,

namely $\prod_{i=1}^{n} \exp(i\vec{q}_i \cdot \vec{R}) = 1$. And umklapp is the price one pays for writing it in the additive form $\sum_{i=1}^{n} \vec{q}_i = \vec{K}$.

2. ELECTRON-PHONON INTERACTION IN METALS

In this section we discuss what we think to be the typical cases of how the electron-phonon interaction modifies the properties of the electrons in a metal. It is not surprising that the basic question turns out to be how the coupling function γ_q^0 itself is modified. Now the <u>Migdal theorem</u> states that up to order κ it is not modified at all, at least under conditions such that the exchanged phonons have not too long a

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wave-length and the electron energies are not too far off from the Fermi surface. It turns out, however, that the typical cases are in a loose sense just exceptions to this theorem. These are the renormalization effects, the pair instability leading to superconductivity and the hydrodynamical limit giving rise to a transport equation.

2.1. Real-time Green functions. Migdal's theorem

The one-electron Green function is defined by

$$G_1^2 = \frac{1}{i} \langle T(a_{k_1}(t_1) a_{k_2}^*(t_2)) \rangle = 1 - 2$$
 (2.1)

Here T is the ordering according to real time,

$$T(A(t) B(t')) = \theta(t - t') A(t) B(t') \pm \theta(t' - t) B(t') A(t)$$
(2.2)

the upper (lower) sign referring to boson (fermion) operators. A(t) is the Heisenberg representation (we put $\hbar = 1$ from here on)

$$A(t) = e^{i \mathscr{U} t} A e^{-i \mathscr{U} t}$$
(2.3)

The average is defined as

$$\langle A \rangle = Tr (e^{\beta(F - \mathscr{X} + \mu N_e)}A)$$
 (2.4a)

where μ is the chemical potential (Fermi energy) and $N_{el} = \sum_{k} a_{k}^{*} a_{k}$

the electron-number operator. $\ {\rm F}$ being the thermodynamic potential defined by

$$\langle 1 \rangle = 1$$
 (2.4b)

Similarly the one-phonon Green function is defined by

$$D(1,2) = \frac{1}{i} \langle T(Q_{q_1}(t_1)Q_{q_2}^*(t_2)) \rangle = 1 - 2$$
 (2.5)

These Green functions depend only on the time difference $t_1 - t_2$ and, according to Eqs (1.52a), (1.53a) and (1.61), conserve momentum, $G_1^2 \propto \delta_{\vec{k}_1\vec{k}_2}$, $D(1, 2) \propto \delta_{\vec{q}_1\vec{q}_2}$. Since \mathscr{H} does not induce spin-flip processes (we did not consider exchange interactions) we have, in addition, $G_1^2 \propto \delta_{\sigma_1,\sigma_2}$. Thus we can write

$$G_1^2 = G(k_1; t_1 - t_2)\delta_{k,k}$$
 (2.6)

In general D(1, 2) cannot be simplified in the same way because \mathscr{H}_{anh}^{i} contains polarization-flip processes, $\mu \rightarrow \mu^{i}$. However, according to Eq.(1.34) these terms are at least of order κ^{4} (the lowest order diagram is ...). Note that \mathscr{H}_{el-ph}^{i} does not induce polarization flips

if umklapp is neglected, since only the longitudinal polarization is coupled. Here we shall neglect umklapp and write the coupling function (1.50b) for $\vec{K} = 0$ simply γ_a^0 . Then

$$D(1, 2) = D(q_1; t_1 - t_2) \delta_{q, q_1} + O(\kappa^4)$$
(2.7)

D(q; t) still contains the renormalization effects due to the electronphonon interaction. Calling G^0 , D^0 the Green function referring to the free Hamiltonian,

$$\mathcal{H}_{0} = \mathcal{H}_{HF} + \mathcal{H}_{harm}$$
 (2.8)

their Fourier transform as defined by

$$G(k; \omega) = \int dt G(k; t)^{i\omega t}$$
 (2.9)

etc., is found to be

$$D^{0}(q;\omega) = \frac{(1+n_{q}^{0})\omega_{q}^{0}}{\omega^{2} - (\omega_{q}^{0} - i\delta)^{2}} - \frac{n_{q}^{0}\omega_{q}^{0}}{\omega^{2} - (\omega_{q}^{0} + i\delta)^{2}} = \qquad (2.10b)$$

where $\delta \rightarrow 0^+$ and

$$f_k^0 = \langle a_k^* a_k \rangle_0 = (e^{\beta \epsilon_k^0} + 1)^{-1}$$
 (2.11a)

$$n_{q}^{0} = \langle b_{q}^{*} b_{q} \rangle_{0} = (e^{\beta \omega_{q}^{0}} - 1)^{-1}$$
 (2.11b)

are the electron and phonon occupation numbers referring to \mathscr{H}_0 . In the limit $T \to 0$, $f_k^0 \to \theta(-\epsilon_k^0)$, $n_q^0 \to 0$, so that

$$G^{0}(k; \omega) \rightarrow \frac{1}{\omega - \epsilon_{k}^{0} + i\delta \operatorname{sign} \epsilon_{k}^{0}}$$
 (2.12a)

$$D^{0}(q; \omega) \rightarrow \frac{\omega_{q}^{0}}{\omega^{2} - \omega_{q}^{02} + i\delta}$$
 (2.12b)

This limit already gives interesting renormalization effects in the electron system. The limit is even necessary if perturbation theory is used for real-time Green functions. At T>0 only the perturbation theory of imaginary-time Green function works properly (see subsections 2.4 and 3.1). We shall not make use of perturbation theory in this section, however. Of course, non-perturbative methods (functional derivatives, equations of motion (see, e.g. Ref. [9])) are always possible.

Because of the θ -functions in the definition of the time-order (2.2) G and D consist of two parts each of which is analytical, respectively, in the upper and lower half ω -plane. While for finite temperature these parts of G and D have cuts all along the real ω -axis (see Eqs (2.14a), (2.14b)), at T = 0 the cuts extend only over the positive and negative real ω axis, respectively. Therefore, at T = 0, G and D have a unique spectral representation (see the contribution of Prof. Lundquist in this book)¹

$$G(\mathbf{k}; \omega) = \int_{-\infty}^{+\infty} \frac{A(\mathbf{k}; \omega^{\dagger}) d\omega^{\dagger}}{\omega - \omega^{\dagger} + i\delta \operatorname{sign} \omega^{\dagger}}$$
(2.13a)

$$D(q; \omega) = \int_{-\infty}^{+\infty} \frac{B(q; \omega') d\omega'}{\omega - \omega' + i\delta \operatorname{sign} \omega'}$$
(2.13b)

Here

$$\mathbf{A}(\mathbf{k}; \omega) = \sum_{ss'} \rho_{s} \{ |\langle \Psi_{s}, |\mathbf{a}_{k}^{*}|\Psi_{s} \rangle|^{2} \delta(\boldsymbol{\xi}_{s}, -\boldsymbol{\xi}_{s} - \omega) + |\langle \Psi_{s}, |\mathbf{a}_{k}|\Psi_{s} \rangle|^{2} \delta(\boldsymbol{\xi}_{s}, -\boldsymbol{\xi}_{s} + \omega) \}$$

$$(2.14a)$$

$$B(q;\omega) = \sum_{ss'} \rho_s \{ |\langle \Psi_{s'} | Q_q^* | \Psi_s \rangle |^2 \delta(\xi_{s'} - \xi_s - \omega) - |\langle \Psi_{s'} | Q_q | \Psi_s \rangle |^2 \delta(\xi_{s'} - \xi_s + \omega) \}$$

$$(2.14b)$$

are the spectral functions at temperature T. Ψ_s , ξ_s are the eigenstates and eigenvalues of \mathcal{H} , Eq.(1.8) and ρ_s is the eigenvalue of the density matrix defined in expressions (2.4).

A and B are real and A is non-negative by construction. Both satisfy a sum rule,

$$\int_{\infty}^{+\infty} A(\mathbf{k}; \omega) d\omega = \sum_{\mathbf{s}} \rho_{\mathbf{s}} \langle \Psi_{\mathbf{s}} | [\mathbf{a}_{\mathbf{k}}^* \mathbf{a}_{\mathbf{k}}]_{+} | \Psi_{\mathbf{s}} \rangle = 1 \qquad (2.15a)$$

$$\int_{\infty}^{\infty} \mathbf{B}(\mathbf{q}; \omega) \, d\omega = \sum_{s} \rho_{s} \langle \Psi_{s} | [\mathbf{Q}_{q} \mathbf{Q}_{q}^{*}] | \Psi_{s} \rangle = 0 \qquad (2.15b)$$

In addition

$$\int_{-\infty}^{\infty} \mathbf{B}(\mathbf{q};\omega)\omega \, \mathrm{d}\omega = \sum_{s} \rho_{s} \langle \psi_{s} | [\mathbf{Q}_{\mathbf{q}}[\mathcal{E}\mathbf{Q}_{\mathbf{q}}^{*}] | \psi_{s} \rangle = \omega_{\mathbf{q}}$$

The effect of renormalization on G and D due to the electron-phonon interaction is contained in the electron and phonon self-energies Σ and Π , respectively. They constitute the one-particle irreducible (or proper) parts of G and D. And the one-particle reducibility of the latter is explicitly exhibited through the Dyson equations (which may also be considered as a definition of Σ and Π)

$$G(\mathbf{k}; \omega) = G^{0}(\mathbf{k}, \omega) + G^{0}(\mathbf{k}, \omega) \Sigma(\mathbf{k}, \omega) G(\mathbf{k}, \omega) \qquad (2.16a)$$

$$D(q, \omega) = D^{0}(q, \omega) + D^{0}(q, \omega) \Pi(q, \omega) D(q, \omega)$$
(2.16b)

¹ Actually, a spectral representation exists also for T > 0 but it is not commonly used. Indeed, with the method presented in Part 3 to derive Eq.(3.11) one finds

$$G(\mathbf{k},\omega) = \int_{-\infty}^{+\infty} \frac{\mathbf{A}_1(\mathbf{k},\omega')\,\mathrm{d}\omega'}{\omega-\omega'+\mathrm{i}\delta} + \int_{-\infty}^{+\infty} \frac{\mathbf{A}_2(\mathbf{k},\omega')\,\mathrm{d}\omega'}{\omega-\omega'-\mathrm{i}\delta}$$

and similarly for $D(q, \omega)$. Here A_1 and A_2 are the two terms of Eq.(2.14a) which in the limit $T \rightarrow 0$ are non-zero only for $\omega > 0$ and $\omega < 0$, respectively.

or in diagrammatic form



Making use of Eqs (2.10a), (2.10b) these equations may be inverted to give

$$G(k, \omega) = \frac{1}{\omega - \epsilon_k^0 - \Sigma(k; \omega)}$$
(2.17a)

$$D(q, \omega) = \frac{\omega_q^0}{\omega^2 - \omega_q^{02} - \omega_q^0 \Pi(q; \omega)}$$
(2.17b)

One obtains a closed set of equations by introducing the renormalized, one-particle irreducible, 3-point vertex (see Ref.[10]):



Here γ_q^0 is the unrenormalized vertex as given by the coupling function (1.50b) for $\vec{K}=0$. From the diagram equations



the additional equations are seen to be (the factors may be determined from the lowest order perturbation theory diagrams)

$$\Sigma(\mathbf{k};\omega) = \frac{1}{\mathrm{iV}} \sum_{\mathbf{q}} \gamma_{\mathbf{q}}^{0} \int \frac{\mathrm{d}\nu}{2\pi} \operatorname{G}(\mathbf{k}+\mathbf{q}, \omega+\nu) \operatorname{D}(\mathbf{q};\nu) \gamma(\mathbf{k}, \omega; \mathbf{q}, \nu)$$
(2.19a)

$$\Pi(\mathbf{q};\nu) = \frac{1}{\mathrm{iV}} \sum_{\mathbf{k}} \gamma_{\mathbf{q}}^{0} \int \frac{\mathrm{d}\omega}{2\pi} \, \mathbf{G}(\mathbf{k}+\mathbf{q};\,\omega+\nu) \, \mathbf{G}(\mathbf{k},\,\omega) \, \gamma\left(\mathbf{k},\,\omega;\,\mathbf{q},\,\nu\right)$$
(2.19b)
Note that these equations involve only exact Green functions G and D and hence are independent of perturbation theory. They just exhibit an internal structure like the Dyson equations and may, in fact, be derived by functional methods (see, e.g. Ref. [15], p.332). If the vertex function is supposed to be given, then Eqs (2.19a), (2.19b) and (2.17a), (2.17b)form a closed system of coupled integral equations.

Now Migdal states [10] that for the values of k, ω , q, ν which are relevant in Eqs (2.19a), (2.19b) (i.e. near the Fermi surface, q, $k \approx k_F$; ω , $\nu \approx \omega_D$ = Debye frequency)

$$\frac{\gamma(\mathbf{k},\omega;\mathbf{q},\nu)}{\gamma_{\mathbf{q}}^{0}} = 1 + O(\kappa^{2})$$
(2.20)

(See also Ref.[12], pp.156-163.) We shall call this the <u>Migdal theorem</u>. It simplifies considerably the calculation of Σ and Π since Σ turns out to vary little with k near the Fermi surface so that according to (2.17a) G can be approximated by G⁰ in Eqs (2.19a), (2.19b). For this reason the Migdal theorem is also called the "weak momentum dependence approximation" (see Ref.[13]).

That the Migdal theorem is not generally true can be seen in explicit examples (see sub-sections 2.3 and 2.4) which are characterized by very small q-values, $q \ll k_F$. The first was pointed out by Engelsberg and Schrieffer (see Ref.[14]). They noticed that the generalized Ward-Takahashi identity

$$\frac{\gamma(\mathbf{k},\,\omega;\,\mathbf{q},\,\nu)}{\gamma_{2}^{0}} = \frac{\mathbf{G}^{-1}(\mathbf{k}+\mathbf{q},\,\omega+\nu)-\mathbf{G}^{-1}(\mathbf{k},\,\omega)}{\nu}$$

taken in the limit "first $q \rightarrow 0$, then $\nu \rightarrow 0$ ",

.

$$\frac{\gamma(\mathbf{k}, \omega; \mathbf{q}, \nu)}{\gamma_{\mathbf{q}}^{0}} \bigg|_{\substack{\mathbf{q} \to 0 \\ \nu \to 0}} = \frac{\partial \mathbf{G}^{-1}(\mathbf{k}, \omega)}{\partial \omega} = 1 - \frac{\partial \Sigma(\mathbf{k}, \omega)}{\partial \omega}$$
(2.21)

may in certain cases lead to a correction $\partial \Sigma / \partial \omega$ of order one.

2.2. Renormalization effects in normal state

If Eqs (2.17a) or (2.17b) are well approximated by one or several poles near the real axis in the ω -plane these poles are called quasi-particles. The location of quasi-electrons is characterized by the renormalized energy ϵ_k and the width $|\Gamma_k|$ such that $\omega = \epsilon_k - i\Gamma_k$. From (2.17a) we then find

$$\epsilon_{k} - \epsilon_{k}^{0} - \operatorname{Re}\Sigma(k, \epsilon_{k} - i\Gamma_{k}) = 0$$
 (2.22a)

$$\Gamma_{k} = |\Gamma_{k}| \operatorname{sign} \epsilon_{k} = -\operatorname{Im} \Sigma(k; \epsilon_{k} - i\Gamma_{k}) \qquad (2.22b)$$

the assumption being that $|\Gamma_k| \ll |\epsilon_k|$.

A development $\overline{\Sigma}(\mathbf{k},\omega)$ in powers of $\omega - \epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}}$ gives

$$\Sigma(\mathbf{k},\omega) = \Sigma(\mathbf{k},\epsilon_{\mathbf{k}}-i\Gamma_{\mathbf{k}}) + (\omega-\epsilon_{\mathbf{k}}+i\Gamma_{\mathbf{k}})\frac{\partial\Sigma}{\partial\omega}\Big|_{\omega=\epsilon_{\mathbf{k}}-i\Gamma_{\mathbf{k}}} + \cdots$$

and one finds from Eq. (2.17a)

$$G^{-1}(k, \omega) = (\omega - \epsilon_k + i\Gamma_k) \left(1 - \frac{\partial \Sigma}{\partial \omega}\Big|_{\omega = \epsilon_k - i\Gamma_k}\right) + \dots$$

which can be written as

$$G(k, \omega) = \frac{z_k}{\omega - \epsilon_k + i\Gamma_k} + G_{reg}(k, \omega)$$
(2.23)

where z_k is defined by (see Ref.[16])

$$z_{k}^{-1} = 1 - \frac{\partial \Sigma}{\partial \omega} \bigg|_{\omega = \epsilon_{k} - i\Gamma_{k}}$$
(2.24)

and G_{reg} is regular in the vicinity of the pole. This formulation of the quasi-particle concept is sufficiently general for most purposes. The spectral function associated with (2.23) is, at T = 0,

$$A(k, \omega) = \frac{z_k}{\pi} \frac{|\Gamma_k|}{(\omega - \epsilon_k)^2 + \Gamma_k^2} + A_{back} \qquad (2.25)$$

where A_{back} describes a background spectrum which is smooth in the vicinity of the pole and determines z_k through the sum rule (2.15a)

$$1 - z_{k} = \int_{-\infty}^{+\infty} d\omega' A_{back} (k, \omega') \qquad (2.26)$$

so that $z_k \leq 1$.

According to Eq. (2.25) a quasi-particle has a Lorentzian line shape superposed on the background. If the latter is negligible the quasiparticle "exhausts the sum rule" and $z_k = 1$. Note that this limit $z_k \approx 1$ would be required by the Migdal theorem if it applied generally, since from the Ward identity (2.21) we have

$$z_{k}^{-1} = \frac{\gamma(k, \epsilon_{k} - i\Gamma_{k}; q, \nu)}{\gamma_{q}^{0}} \Big|_{\substack{q \to 0 \\ \nu \to 0}}$$

In order to show that Eq.(2.25) inserted in Eq.(2.13a) leads to Eq.(2.23) we use the identity

$$\int_{-\infty}^{+\infty} \frac{f(\omega') d\omega'}{\omega - \omega' + i\delta \operatorname{sign} \omega'} = \int_{-\infty}^{+\infty} \frac{f(\omega') d\omega'}{\omega - \omega' \pm i\delta} \pm 2\pi i f(\omega) \theta(\mp \omega)$$

which is obtained by using

$$\frac{1}{\omega' - \omega \mp i\delta} = \frac{P}{\omega' - \omega} \pm i\pi \,\delta(\omega' - \omega)$$

for the second term on the right-hand side. Now we put

$$\mathbf{f}(\omega) = \frac{\mathbf{z}_{\mathbf{k}}}{\pi} \frac{\left| \boldsymbol{\Gamma}_{\mathbf{k}} \right|}{(\omega - \epsilon_{\mathbf{k}})^2 + \boldsymbol{\Gamma}_{\mathbf{k}}^2}$$

and use the upper (lower) sign of the identity for $\epsilon_k > 0$ ($\epsilon_k < 0$). The first integral on the r.h.s. of the identity can be integrated in the complex ω '-plane (see figure) and leads to the first term in Eq. (2.23).



The second term is non-singular because ω and ε_k have opposite signs by assumption. It may thus be added to the integral over A back which together give G_{reg} in Eq.(2.23). In the limit $|\Gamma_k| \rightarrow \delta = 0^+$ we have, at T = 0, a stable quasi-particle

(see the contribution by Lundquist in this book)

$$A(k; \omega) = z_k \delta(\omega - \epsilon_k) + A_{back} \qquad (2.27a)$$

$$G(\mathbf{k}; \omega) = \frac{z_k}{\omega - \epsilon_k + i\delta \operatorname{sign} \epsilon_k} + G_{\operatorname{reg}}$$
(2.27b)

$$z_{k}^{-1} = 1 - \frac{\partial \text{Re}\Sigma}{\partial \omega} \bigg|_{\omega = \epsilon_{k}}$$
(2.27c)

Since now $z_k^{-1}(G - G_{reg})$ has exactly the form of G_0 we can introduce quasi-particle creation and annihilation operators A_k^* , A_k and call $\sqrt{z_k} \cdot A_k^* | 0 >$ the quasi-particle wave function (in analogy to (1.22)). Hence z_k is the wave function renormalization factor (see Ref. [16]). With the correction factor z_k the quasi-particle picture is a good approximation as long as Im(k; ω) is small (see Ref.[17]).

Differentiation of (2.22a) with respect to \vec{k} gives in the limit $|\Gamma_{\mathbf{k}}| \rightarrow \delta$

$$\frac{\partial \epsilon}{\partial \vec{k}} - \frac{\partial \epsilon_k^0}{\partial \vec{k}} - \frac{\partial \operatorname{Re} \Sigma}{\partial \vec{k}} \bigg|_{\omega = \epsilon_k} - \frac{\partial \operatorname{Re} \Sigma}{\partial \omega} \bigg|_{\omega = \epsilon_k} \frac{\partial \epsilon_k}{\partial \vec{k}} = 0$$

or for spherical bands (see Ref. [18])

$$\frac{\mathbf{v}_{k}}{\mathbf{v}_{k}^{0}} = \mathbf{z}_{k} \left(1 + \frac{1}{\mathbf{v}_{k}^{0}} \left. \frac{\partial \operatorname{Re} \Sigma}{\partial k} \right|_{\omega = \epsilon_{k}} \right)^{-1} \cong \mathbf{z}_{k} < 1$$
(2.28)

where $\vec{v}_k = \partial \epsilon_k / \partial \vec{k}$ and \vec{v}_k^0 are the electron velocities. The simplification on the r.h.s. is a consequence of the Migdal theorem. Indeed, by putting $\gamma = \gamma^0$ in Eq.(2.19a) it can be shown (see, e.g. Ref. [17], p.162) that near the Fermi surface Re Σ is also small and depends only very little on \vec{k} so that

$$\frac{1}{\mathbf{v}_{\mathbf{k}}^{0}} \left. \frac{\partial \operatorname{Re} \Sigma}{\partial \mathbf{k}} \right|_{\boldsymbol{\omega} = \epsilon_{\mathbf{k}}} = O\left(\frac{\operatorname{Re} \Sigma}{\mu}\right) \ll 1$$

In spite of these properties $\operatorname{Re}\Sigma$ may depend strongly on ω , so that $z_k \neq 1$.

If an effective mass approximation is valid for the valence band, so that

$$\epsilon_{k}^{0} = \frac{k^{2} - k_{F}^{2}}{2m_{B}}$$

then the electron-phonon interaction gives rise to a mass renormalization such that

$$\epsilon_{k} = \frac{k^2 - k_F^2}{2(m_B + \delta m_k)}$$

From Eqs (2.28), (2.27c) we find

$$\frac{\mathbf{v}_{\rm F}^{\rm o}}{\mathbf{v}_{\rm F}} = 1 + \frac{\delta m}{m_{\rm B}} \cong z^{-1} \tag{2.29}$$

where $z = z_{k_{E}}$, $\delta m = \delta m_{k_{E}}$. It follows that

$$k_{F} = (m_{B} + \delta m)v_{F} = m_{B}v_{F}^{0}$$

i.e. no renormalization effect on k_{F} .

Since renormalization effects die off for $|\epsilon_k| \gg \omega_D$ the situation is as described in the figure where $\mu^0 = k_F^2/2m_B$ is the unrenormalized Fermi energy.



Similarly, the effect of renormalization on the density of states is essentially described by z_k^{-1} :

$$N^{0}(\omega) = \frac{1}{V} \sum_{k} \delta(\omega - \epsilon_{k}^{0}) = \frac{1}{\pi^{2}} \left(k^{2} \frac{dk}{d\epsilon_{k}^{0}}\right)_{\epsilon_{k}^{0} = \omega}$$

$$N(\omega) = \frac{1}{V} \sum_{k} \delta(\omega - \epsilon_{k}) = \frac{1}{\pi^{2}} \left(k^{2} \frac{dk}{d\epsilon_{k}} \right)_{\epsilon_{k}} = \omega$$

(a factor of 2 comes from the spin sum). Now for ω -values of the order of phonon frequencies ω_q , k-k_F \cong q $v_{ph}/v_F \ll k_F$, i.e. k is almost constant. Hence (see Ref.[17])

$$\frac{N(\omega)}{N^{0}(\omega)} \approx \frac{v_{k}^{0}}{v_{k}} \bigg|_{\epsilon_{k}} = \epsilon_{k}^{0} = \omega} \approx z^{-1}$$
(2.30)

Numerical calculations of $\delta m/m_B$ and $N(\omega)/N^0(\omega)$ have been made for sodium by Grimval [19].

From Eqs (2.29) and (2.30) it follows that

$$\frac{N(\omega)}{m_B + \delta m} = \frac{N^0(\omega)}{m_B}$$
(2.31)

The shift $\delta \mu$ of the Fermi energy is determined by

$$\int_{0}^{\mu^{0}+\delta\mu} N(\omega) d\omega = \int_{0}^{\mu^{0}} N^{0}(\omega) d\omega$$

so that (see the figure above)

$$|\delta\mu/\mu_0| \lesssim \omega_D/\mu_0 \ll 1$$

On the other hand, the wave function renormalization implies that the ratio of electronic matrix elements with and without renormalization effects is

$$\frac{M}{M^0} = z$$
 (2.32)

Hence (see Ref.[13])

$$\begin{cases} N(m_{B} + \delta m) |M|^{2} = N^{0}m_{B} |M^{0}|^{2} \\ N \cdot M = N^{0}M^{0} \end{cases}$$
(2.33)

From these and similar considerations Table I is obtained (see Refs [18, 23]).

2.3. Pair interaction and superconductivity

The electron-phonon interaction

$$\mathcal{H}_{el-ph}^{\prime} = \sum_{kq} \gamma_{q}^{0} a_{k+q}^{*} a_{k} Q_{q} \qquad (2.34)$$

Physical quantity .	Electron-phonon renormalization effect	
	Yes	No
Electronic band mass	$m_B^+ \delta m \propto z^{-1}$	
Electron velocity	v _k ∝z	
Shape of Fermi surface]	$\mathbf{k}_{F}\cong\mathbf{m}_{B}\mathbf{v}_{F}$
Fermi energy		$\delta\mu/\mu \cong 0$
Phonon velocity		$v_{\rm ph} \cong \partial \omega_{\rm q} / \partial {\rm q}$
Electronic specific heat	$c_e/T \propto N \propto z^{-1}$	
Phonon specific heat		с _{рһ}
Para-diamagn, spin susceptibility		$\chi \propto \partial f_k / \partial \mu$
Cyclotron frequency	$\omega_{\rm c} \propto (m_{\rm B} + \delta m)^{-1} \propto z$	
Amplitude de Haas-van Alphen effect	present	
Amplitude of Kohn anomaly	present	
Electronic matrix elements	Μ∝z	
Nuclear spin-lattice relaxation		$T_1 \propto m_B/N$
Ultrasonic alternation		$\alpha \propto N_0^2 M_0 ^2$
Positron annihilation	$a \propto N \propto z^{-1}$	
Tunnelling rate		present
Electronic mobilities and mean free paths		$\ell \propto \tau \left m_B \propto \frac{1}{m_B N_0 \left M_0 \right ^2} \right.$
Mean free times	$\tau \propto \frac{1}{N M ^2} \propto z^{-1}$	
Transport processes: dc electric conductivity thermal conductivity viscosity, spin diffusion coefficient thermopower		present

TABLE I. ELECTRON-PHONON RENORMALIZATION EFFECT ON VARIOUS PHYSICAL QUANTITIES

gives rise to an effective electron-electron interaction which may be obtained by a canonical transformation $\mathscr{H} \xrightarrow{\rightarrow} \widetilde{\mathscr{H}}$ given by

$$\begin{aligned} \widetilde{\mathcal{H}} &= e^{S} \, \mathscr{H}e^{-S} = \mathscr{H} + [S, \, \mathscr{H}] + \frac{1}{2!} [S[S, \mathscr{H}]] + \dots \\ &= \mathscr{H}_{0} + \mathscr{H}_{el-ph}' + [S, \, \mathscr{H}_{0}] + [S, \, \mathscr{H}_{el-ph}'] + \frac{1}{2} [S[S, \, \mathscr{H}_{0}]] + \dots \end{aligned}$$

We determine S so as to eliminate \mathcal{H}_{el-ph} to first order,

$$\mathcal{H}_{el-ph}^{\dagger} + [S, \mathcal{H}_0] = 0 \qquad (2.35)$$

Thus \mathcal{H} may be written as

$$\widetilde{\mathscr{H}} = \mathscr{H}_0 + \frac{1}{2} [S, \mathscr{H}'_{el-ph}] + \dots$$

 $\langle 0 | \tilde{\mathcal{H}} | 0 \rangle_{\rm ph} = \mathcal{H}_{\rm HF} + \mathcal{H}_{\rm eff} + \dots$

Taking the phonon vacuum of this equation we have

where

 $\mathcal{H}_{eff} = \frac{1}{2} \langle 0 | [S, \mathcal{H}_{el-ph}] | 0 \rangle_{ph}$ (2.36)

is the effective interaction we are looking for. Introducing the interaction representation

$$A[t] = e^{i \mathscr{H}_0 t} A e^{-i \mathscr{H}_0 t}$$
(2.37)

Eq.(2.35) may be written as

$$\mathcal{H}'_{el-ph}[t] = - [S[t], \mathcal{H}_0] = -iS[t]$$

which can immediately be integrated,

$$S[t] = S + i \int_{0}^{t} dt' e^{-\delta t'} \mathscr{H}_{el-ph}^{i} [t']$$

Assuming adiabatic switching of \mathscr{H}_{el-ph}^{t} at $t = +\infty$ (or $-\infty$) such that $S[+\infty] = 0$ we have

$$S = -i \int_{0}^{\infty} dt e^{-\delta t} \mathscr{H}_{el-ph}^{t} [t]$$
 (2.38)

Inserting this into Eq. (2.36) we find the explicit expression

$$\mathcal{H}_{eff}^{\prime} = -\frac{i}{2} \int_{0}^{\infty} dt \, e^{-\delta t} \langle 0 | \left[\mathcal{H}_{el-ph}^{\prime} \left[t \right], \mathcal{H}_{el-ph}^{\prime} \left[0 \right] \right] | 0 \rangle_{ph}$$
(2.39)

which is just the expectation value of the retarded commutator.

As compared with the usual algebraic method, the method used here to determine $\mathscr{H}_{\rm eff}$ has the advantage of containing a prescription how to go around a singularity, which is often useful (see Ref.[20]). The evaluation is straightforward, noting that

$$<0|[\mathscr{U}_{el-ph}[t]], \mathscr{U}_{el-ph}[0]]|0>_{ph}$$

$$= \frac{1}{2}e^{i(\epsilon_{k+q}^{0}-\epsilon_{k}^{0})t} \sum_{kk'q} |\gamma_{q}^{0}|^{2}\{a_{k+q}^{*}a_{k}a_{k'-q}^{*}a_{k'}e^{-i\omega_{q}^{0}t} - a_{k'-q}^{*}a_{k'}a_{k+q}^{*}a_{k}e^{+i\omega_{q}^{0}t}\}$$

One obtains, after relabelling the summation indices in the second term,

$$\mathcal{H}_{eff}^{I} = \frac{1}{2} \sum_{kk'q} \langle k' - q, k + q | V_{eff} | k'k \rangle a_{k+q}^{*} a_{k} a_{k'-q}^{*} a_{k'}$$
(2.40a)

where

$$\langle \mathbf{k}^{\prime} - \mathbf{q}, \mathbf{k} + \mathbf{q} | \mathbf{V}_{eff} | \mathbf{k}^{\prime} \mathbf{k} \rangle = \frac{|\gamma_{q}^{0}|^{2}}{2} \left\{ \frac{1}{\epsilon_{\mathbf{k}+q}^{0} - \epsilon_{\mathbf{k}}^{0} - \omega_{q}^{0} + i\delta} - \frac{1}{\epsilon_{\mathbf{k}^{\prime}-q}^{0} - \epsilon_{\mathbf{k}^{\prime}}^{0} + \omega_{q}^{0} + i\delta} \right\}$$

$$(2.40b)$$

is the effective coupling function corresponding to the 4-vertex of the figure.

The electron pairs most important for superconductivity, (\vec{k}, σ) and $(-\vec{k}, -\sigma)$, have a coupling function

$$\langle -\vec{k} - \vec{q}, -\sigma, \vec{k} + \vec{q}, \sigma | V_{eff} | \vec{k}, \sigma, -\vec{k}, -\sigma \rangle = |\gamma_q^0|^2 \frac{\omega_q^{02}}{(\epsilon_{k+q}^0 - \epsilon_k^0 + i\delta)^2 - \omega_q^{02}}$$
 (2.40c)

the real part of which has the behaviour of the figure. Since $|\epsilon_{k+q}^0 - \epsilon_k^0| \gtrsim \omega_q^0$, the attractive part of the interaction dominates.



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Now repeated action of this attractive electron-electron interaction may lead to an instability of the normal ground state against formation of coherent electron pairs (Coulomb repulsion prevents a bound state). The corresponding diagrams are the ladders with arbitrary number of phonon lines.



Such a ladder diagram contributes to the self-energy Σ the term



which when written in the form φ gives rise to a vertex part γ



which is obviously different from γ_0 . The instability of the normal ground state against pair formation may be understood as piling up of such ladder contributions to γ (see Ref.[12], section 7-1). Hence γ in this case is another exceptional case to the Migdal theorem. (Actually, one would have to prove that the ladders are of order κ^0 .)

2.4. Hydrodynamical limit and transport equation

The Boltzmann equation for the distribution function $f_k(\vec{r}, t)$ of the electrons is

$$\frac{\partial f_k}{\partial t} + \frac{\partial f_k}{\partial \vec{r}} \cdot \frac{\partial \epsilon_k}{\partial \vec{k}} - \frac{\partial f_k}{\partial \vec{k}} \cdot \frac{\partial \phi}{\partial \vec{r}} = I(\delta f_k)$$
(2.41a)

Here $\phi(\vec{r}, t)$ is an external potential and $I(\delta f_k)$ the collision integral. If we write

$$f_k(\vec{r}, t) = f_k^0 + \delta f_k(\vec{r}, t)$$
 (2.42)

where f_k^0 is the equilibrium distribution function, then the linearized form of Eq.(2.41a) is

$$\frac{\partial (\delta f_k)}{\partial t} + \frac{\partial (\delta f_k)}{\partial \vec{r}} \cdot \vec{\nu}_k - \frac{\partial f_k^0}{\partial \vec{k}} \cdot \frac{\partial \phi}{\partial \vec{r}} = I_1(\delta f_k) \qquad (2.41b)$$

or after Fourier transformation

$$-i(\nu - \vec{q} \cdot \vec{\nu}_{k})\delta f_{k}(\vec{q}, \nu) - i\vec{q} \cdot \vec{\nu}_{k} \frac{\partial f_{k}^{0}}{\partial \epsilon_{k}}\phi(\vec{q}, \nu) = I_{1}(\delta f_{k})$$
(2.43)

On the other hand, starting from quantum statistical mechanics the time. evolution is described by the Liouville equation for the density matrix

$$i \frac{\partial \rho_t}{\partial t} = [\mathcal{H} + \mathcal{H}_t, \rho_t]$$
(2.44)

where

$$\mathscr{H}_{t}^{*} = \int d^{3}r \,\phi(\vec{r},t) \,n(\vec{r}) = \nabla^{-1} \sum_{k} \phi(\vec{q},\nu) \,n(-\vec{q}) \qquad (2.45)$$

is the interaction of the electrons with the external potential $\phi(\vec{r}, t)$. Here $n(\vec{q})$ is the Fourier transformed electron density

$$n(\vec{q}) = \sum_{k} n_{k}(\vec{q}) \qquad (2.46a)$$

where

$$n_k(\vec{q}) = a_k^* a_{k+q}$$
 (2.46b)

The solution of Eq. (2.44) under the initial condition

$$\rho_{t=-\infty} = \rho^0 \equiv e^{\beta(F - \mathscr{H} + \mu N_{el})}$$

is (see the contribution of des Cloizeaux in this book)

$$\rho_{t} = \rho^{0} + i \left[\rho^{0}, \int_{0}^{\infty} dt' e^{-\delta t'} \mathscr{H}_{t-t'}(-t') \right]$$
(2.47)

The quantum statistical definition of the function (2.42) then is

$$f_{k}^{0} = \langle n_{k}(\vec{r}) \rangle \qquad (2.48)$$

$$\delta f_k(\vec{r}, t) = Tr((\rho_t - \rho^0) n_k(\vec{r}))$$
 (2.49a)

or

$$\delta f_{k}(\vec{q},\nu) = \frac{i}{V}\phi(\vec{q},\nu)\int_{0}^{\infty} dt \, e^{(i\nu-\delta)t} \langle [n(-\vec{q}), n_{k}(\vec{q},t)] \rangle \qquad (2.49b)$$

where the average is defined by expression (2.4a) and the time dependence of the operators by (2.3). Introducing the retarded 2-particle Green function

$$K_k^R(\vec{r},t) = \theta(t) \langle [n(-\vec{q}), n_k(\vec{q},t)] \rangle e^{-\delta t}$$

Function (2.49b) may be written as the Fourier transform

$$\delta f_{k}(\vec{q},\nu) = \frac{i}{V}\phi(\vec{q},\nu) \cdot K_{k}^{R}(\vec{q},\nu) \qquad (2.49c)$$

 $K_k^{\mathbb{R}}(\vec{q},\nu)$ is analytically connected, in the variable ν , with the imaginarytime 2-particle Green function (see sub-section 3.1), which is then analysed (see Ref.[21]). Now in the domain of applicability of a transport equation, ν and $\vec{q} \cdot \vec{\nu}_k$ are so small that they are of the same order as the width $|\Gamma_k|$. This is the definition of the hydrodynamical limit. It turns out that in this limit the particle-hole ladders



contribute to $K_k^R(\vec{q},\nu)$ to order κ^0 , independently of the number of steps. Therefore all the ladders have to be summed in order to get a good approximation of $K_k^R(\vec{q},\nu)$ (see Ref.[22]). Thus we see that the transport equation is still another example of an exception to the Migdal theorem, since by simply attaching a vertex γ^0 to the right of the ladder we get the ladder approximation of γ (which is quite different from the one responsible for superconductivity):



The analytical continuation in ν is quite delicate and one would like to arrive at the same result by using real-time Green functions only. It works to a certain extent, and we shall sketch the method.

First rewrite Eq. (2.49b) with the help of the Kubo identity

$$i[A, \rho^0] = \beta \rho^0 \tilde{A}$$

where

$$\widetilde{\mathbf{A}} \equiv \beta^{-1} \int_{0}^{\beta} \mathbf{A}(-\mathbf{i}\tau) \mathrm{d}\tau$$

(2.50)

We find after a partial integration over t

$$\delta f_{k} = \delta f_{k}^{L} + \delta f_{k}^{D}$$
 (2.51a)

where

$$\delta f_{k}^{L}(\vec{q}, \nu) = -\frac{\beta}{V} \phi(\vec{q}, \nu) \langle \delta \tilde{n}_{k}(\vec{q}) \delta n(-\vec{q}) \rangle \qquad (2.51b)$$

is the "local equilibrium variation" and

$$\delta f_{k}^{D}(\vec{q},\nu) = -i\nu \frac{\beta}{V} \phi(\vec{q},\nu) \int_{0}^{\infty} dt \, e^{(i\nu-\delta)t} \sum_{k'} \langle T(\delta \tilde{n}_{k}(\vec{q}\,t)\,\delta n_{k'}(-\vec{q})) \rangle \qquad (2.51c)$$

the "dissipative variation" (see Refs [23, 24]). Here we used the abbreviation $\delta A = A - \langle A \rangle$ and we inserted the real-time ordering T (which is unity in the interval of integration). Now the difficulty is that we have again real and imaginary time arguments (t and $-i\tau$) mixed together which prevents development of a perturbation theory in the usual way because a simultaneous ordering according to real and imaginary time is impossible. One possibility is to define a generalized ordering along an arbitrary path in the complex t-plane (see Ref. [24]). This, however, is rather cumbersome. Here we shall simply assume that the average (2, 50) can be neglected, which amounts to a high temperature approximation.

Now the ladder sum mentioned above is just the solution of the Bethe-Salpeter equation

$$\begin{array}{c} 1' & \overbrace{}{} \\ 1 & \overbrace{}{} \\ \end{array} \begin{array}{c} K \\ 2 \end{array} = \begin{array}{c} 1' & \overbrace{}{} \\ 1 \end{array} \begin{array}{c} 2' \\ 2 \end{array} + \begin{array}{c} 1' & \overbrace{}{} \\ 1 \end{array} \begin{array}{c} 3' \\ 4' \\ 1 \end{array} \begin{array}{c} K \\ 4' \\ 4 \end{array} \begin{array}{c} K \\ 2 \end{array} \begin{array}{c} 2' \\ 2 \end{array}$$
 (2.52)

where $\begin{pmatrix} 1' \\ 1 \\ \end{pmatrix} \\ \begin{pmatrix} 2' \\ 2 \\ \end{pmatrix} \\ \begin{pmatrix} 1' \\ 2 \\ \end{pmatrix} \\ \begin{pmatrix} 2' \\ 1 \\ \end{pmatrix} \\ \begin{pmatrix} 2' \\ 1 \\ \end{pmatrix}$ is the time-Fourier transform of

 $\langle T(a_{k_1}^*(t_1)a_{k_1'}(t_1), a_{k_2'}^*(t_2) \rangle$. Similarly to Eqs (2.16a), (2.19a), etc., this Bethe-Salpeter equation simply exhibits the 2-particle structure of K. L is the 1- and 2-particle irreducible 4-vertex



(2.52) is thus again independent of perturbation theory and can be obtained, e.g. by functional methods (see, e.g. Ref. [11], p.337).

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Taking into account energy and momentum conservation we can write, using the abbreviation $1 = (k_1, \omega_1)$, etc.

$$1 \xrightarrow{1^{\prime}} K \xrightarrow{2^{\prime}} 2 = K(1; 2; 1^{\prime} - 1) \delta_{1^{\prime} - 1, 2^{\prime} - 2}$$

$$1 \xrightarrow{1^{\prime}} L \xrightarrow{4^{\prime}} 2 = L(1; 4; 1^{\prime} - 1) \delta_{1^{\prime} - 1, 4^{\prime} - 4}$$

Then the identification with the Green function in Eq. (2.51c) is

$$\langle T(\delta n_{k}(\vec{q},t) \, \delta n_{k'}(-\vec{q})) \rangle = \int \frac{d\omega}{2\pi} \int \frac{d\omega^{\prime}}{2\pi} \int \frac{d\nu^{\prime}}{2\pi} e^{-i\nu't} K(k,\omega; k'-q,\omega'; \vec{q},\nu')$$
(2.54)

and the Bethe-Salpeter equation (2.52) becomes

$$K(1; 2; 1'-1) = G_1G_1 \left\{ \delta_{12} + \sum_{4} L(1; 4; 1'-1)K(4; 2; 1'-1) \right\} (2.55)$$

The ladder solution is obtained by taking only L_0 in Eq.(2.53). The fact that this ladder solution in the hydrodynamic limit is of order κ^0 comes from the structure of G_1G_1 in this limit. Indeed, adopting for G_1 and G_1 the form (2.23) with the identification $k_1 = k; \ \omega_1 = \omega; \ k_1 = k + q; \ \omega_1 = \omega + \nu$, we see that in the hydrodynamical limit $|\nu| \cong |\vec{q} \cdot \vec{\nu}_k| \cong |\Gamma_k|$ we can neglect the q-dependence in $z_{k+q} \in_{k+q}$ and $|\Gamma_{k+q}|$ but not in $\Gamma_{k+q} \cong |\Gamma_k|$ sign ε_{k+q} and $\varepsilon_{k+q} - \varepsilon_k \cong \vec{q} \cdot \vec{\nu}_k$. Hence

$$G_{1}G_{1'} \cong \frac{z_{k}^{2}}{\nu - \vec{q} \cdot \vec{\nu}_{k} + i |\Gamma_{k}| (\operatorname{sign} \epsilon_{k+q} - \operatorname{sign} \epsilon_{k})} \\ \times \left\{ \frac{1}{\omega - \epsilon_{k} - i |\Gamma_{k}| \operatorname{sign} \epsilon_{k}} - \frac{1}{\omega - \epsilon_{k} + i |\Gamma_{k}| \operatorname{sign} \epsilon_{k+q}} \right\}$$

The last bracket vanishes unless sign $\varepsilon_{k+q}\text{=}-\operatorname{sign}\varepsilon_k$, in which case we have

$$G_{1}G_{1} \approx -\frac{2\pi i z_{k}[A(k,\omega) - A_{back}(k,\omega)]}{\nu - \vec{q} \cdot \vec{v}_{k} + 2i\Gamma_{k}}$$
(2.56)

Now with

$$1^{'} \underbrace{L_{0}}_{1} \underbrace{L_{0}}_{\gamma 0} \underbrace{4^{'}}_{4} = \underbrace{1^{'} \underbrace{\gamma^{0}}_{\gamma 0} \underbrace{4^{'}}_{1}}_{\gamma 0} = |\gamma^{0}_{k_{4}-k_{1}}|^{2} D(k_{4}-k_{1}, \omega_{4}-\omega_{1})$$

we see that each step



added to the ladder brings in a factor $G_1G_1, |\gamma^0|^2 D$ which, according to Eq.(2.56) is proportional, in the hydrodynamic limit, to $|\gamma^0_q, |^2/|\Gamma_k|$. But to lowest order of perturbation theory



Hence $G_1G_1 \cdot |\gamma^0|^2 D \propto \kappa^0$ as indicated before. The transport equation is now obtained from the ladder approximation of Eq.(2.55) in the following way. Put $k_2 = k' - q$; $\omega_2 = \omega'$; $k_2 = k'$; $\omega_2 = \omega' + \nu$; $k_4 = k''$; $\omega_4 = \omega''$; $k_4 \cdot = k'' + q$; $\omega_4 \cdot = \omega'' + \nu$ and

$$M(k\omega; \vec{q}\nu) = \sum_{k'} \int \frac{d\omega'}{2\pi} K(k, \omega; k' - q, \omega'; \vec{q}, \nu) \quad (2.57)$$

then with Eq. (2.56) and L = $L_{\,0}$ the Bethe-Salpeter equation (2.55) may be written in terms of M,

$$M(\mathbf{k}\omega; \vec{q}\nu) = \frac{z_{\mathbf{k}}[A(\mathbf{k},\omega) - A_{back}(\mathbf{k},\omega)] \operatorname{sign} \epsilon_{\mathbf{k}}}{i(\nu - \vec{q} \cdot \vec{\nu}_{\mathbf{k}}) - 2\Gamma_{\mathbf{k}}} \times \left\{ 1 + 2\pi \sum_{\mathbf{k}''} \int d\omega'' |\gamma_{\mathbf{k}''-\mathbf{k}}^{0}|^{2} D(\mathbf{k}''-\mathbf{k}, \omega''-\omega) M(\mathbf{k}''\omega''; \vec{q}\nu) \right\}$$
(2.58)

It follows that

$$M(k\omega; \vec{q}\nu) \propto A(k\omega) - A_{back}(k\omega) \cong z_k \delta(\omega - \epsilon_k)$$

Thus putting

$$M(k\omega; \vec{q}\nu) = \varphi_k(\vec{q}, \nu) \,\delta(\omega - \epsilon_k) \qquad (2.59)$$

Eq. (2.58) becomes, after rearranging terms,

$$- i(\nu - \vec{q} \cdot \vec{\nu}_{k}) \varphi_{k}(\vec{q}, \nu) + z_{k}^{2} = - 2 |\Gamma_{k}| \varphi_{k}(\vec{q}, \nu) - 2\pi z_{k}^{2}$$

$$\times \sum_{k''} |\gamma_{k''-k}^{0}|^{2} D(k''-k, \epsilon_{k''} - \epsilon_{k}) \varphi_{k''}(\vec{q}, \nu) \qquad (2.60)$$

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From Eqs (2.54), (2.57), (2.59) we find for the dissipative variation (2.51c)

$$\delta f_{\mathbf{k}}^{\mathrm{D}}(\vec{\mathbf{q}},\nu) = \frac{\beta}{V} \phi(\vec{\mathbf{q}},\nu) \nu \int \frac{\mathrm{d}\nu'}{2\pi} \frac{\varphi_{\mathbf{k}}(\vec{\mathbf{q}},\nu')}{\nu - \nu' + \mathrm{i}\delta} \qquad (2.61)$$

If $\varphi_k(\vec{q}, \nu)$ can be assumed regular in ν (without this assumption the analysis is somewhat more complicated) we simply have

$$\delta \mathbf{f}_{k}^{D}(\vec{\mathbf{q}},\nu) = -i\frac{\beta}{V}\phi(\vec{\mathbf{q}},\nu)\nu\varphi_{k}(\vec{\mathbf{q}},\nu) \qquad (2.62)$$

so that we see from (2.60) that $\delta f_k^p(\vec{q},\nu)$ satisfies indeed the transport equation (2.43). The two terms on the right-hand side of Eq. (2.60) describe, respectively, the scatterings out of and into the state k, contained in the collision integral I_1 . One difference is that the inhomogeneous term proportional to the potential ϕ turns out to be proportional not to $\vec{q} \cdot \vec{\nu}_k$ but to ν (see Ref.[21]). But since the values of ν and $(\vec{q} \cdot \vec{\nu}_k)$ are close this is not so important.

It should be mentioned that Kadanoff and Baym have given a quite different derivation of the Boltzmann equation by the equation of motion method (see Ref. [9], chapter 9).

Finally we remark that if we use in the Bethe-Salpeter equation the term L_b^{1} of Eq. (2.53) instead of L_0 the ladders are replaced by the chains



which are equivalent to a random phase approximation. In the case of repulsive effective 2-particle interactions this approximation is known to lead to a collective mode (plasma or zero sound). Now, in cases where such a collective mode exists it will be dominated by the hydrodynamical excitations, except at sufficiently low temperatures where the chain solution of the Bethe-Salpeter equation may dominate the ladder solution. This possibility may be realized in second sound which at the usual frequencies of observation is a hydrodynamical mode (see section 3.4) but for $\omega \rightarrow 0$ may gradually go over into a collective mode

3. PHONON-PHONON INTERACTION IN INSULATORS

The phonon-phonon interaction has a much more complicated structure than the electron-phonon interaction and information about the coupling function $C_{q_1}^{(n)}$ is difficult to obtain. One source of information are the elastic constants, as will be discussed in section 3.2.

For phonons the limit $T \rightarrow 0$ is obviously not a good approximation. On the other hand, perturbation theory at finite temperatures is a reasonable approach. This leads naturally to the "imaginary-time" Green functions discussed in section 3.1.

Experimental information on renormalization effects (frequency shifts and widths) are available mainly from neutron diffraction and ultrasonic attenuation. But the new technique of heat pulses seems promising as the discovery of second sound has shown (see section 3.4).

3.1. Imaginary-time Green functions and perturbation theory

As remarked in section 2, perturbation theory at finite temperature necessitates an ordering according to imaginary times or reciprocal temperatures. This can be done both for electrons and phonons, but here we will concentrate on the phonon Green function as defined by

$$\mathscr{D}(1,2) = \langle \mathscr{I}\left(Q_{q_1}(-i\tau_1) Q_{q_2}^*(-i\tau_2)\right) \rangle = 1 - 2 \qquad (3.1a)$$

where $Q_{q_1}(-i\tau_1)$, etc. is the Heisenberg representation (2.3) with imaginary time argument, taken with the Hamiltonian (1.24), which in this section will be written as $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}'$ (gothic letters and straight lines will be used to represent the Green functions of this section). τ_1 etc. varies in the interval $0 < \tau_1 < \beta$ and the \mathcal{T} -ordering is defined by

$$\mathcal{F}\left(\mathbf{A}(-\mathbf{i}\tau)\mathbf{B}(-\mathbf{i}\tau')\right) = \theta\left(\tau - \tau'\right)\mathbf{A}(-\mathbf{i}\tau)\mathbf{B}(-\mathbf{i}\tau')$$

$$\pm \theta\left(\tau' - \tau\right)\mathbf{B}(-\mathbf{i}\tau')\mathbf{A}(-\mathbf{i}\tau)$$
(3.1b)

(lower sign: fermions) which is quite different from Eq.(2.2). It is useful also to define oriented phonon lines analogous to the electron Green functions,

$$\mathscr{G}_{1}^{2} = \langle \mathscr{F} \left(\mathsf{b}_{\mathsf{q}_{1}}(-i\tau_{1}) \mathsf{b}_{\mathsf{q}_{2}}^{*}(-i\tau_{2}) \right) \rangle = 1 \underbrace{\longleftarrow} 2 \qquad (3.1c)$$

From now on we will drop the restriction to Bravais lattices introduced in section 1 so that the index μ in $\pm q = (\pm \vec{q}, \mu)$ now runs over 3B values corresponding to the three polarizations for the B branches (1 acoustic and B-1 optical). B is the number of basis atoms of mass M_b and equilibrium positions $\vec{R}_1^0 + \vec{r}_b$ (b = 1, ..., B). The orthonormality (1.33) has then to be modified as follows;

$$B^{-1} \sum_{b=1}^{B} \vec{e}_{\vec{q},\mu}^{*}(\vec{r}_{b}) \vec{e}_{\vec{q},\mu}^{*}(\vec{r}_{b}) = \delta_{\mu\mu},$$

As in section 2.1, we can write

$$\mathcal{D}(1,2) = \mathcal{D}_{\mu_1\mu_2}(\vec{q}_1;\tau_1,\tau_2) \delta_{\vec{q}_1\vec{q}_2}$$
(3.2a)

$$\mathscr{G}_{1}^{2} = \mathscr{G}_{\mu_{1}\mu_{2}}(\overrightarrow{q}_{1}; \tau_{1} - \tau_{2}) \delta_{\overrightarrow{q}_{1}\overrightarrow{q}_{2}}$$
(3.2b)

Thus $\tau_1 - \tau_2$ varies between $-\beta$ and $+\beta$. It is, however, sufficient to consider the matrices $\mathscr{D}(\vec{q}; \tau)$ and $\mathscr{G}(\vec{q}; \tau)$ in the interval $0 \rightarrow \beta$ because of the important periodicity property

$$\mathscr{D}(\vec{q};\tau) = \mathscr{D}(\vec{q};\tau-\beta); \ 0 < \tau < \beta \tag{3.3}$$

and similarly for $\mathscr G$. To prove (3.3) we notice that for such τ (writing $q' = (\vec{q}, \mu)$

$$\mathcal{D}_{\mu\mu}(\vec{q};\tau) = \langle Q_{q}(-i\tau) Q_{q'}^{*}(0) \rangle$$
$$\mathcal{D}_{\mu\mu}(\vec{q};\tau-\beta) = \langle Q_{q'}^{*}(0) Q_{q}(-i(\tau-\beta)) \rangle$$

Using the identity (which is a simple consequence of the cyclic property of the trace (2.4a))

$$\langle A(a)B(b) \rangle = \langle B(b)A(a+i\beta) \rangle$$
 (3.4)

valid for any operators A, B and complex "times" a, b, Eq.(3.3) readily follows.

In this interval \mathscr{D} and \mathscr{G} may be expanded into a Fourier series

$$\mathscr{D}(\vec{q};\tau) = \sum_{\sigma} \mathscr{D}(\vec{q};\sigma) e^{i\sigma\tau}$$
 (3.5a)

(and similarly for \mathscr{G}) where σ is defined by

$$e^{i\sigma\beta} = 1, \quad \sigma = \pm \frac{2\pi}{\beta} \times \text{integer}$$
 (3.5b)

(for fermions $\frac{1}{2}$ is to be added to the integer). The inverse of expression (3.5a) is

$$\mathscr{D}(\vec{\mathbf{q}};\sigma) = \beta^{-1} \int_{0}^{\beta} d\tau \ \mathscr{D}(\vec{\mathbf{q}};\tau) e^{-i\sigma\tau}$$
(3.5c)

The zero-order, i.e. harmonic, Green functions are again easy to calculate. First we notice that

$$\mathscr{D}^{0}(\vec{\mathbf{q}};\tau) = \frac{1}{2} \left\{ \mathscr{G}^{0}(\vec{\mathbf{q}};\tau) + \mathscr{G}^{0}(-\vec{\mathbf{q}};-\tau) \right\}$$
(3.6a)

Using expression (3.5) for $\mathscr{G}^{0}(-\vec{q}; -\tau)$ we find

$$\mathscr{D}^{0}(\vec{\mathbf{q}};\sigma) = \frac{1}{2} \left\{ \mathscr{G}^{0}(\vec{\mathbf{q}};\sigma) + \mathscr{G}^{0}(-\vec{\mathbf{q}};-\sigma) \right\}$$
(3.6b)

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Now with Eq.(2.11)

$$\mathscr{G}^{0}_{\mu\mu'}(\vec{q};\sigma) = \beta^{-1} \frac{1}{i\sigma + \omega_{q}^{0}} \delta_{\mu\mu'} \equiv \mathscr{G}^{0}(q;\sigma) \delta_{\mu\mu'}$$
(3.7)

so that

$$\mathscr{D}^{0}_{\mu\mu}(\vec{q};\sigma) = \beta^{-1} \frac{\omega_{q}^{0}}{\sigma^{2} + \omega_{q}^{02}} \delta_{\mu\mu}^{} \equiv \mathscr{D}^{0}(q;\sigma) \delta_{\mu\mu}^{}, \qquad (3.8)$$

As remarked in section 2.1, the spectral representations (2.13a), (2.13b) cease to be valid at $T \neq 0$. However, $\mathscr{D}(\vec{q}; \sigma)$ does have a <u>spectral</u> <u>representation</u> with the same spectral function $B(\vec{q}; \omega)$, Eq. (2.14b). To see this let us write \mathscr{D} in the representation by exact eigenfunctions of \mathscr{H} , Eqs (1.7) and (1.7a). We find

$$\mathscr{D}(\vec{q};\sigma) = \beta^{-1} \left\{ \varphi^{+}(-i\sigma) + \varphi^{-}(-i\sigma) \right\}$$
(3.9a)

where

$$\varphi^{\pm}(\omega) = \sum_{\mathbf{n}\mathbf{n}'} e^{\beta(\mathbf{F}\cdot\mathbf{\Omega}_{\mathbf{n}})} \frac{\alpha^{\pm}(\mathbf{n},\mathbf{n}')}{\Omega_{\mathbf{n}'} - \Omega_{\mathbf{n}}^{\pm}\omega}$$
(3.9b)

again are matrices in μ , μ ' and

$$\alpha^{+}_{\mu\mu}(\mathbf{n},\mathbf{n}^{\dagger}) = \langle \mathbf{n} | \mathbf{Q}_{\overrightarrow{\mathbf{q}}\,\mu} | \mathbf{n}^{\dagger} \rangle \langle \mathbf{n}^{\dagger} | \mathbf{Q}_{\overrightarrow{\mathbf{q}}\,\mu}^{*} | \mathbf{n} \rangle$$

$$\alpha^{-}_{\mu\mu'}(\mathbf{n},\mathbf{n}^{\dagger}) = \alpha^{+}_{\mu\mu'}(\mathbf{n}^{\dagger},\mathbf{n})$$

$$(3.9c)$$

Both ϕ^+ and ϕ^- are analytic in each of the half planes $\operatorname{Im} \omega > 0$ and $\operatorname{Im} \omega < 0$. In order to connect the two pieces through the real ω axis we may write ϕ^+ as sum of two functions defined by splitting

$$\sum_{nn'} \text{ into a part with } \Omega_{n'} > \Omega_{n}$$

and another with $\Omega_{n'} < \Omega_n$. Each of these new functions then has a cut only along half of the real ω axis and is analytic in the entire cut ω -plane. Using Cauchy's formula for them and going back to ϕ^{\dagger} and $\bar{\phi}$ we find

$$\varphi^{\pm}(\omega) = \pm \int_{-\infty}^{\infty} \frac{d\omega^{\dagger}}{\omega^{\dagger} - \omega} \sum_{n, n'} e^{\beta (F - \Omega_n)} \times \alpha^{\pm}(n, n') \delta (\Omega_n^{-} \Omega_{n'}^{-} \pm \omega')$$
(3.10)

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Combining Eqs (3.9a), (3.10) we find immediately

$$\mathscr{D}(\vec{q};\sigma) = \beta^{-1} \int_{-\infty}^{+\infty} \frac{d\omega'}{\omega' + i\sigma} B(\vec{q};\omega')$$
(3.11)

where $B(\vec{q};\omega)$ is given by Eq.(2.14b) with Ψ_s , ξ_s replaced by $|n\rangle$, Ω_n and the labels $\mu \mu'$ are put correctly. It is important to note that although the real-time Green function $D(q;\mu)$ has no spectral representation (2.13b) for finite τ the Fourier transform of the <u>retarded Green function</u>

$$D_{\mu\mu'}^{\text{ret}}(\vec{q};t) = \theta(t) \langle \left[Q_{\vec{q}\mu}(t), Q_{\vec{q}\mu'}^*(0) \right] \rangle$$
(3.12)

has, at any temperature, the spectral representation

$$\mathbf{D}^{\mathsf{ret}}(\vec{\mathbf{q}};\omega) = \int_{-\infty}^{+\infty} \frac{\mathbf{B}(\vec{\mathbf{q}};\omega')}{\omega - \omega' + i\delta} d\omega' \qquad (3.13)$$

which is similar to Eq. (2.13b). Equation (3.13) is easy to prove by expressing $D^{ret}(\vec{q};\omega)$ again in terms of ϕ^{\dagger} and ϕ^{-} . (The analogous results are of course true for $\mathscr{G}(\vec{q};\sigma)$ but also for the electronic Green functions where the definition analogous to Eq. (3.12) contains an anticommutator.)

The practical importance of the connection between \mathscr{D} and D^{ret} through their common spectral function B lies in the fact that \mathscr{D} can be calculated, e.g. by finite temperature perturbation theory (see below), thus determining B. But B then determines D^{ret} which is the function describing causal responses. Now the derivation of the spectral representations (3.11), (3.13) did not make use at all of the particular nature of the operators Q_{\downarrow} . In fact, any pair of operators could have been used in (3.9c) instead of $Q_{q\mu}^{q}$, $Q_{q\mu}^{a}$. Therefore the connection between \mathscr{D} and D^{ret} through B is much more general. An example of a more general retarded function is given in (2.49b). In fact, this is the general form (Kubo formula) of a transport coefficient (see the contribution of des Cloizeaux in this book). Thus the spectral function plays an important role in the calculation of physical quantities.

We now describe the procedure of perturbation theory. A typical quantity to be calculated is of the form

$$\mathcal{T}_{1\dots r} \equiv \left\langle \mathcal{T}(A_1(-i\tau_1) - A_r(-i\tau_r)) \right\rangle$$
(3.14a)

where the A_i ($r \ge 0$) are any linear combinations of Q_q or b_q , b_q^* Since in perturbation theory we make a development in powers of the interaction \mathscr{H}_{anh}^i , the passage from the Heisenberg representation (2.3) to the interaction representation (2.37) is the natural starting point. It may be written as

$$A(-i\tau) = S(0;\tau) A[-i\tau] S(\tau;0)$$
(3.14b)

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Similarly

$$\rho = e^{\beta (F - F^0)} \rho^0 S(\beta; 0)$$
 (3.14c)

where $\rho = \exp \beta (F - \mathcal{H})$ and $\rho^0 = \exp \beta (F^0 - \mathcal{H}_0)$ and where we have used the definition

$$S(\tau_1; \tau_2) = e^{+\tau_1 \mathscr{U}_0} e^{-\tau_1 \mathscr{U}_1} e^{+\tau_2 \mathscr{U}_2} e^{-\tau_2 \mathscr{U}_0}$$
(3.15a)

This operator has the property

$$S(\tau_1; \tau_2) S(\tau_2; \tau_3) = S(\tau_1; \tau_3)$$
 (3.15b)

and may be expressed in terms of the interaction $\mathscr{J}_{anh}^{\dagger}$ as imaginary – time ordered exponential (defined as formal power series)

$$S(\tau_1;\tau_2) = \mathcal{T} \exp\left\{-\int_{\tau_2}^{\tau_1} d\tau \, \mathscr{H}_{anh}^{\dagger}[-i\tau]\right\}; \, \tau_1 \ge \tau_2 \quad (3.15c)$$

(3.15c) may be verified by comparing its derivative and its value at $\tau_1 = \tau_2$ with those of (3.15a). With (3.14b), (3.14c), (3.15b) the expression (3.14a) may be written

$$\mathcal{F}_{1,\ldots,r} = e^{\beta(F-F^{0})} \langle \mathcal{F} \left\{ S(\beta;\tau_{1}) A_{1}[-i\tau_{1}] S(\tau_{1};\tau_{2}) - \cdots \right\}$$
$$= S(\tau_{r-1};\tau_{r}) A_{r}[-i\tau_{r}] S(\tau_{r};0) \right\} \rangle_{0}$$

where $\langle \rangle_0$ refers to ρ_0 . In this expression all operators are strictly τ -ordered, as is seen from (3.15c). Therefore we can gather all S-operators together and use (3.15b). Hence

$$\mathcal{T}_{1_{--}r} = e^{\beta(F-F^0)} \langle \mathcal{T} \left(A_1[-i\tau_1] - ... A_r[-i\tau_r] S(\beta;0) \right) \rangle_0$$

Inserting (3.15c) and the expression (1.26), (1.29) for \mathscr{J}_{anh}^{1} one sees that $\mathscr{T}_{1__1}$ is a sum of integrals of expressions $\langle \mathscr{T}(A_1[-i\mathscr{T}_1]___A_s[-i\tau_s]) \rangle_0$, (s ≥ r) multiplied with coupling functions $C_{q___-q_n}^{(n)}$. Now it can be shown ("Wick's theorem", see, e.g., Ref. 1) that

$$\langle \mathcal{T}(A_{1}[-i\tau_{1}] - -A_{s}[-i\tau_{s}]) \rangle_{0} = \sum_{\text{all pairings } (j j')} \prod_{j} \langle \mathcal{T}(A_{j}[i\tau_{j}]A_{j'}[-i\tau_{j'}]) \rangle_{0}$$

(3.16a)

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In \mathscr{T}_{1--r} part of these propagator-lines are linked together in the vertices $C^{(n)}$ but some have free ends due to the presence of $A_1 \ldots A_r$ in \mathscr{T}_{1--r} . This leads to diagrams (see the examples in sections 3.2 and 3.3).

An important simplification comes from the fact that all diagrams in $\mathcal{F}_{1...r}$ which have no free ends ("equilibrium diagrams") contribute the same disconnected part to each diagram with given free ends. Therefore this disconnected part, which is just $\langle s(\beta; 0) \rangle_0$, can be factored out, and we are left with only the connected part of each diagram. Since, according to (3.14c),

1 =
$$\langle 1 \rangle$$
 = $e^{(F - F^0)} \langle S(\beta; 0) \rangle_0$

the disconnected parts just cancel the factor $\exp\beta({\tt F}\,{\tt F}^0)$ in $\mathscr{T}_{1\ldots\,r}$ so that we arrive at the result

$$\langle \mathscr{T} (A_{1}(-i\tau_{1})--A_{r}(-i\tau_{r})) \rangle$$

= $\langle \mathscr{T} (A_{1}[-i\tau_{1}]--A_{r}[-i\tau_{r}] S(\beta; 0)) \rangle_{0, \text{ conn.}}$ (3.16b)

Finally the argument about disconnected parts can also be applied to the equilibrium diagrams of $\langle S(\beta; 0) \rangle_0$. The result is (see, e.g. Ref. [26]))

$$\langle S(\beta; 0) \rangle_{0} = \exp \left\{ \langle S(\beta; 0) \rangle_{0, \text{ conn.}} = 1 \right\}$$
 (3.17a)

or also (see, e.g. Ref. [27]))

F - F⁰ = -
$$\beta^{-1} \left\{ \langle S(\beta; 0) \rangle_{0, \text{ conn.}} = 1 \right\}$$
 (3.17b)

Eqs (3.15c), (3.16a), (3.16b) and (3.17b) form the basis of any perturbation calculation. Examples are given in the next two sections.

3.2. Thermal and elastic properties

As a first application of the perturbation theory developed in the last section, let us calculate the lowest order anharmonic correction to the free energy, Eq.(3.17b). Insertion of expression (3.15c) gives, remembering the definitions (1.26), (1.29) of \mathscr{J}_{anh}^{*}

$$\beta(\mathbf{F} - \mathbf{F}_0) = 1 - \langle \mathcal{F} \exp \left\{ - \int_0^\beta d\tau \left(\mathscr{H}_3^{\dagger} \left[-i\tau \right] + \mathscr{H}_4^{\dagger} \left[-i\tau \right] + \dots \right) \right\} \right\}_{0, \text{ conn.}}$$

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$$= \int_{0}^{\beta} d\tau \left\langle \mathscr{H}_{4}^{\dagger} \left[-i \tau \right] \right\rangle_{0, \text{ conn.}}$$

$$- \frac{1}{2} \int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau' \left\langle \mathscr{T} \left(\mathscr{H}_{3}^{\dagger} \left[-i \tau \right] \mathscr{H}_{3}^{\dagger} \left[-i \tau' \right] \right) \right\rangle_{0, \text{ conn.}} + \dots$$

$$= \beta \left(F_{1} + F_{2} + \dots \right) \qquad (3.18)$$

Now

$$\langle \mathscr{H}_{4}^{\dagger}[-i\tau] \rangle_{0,\,\mathrm{conn.}} = \langle \mathscr{H}_{4}^{\dagger} \rangle_{0,\,\mathrm{conn.}}$$

$$=\frac{1}{4!}\sum_{q_1\cdots q_4} C_{q_1\cdots q_4}^{(4)} \langle \mathscr{T}\left(Q_{q_1}[-i\tau_1]\cdots Q_{q_4}[-i\tau_4]\right) \rangle_{0, \text{ conn.}} \Big|_{\tau_1} = \cdots = \tau_4 = 0$$

But according to (3.16a)

$$\langle \mathcal{T}(Q_{q_1}[-i\tau_1]\dots Q_{q_4}[-i\tau_4]) \rangle_{0, \text{ conn.}}$$

$$= 3 \mathscr{D}^{0}(q_{1}; \tau_{1} - \tau_{2}) \delta_{q_{1}, - q_{2}} \mathscr{D}^{0}(q_{3}; \tau_{3} - \tau_{4}) \delta_{q_{3}, - q_{4}}$$

corresponding to the Fourier transform of the \mathscr{D}^0 -lines in the diagram F_1 , taken in the three distinct combinations. Hence



$$F_{1} = \frac{3}{4!} \sum_{q_{1}, q_{3}} C_{q_{1}, -q_{1}, q_{3}, -q_{3}}^{(4)} \mathscr{D}^{0}(q_{1}, 0) \mathscr{D}^{0}(q_{3}, 0)$$

According to Eq.(2.11b),

$$\mathscr{D}^{0}(q;0^{+}) = \langle Q_{q} Q_{q}^{*} \rangle_{0} = n_{q}^{0} + \frac{1}{2}$$

so that

$$F_{1} = \frac{1}{8} \sum_{qq'} C_{q,-q,q',-q'}^{(4)} \left(n_{q}^{0} + \frac{1}{2} \right) \left(n_{q'}^{0} + \frac{1}{2} \right)$$
(3.19)

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For the second term in Eq.(3.18) we have to calculate

$$\langle \mathscr{T}\left(\mathscr{Y}_{3}^{!}\left[-i\left(\tau-\tau^{\dagger}\right)\right]\mathscr{Y}_{3}^{!}\left[0\right]\right)\rangle_{0, \text{ conn.}}$$

$$= \cdot\left(\frac{1}{3!}\right)^{2}\sum_{q_{1}\cdots q_{3}^{\prime}}C_{q_{1}q_{2}q_{3}}^{(3)}C_{q_{1}^{\prime}q_{2}^{\prime}q_{3}}^{(3)} < \mathscr{T}\left(Q_{q_{1}}\left[-i\left(\tau-\tau^{\dagger}\right]\ldots Q_{q_{3}^{\prime}}\left[0\right]\right)\right)_{0, \text{ conn.}}$$

Applying Eq. (3.16a) one finds that there are two possible diagrams:



contributing with combinatorial factors 3×3 , and 3×2 , respectively, so that F_2 = F_2^1 + $F_2^{\prime\prime}$ and

$$\begin{aligned} \mathbf{F}_{2}^{\prime} &= -\frac{1}{2\beta} \left(\frac{1}{3!}\right)^{2} \sum_{\mathbf{q}_{1}\mathbf{q}_{2}\mathbf{q}_{2}^{\prime}} \mathbf{C}_{\mathbf{q}_{1},\mathbf{q}_{2},\mathbf{q}_{2}}^{(3)} \mathbf{C}_{-\mathbf{q}_{1},\mathbf{q}_{2}^{\prime},\mathbf{q}_{2}^{\prime}}^{(3)} \\ &\times 9 \int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau^{\prime} \mathscr{D}^{0}(\mathbf{q}_{1};\tau-\tau^{\prime}) \mathscr{D}^{0}(\mathbf{q}_{2};0) \mathscr{D}^{0}(\mathbf{q}_{2}^{\prime};0) \\ \\ \mathbf{F}_{2}^{\prime\prime} &= -\frac{1}{2\beta} \left(\frac{1}{3!}\right)^{2} \sum_{\mathbf{q}_{1}\mathbf{q}_{2}\mathbf{q}_{3}} \mathbf{C}_{\mathbf{q}_{1}\mathbf{q}_{2}\mathbf{q}_{3}}^{(3)} \mathbf{C}_{\mathbf{q}_{1}^{\prime},\mathbf{q}_{2}^{\prime},\mathbf{q}_{3}}^{(3)} \\ &= 6 \int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau^{\prime} \mathscr{D}^{0}(\mathbf{q}_{1};\tau-\tau^{\prime}) \mathscr{D}^{0}(\mathbf{q}_{2};\tau-\tau^{\prime}) \mathscr{D}^{0}(\mathbf{q}_{3};\tau-\tau^{\prime}) \end{aligned}$$

In F' crystal momentum conservation (1.47) implies that $\vec{q}_1 = 0$. However, $C_{0\mu}^{(3)}, q', -q' = 0$ for any $\vec{q'}$ (see Ref. [28]). Hence

$$F_2' = 0$$
 (3.20)

To proceed further with $F_2^{"}$ it is best to introduce the Fourier transformed \mathscr{D}^0 by (3.5). Then

$$\int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau' \mathcal{D}^{0}(q;\tau-\tau') \mathcal{D}^{0}(q';\tau-\tau') \mathcal{D}^{0}(q'';\tau-\tau')$$
$$= \beta^{2} \sum_{\sigma\sigma'} \mathcal{D}^{0}(q;\sigma) \mathcal{D}^{0}(q';\sigma') \mathcal{D}^{0}(q'';\sigma+\sigma')$$

2

For the evaluation of such sums one may either use the method of partial fractions or the identity

1.5

$$\beta^{-1} \sum_{\alpha} f(i\sigma) = \frac{1}{2\pi i} \int_{C} \frac{f(\omega) d\omega}{e^{\beta \omega} - 1}$$
(3.21)

(3.21)

where C is the contour shown in the figure and $f(\omega)$ is supposed to be regular inside and on C. (3.21) is due to the fact seen from (3.5b) that for $\omega = i\sigma$ the denominator vanishes. Thus, choosing

$$f(\omega) = \frac{1}{-(\omega - \nu)^{2} + \omega_{q}^{02}} \frac{1}{-(\omega - \nu^{\dagger} + i\sigma)^{2} + \omega_{q}^{02}}$$

and taking $\omega_q^0 \neq \pm \nu$, $\omega_{q'}^0 \neq \pm \nu'$ (the excluded values can be reached as a limit of the result) we see that $f(\omega)$ has only poles outside C. By deforming the contour C as indicated in the figure, we find, making use of Eq.(3.8)



$$2 \sum_{\sigma'} \mathscr{D}^{0}(\mathbf{q};\sigma'+\mathbf{i}\nu) \mathscr{D}^{0}(\mathbf{q}';\sigma+\sigma'+\mathbf{i}\nu')$$

$$= n(\nu+\omega_{\mathbf{q}}^{0}) \mathscr{D}^{0}(\mathbf{q}';\sigma-\mathbf{i}\omega_{\mathbf{q}}^{0}-\mathbf{i}\nu+\mathbf{i}\nu')$$

$$- n(\nu-\omega_{\mathbf{q}}^{0}) \mathscr{D}^{0}(\mathbf{q}';\sigma+\mathbf{i}\omega_{\mathbf{q}}^{0}-\mathbf{i}\nu+\mathbf{i}\nu')$$

$$+ n(\nu'+\omega_{\mathbf{q}'}^{0}) \mathscr{D}^{0}(\mathbf{q};\sigma+\mathbf{i}\omega_{\mathbf{q}'}^{0}-\mathbf{i}\nu+\mathbf{i}\nu')$$

$$- n(\nu'-\omega_{\mathbf{q}'}^{0}) \mathscr{D}^{0}(\mathbf{q};\sigma-\mathbf{i}\omega_{\mathbf{q}'}^{0}-\mathbf{i}\nu+\mathbf{i}\nu') \qquad (3.22)$$

where $n(\omega) \equiv (\exp \beta \omega - 1)^{-1}$. Applying the same identity to the σ -sum we finally find, making use of hermiticity, Eq.(1.31),

$$F_{2}^{"} = -\frac{1}{48} \sum_{q,q',q''} \left| C_{q,q',q''}^{(3)} \right|^{2} \\ \times \left\{ \frac{n_{q}^{0}(n_{q'}^{0}+1) + n_{q'}^{0}(n_{q''}^{0}+1) + n_{q''}^{0}(n_{q''}^{0}+1)}{\omega_{q}^{0} + \omega_{q'}^{0} + \omega_{q''}^{0}} \right. \\ + \frac{n_{q}^{0}(n_{q'}^{0}+n_{q''}^{0}+1) - n_{q'}^{0}n_{q''}^{0}}{-\omega_{q}^{0} + \omega_{q'}^{0} + \omega_{q''}^{0}} + \frac{n_{q'}^{0}(n_{q''}^{0}+n_{q}^{0}+1) - n_{q''}^{0}n_{q}^{0}}{\omega_{q}^{0} - \omega_{q'}^{0} + \omega_{q''}^{0}} \\ + \frac{n_{q''}^{0}(n_{q'}^{0}+n_{q'}^{0}+1) - n_{q}^{0}n_{q''}^{0}}{\omega_{q}^{0} - \omega_{q'}^{0} + \omega_{q''}^{0}} \right\}$$
(3.23)

From (3.19), (3.20), (3.23) the lowest order anharmonic corrections to the entropy S = - $(\partial F/\partial T)_v$ and the specific heat (heat capacity per unit volume) $C_v = -(T/V) (\partial^2 F/\partial T^2)_v$ may be obtained (see, e.g. Ref. [2]).

The coupling functions $C^{(n)}$, on the other hand, may in principle be obtained from the elastic constants. They determine the change per unit volume of the potential energy U in Eq.(1.3) due to macroscopic strains. For given strains $u_{\nu\mu}$ the macroscopic displacements \vec{u}_{I}^{c} (the index C indicates that these are C-numbers) are

$$u_{1\nu}^{c} = \sum_{\mu} u_{\nu\mu} R_{1\mu}^{0}$$
 (3.24)

In elasticity theory one defines the deformation tensor by

$$\eta_{\nu\mu} = \eta_{\mu\nu} = \frac{1}{2} \left(u_{\nu\mu} + u_{\mu\nu} + \sum_{\alpha} u_{\nu\alpha} u_{\alpha\mu} \right)$$
(3.25)

Then the potential energy change per unit volume may be written

$$\frac{\Delta U}{V} = V^{-1} \left\{ U(R^{0} + u^{C}) - U(R^{0}) \right\}$$

$$(3.26)$$

$$= \sum_{\nu \mu} C_{\nu \mu} \eta_{\nu \mu} + \frac{1}{2!} \sum_{\nu \mu} C_{\nu \mu \nu' \mu} \eta_{\nu \mu} \eta_{\nu' \mu} + \frac{1}{3!} \sum_{\nu} C_{\nu \mu \nu' \mu' \nu' \mu''} \eta_{\nu \mu} \eta_{\nu' \mu} + \dots$$

Here $C_{\nu\mu}$, $C_{\nu\mu\nu'\mu'}$, $C_{\nu\mu\nu'\mu'\nu''\mu''}$, ... are the first, second, third, order elastic constants, respectively. In terms of the $u_{\nu\mu}$, Eq.(3.25), we have

$$\frac{\Delta U}{V} = \sum_{\nu} C_{\nu\mu} u_{\nu\mu} + \frac{1}{2!} \sum_{\nu} \left\{ C_{\nu\mu\nu'\mu'} + C_{\nu\mu'} \delta_{\nu'\mu} \right\} u_{\nu\mu} u_{\nu'\mu'} + \frac{1}{3!} \sum_{\nu} \left\{ C_{\nu\mu\nu'\mu'} + \frac{3}{2} \left(C_{\nu\mu\nu'\mu''} \delta_{\nu''\mu''} + C_{\nu\mu''\nu'\mu'} \delta_{\nu''\mu'} + C_{\nu\mu''\nu'\mu'} \delta_{\nu''\mu'} \right) \right\} \times u_{\nu\mu} u_{\nu'\mu'} u_{\nu''\mu''} + \dots$$
(3.27)

Insertion of (3.24) into the expansion of $U(R^0 + u^C)$ given in section 1.2 gives, on the other hand, (we assume a Bravais lattice for a moment)

$$\Delta U = \sum U_{I\nu} R_{I\mu}^{0} u_{\nu\mu}$$

$$= \frac{1}{2!} \sum U_{I\nu I'\nu'} R_{I\mu}^{0} R_{I'\mu}^{0}, u_{\nu\mu} u_{\nu'\mu'},$$

$$+ \frac{1}{3!} \sum U_{I\nu I'\nu' I''\nu''} R_{I\mu}^{0} R_{I'\mu}^{0}, R_{I''\mu'}^{0}, u_{\nu\mu} u_{\nu'\mu'}, u_{\nu''\mu''} + \dots \qquad (3.28)$$

Comparison of Eqs (3.27) and (3.28) then gives the relation between the force constants $U_{I\nu,...}$ and the elastic constants $C_{\nu\mu...}$ (see, e.g. Ref. [29]

$$C_{\nu\mu} = \sum_{I} \left\{ U_{I\nu} R_{I\mu}^{0} \right\} C_{\nu\mu\nu'\mu'} + C_{\nu\mu'}\delta_{\nu'\mu}$$

$$= \sum_{II'} \left\{ U_{I\nu\Gamma'\nu'} R_{I\mu}^{0} R_{I'\mu'}^{0} \right\} C_{\nu\mu\nu'\mu'\nu'\mu''} + \frac{3}{2} \left(C_{\nu\mu\nu'\mu''}\delta_{\nu''\mu'} + C_{\nu\mu''\nu'\mu'} \delta_{\nu''\mu} \right)$$

$$= \sum_{II'I''} \left\{ U_{I\nu\Gamma'\nu'\Gamma''\nu''} R_{I\mu}^{0} R_{I'\mu'}^{0} R_{I''\mu'}^{0} \right\} \text{ etc.} \qquad (3.29)$$
where $\left\{ \right\}$ means appropriate symmetrization.

3.3. Phonon renormalization effects

In section 2.1 we freed ourselves from the complication of polarization flips $\mu \rightarrow \mu'$ by neglecting the anharmonic interactions, Eq.(2.7). But here we have to take the problem seriously. In addition, μ now has 3B values. The Dyson equation, which evidently also holds for imaginary-time Green functions, is now a 3B by 3B matrix equation

$$\mathscr{D} = \mathscr{D}^{0} + \mathscr{D}^{0}\Pi \mathscr{D} = \mathscr{D}^{0} + \mathscr{D}^{0}\Pi \mathscr{D}^{0} + \mathscr{D}^{0}\Pi \mathscr{D}^{0}\Pi \mathscr{D}^{0} + \dots$$
(3.30)

With (3.8) the inversion of expression (3.30) is

$$\mathcal{D}_{\mu\mu'}^{-1}(\vec{\mathbf{q}};\sigma) = \beta \frac{\sigma^2 + \omega_q^{02}}{\omega_q^0} \delta_{\mu\mu'} - \Pi_{\mu\mu'}(\vec{\mathbf{q}};\sigma)$$
(3.31)

In order to obtain renormalized phonons or quasiparticles Eq. (3, 31) has first to be diagonalized in $\mu\mu^{i}$. This, however, is not generally possible by unitary matrices because Π contains an antihermitian part which gives rise to a width or finite life-time of the quasi-phonons. If the antihermitian part is sufficiently small one can diagonalize just the hermitian part of Eq. (3, 31). The result of this procedure is usually called the quasi-harmonic approximation (see Ref. [27]).

A more practical way of diagonalizing (3.31) is to separate Π into diagonal and non-diagonal parts (see Ref. [28]).

$$\Pi_{\mu\mu}, (\vec{q}; \sigma) = \Pi_{q} (i\sigma) \delta_{\mu\mu}, + \Pi_{\mu\mu}^{N}, (\vec{q}; \sigma)$$
(3.32)

with $\Pi_{\mu\mu}^{N} = 0$. Defining a diagonal matrix d by

$$\left(d^{-1}\right)_{\mu\mu'} = \left\{ \left(\mathscr{D}^{0}(q;\sigma)\right)^{-1} - \Pi_{q}(i\sigma) \right\} \delta_{\mu\mu'}, \qquad (3.33a)$$

or

$$d_{\mu\mu'} \equiv d_{q}(i\sigma) \,\delta_{\mu\mu'} = \beta^{-1} \frac{\omega_{q}^{0}}{\sigma^{2} + \omega_{q}^{02} - \frac{\omega_{q}^{0}}{\beta} \,\Pi_{q}(i\sigma)} \,\delta_{\mu\mu'} \qquad (3.33b)$$

(3.31) may be solved by iteration

$$\mathcal{D} = (1 - d\Pi^{N})^{-1} d = d + d\Pi^{N} d + d\Pi^{N} d\Pi^{N} d + \dots$$
(3.34)

By comparing expression (3.33b) with expression (2.17b) we see that the approximation made in Eq. (2.7) is equivalent to retaining only the first term in the analogue of the development (3.34). In this same approximation the quasi-phonons are determined by the poles of $d_q(\omega)$. If near a pole

$$\big|\,\Pi_q(\omega)\,\big|\ll 2\beta\omega_q^0$$
 we find from Eq.(3.33b)

$$d_{q}(\omega) \stackrel{\simeq}{=} \frac{1}{2\beta} \left\{ \frac{1}{-\omega + \omega_{q}^{0} - \Pi_{q}(\omega)/2\beta} + \frac{1}{+\omega + \omega_{q}^{0} - \Pi_{q}(\omega)/2\beta} \right\}$$
(3.35)

But the poles of the two terms should describe the same quasi-phonon but with opposite sign of the renormalized frequence ω_q . This implies $\Pi_q^*(-\omega) = \Pi_q(\omega^*)$, so that the location of the poles is $\omega = \pm \omega_q - i\Gamma_q$. The renormalized frequency $\omega_q > 0$ and the width $\Gamma_q > 0$ are determined by

$$\omega_{q} = \omega_{q}^{0} - \frac{1}{2\beta} \operatorname{Re} \Pi_{q} (\omega_{q} - i\Gamma_{q}) \qquad (3.36a)$$

$$\Gamma_{q} = \frac{1}{2\beta} \operatorname{Im} \Pi_{q} (\omega_{q} - i \Gamma_{q})$$
(3.36b)

They are both temperature dependent and may be obtained from neutron diffraction experiments.

Expanding $\Pi_q(\omega)$ in the vicinity of the poles

$$\Pi_{\mathbf{q}}(\omega) = \Pi_{\mathbf{q}}(\pm \omega_{\mathbf{q}} - i\Gamma_{\mathbf{q}}) \mp (\mp \omega + \omega_{\mathbf{q}} \mp i\Gamma_{\mathbf{q}}) \frac{\partial \Pi_{\mathbf{q}}}{\partial \omega} \bigg|_{\omega^{\pm} \pm \omega_{\mathbf{q}} - i\Gamma_{\mathbf{q}}} + \dots$$

we find for expression (3.35), in analogy with Eq. (2.23)

$$\mathbf{d}_{\mathbf{q}}(\omega) \cong \frac{1}{2\beta} \left\{ \frac{Z_{\mathbf{q}}^{\dagger}}{-\omega + \omega_{\mathbf{q}} - i\Gamma_{\mathbf{q}}} + \frac{Z_{\mathbf{q}}^{-}}{\omega + \omega_{\mathbf{q}} + i\Gamma_{\mathbf{q}}} \right\} + \mathbf{d}_{\mathbf{q}}^{\mathrm{reg}}(\omega)$$
(3.37)

where Z_q^{\pm} is defined by

$$\left(Z_{\mathbf{q}}^{\pm}\right)^{-1} = 1 \pm \frac{1}{2\beta} \frac{\partial \Pi_{2}}{\partial \omega} \bigg|_{\omega^{\pm} \pm \omega_{\mathbf{q}}^{-1} \Gamma_{\mathbf{q}}}$$
(3.38)

The spectral function which leads to Eq. (3.38) through Eq. (3.11) then is

$$\mathbf{b}_{q}(\omega) = \frac{1}{2\pi} \left\{ \frac{Z_{q}^{\dagger} \Gamma_{q}}{(\omega - \omega_{q})^{2} + \Gamma_{q}^{2}} - \frac{Z_{q}^{\dagger} \Gamma_{q}}{(\omega + \omega_{q})^{2} + \Gamma_{q}^{2}} \right\} + \mathbf{b}_{q}^{\mathrm{back}}(\omega)$$
(3.39)

and the sum rule (2.15b, c) gives

$$\frac{1}{2}\left(Z_{q}^{+}-Z_{q}^{-}\right)=-\int b_{q}^{back}(\omega) d\omega \qquad (3.40a)$$

$$\frac{1}{2} \left(Z_{q}^{*} + Z_{q}^{*} \right) = 1 - \int b_{q}^{\text{back}} \left(\omega \right) \frac{\omega}{\omega_{q}} d\omega \qquad (3.40b)$$

or

$$Z_{q}^{\pm} = 1 - \int b_{q}^{back} (\omega) \left(\frac{\omega}{\omega_{q}} \pm 1 \right) d\omega$$
(3.40b)

In the limit $\Gamma_q \rightarrow \delta = 0^+$ we have

$$\mathbf{b}_{\mathbf{q}}(\omega) = \frac{1}{2} \left\{ Z_{\mathbf{q}}^{\dagger} \delta(\omega - \omega_{\mathbf{q}}) - Z_{\mathbf{q}} \delta(\omega + \omega_{\mathbf{q}}) \right\} + \mathbf{b}_{\mathbf{q}}^{\mathsf{back}}(\omega)$$
(3.41)

and in the harmonic approximation $Z_q^{\dagger} = Z_q^{-} = 1$ and $b_q^{back}(\omega) = 0$. As an application let us calculate the lowest-order contributions to the self-energy Π as defined by Eq.(3.30). According to the prescription (3.16) we have, with $\pm q' \equiv (\pm \vec{q}, \mu')$,

$$\mathcal{D}(\vec{q};-i\tau) = \langle \mathcal{F}\left(Q_{q}\left[-i\tau\right]Q_{-q'}\left[0\right]\right) \\ \times \exp\left\{-\int_{0}^{\beta} d\tau'\left(\mathscr{H}_{3}^{\dagger}\left[-i\tau^{\dagger}\right] + \mathscr{H}_{4}^{\dagger}\left[-i\tau^{\dagger}\right] + \dots\right)\right\}\right)_{0, \text{ conn.}} \\ = \mathcal{D}^{0}(\vec{q};-i\tau) - \int_{0}^{\beta} d\tau' \langle \mathcal{F}(Q_{q}\left[-i\tau\right]Q_{-q'}\left[0\right]\mathscr{H}_{4}^{\dagger}\left[-i\tau^{\dagger}\right]\right)\rangle_{0, \text{ conn.}} \\ + \frac{1}{2}\int_{0}^{\beta} d\tau'\int_{0}^{\beta} d\tau'' \langle \mathcal{F}(Q_{q}\left[-i\tau\right]Q_{-q'}\left[0\right]\mathscr{H}_{3}^{\dagger}\left[-i\tau^{\dagger}\right]\mathscr{H}_{3}^{\dagger}\left[-i\tau''\right]\right)\rangle_{0, \text{ conn.}} + \dots \\ = \mathcal{D}^{0} + \mathcal{D}^{1} + \mathcal{D}^{2} + \dots \qquad (3.42)$$

Now

$$\mathcal{D}^{1}(\vec{q},\tau) = -\frac{1}{4!} \sum_{q_{1}\cdots q_{4}} C_{q_{1}\cdots q_{4}}^{(4)} \int_{0}^{\beta} d\tau' \langle \mathcal{F}(Q_{q}[-i\tau] Q_{-q'}[0]) \rangle$$

$$\times Q_{\mathfrak{q}_1}[-i\tau'] \ldots Q_{\mathfrak{q}_4}[-i\tau']) \rangle_{0, \text{ conn.}}$$

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$$= -\frac{1}{4!} \sum_{q_{1}\cdots q_{4}} C_{q_{1}\cdots q_{4}}^{(4)} \int_{0}^{\beta} d\tau' \, 4.3 \, \mathscr{D}^{0}(q;\tau - \tau')$$

$$\times \mathscr{D}^{0}(q_{2};\tau') \mathscr{D}^{0}(q_{3};0) \, \delta_{q_{1}} - q_{1} \, \delta_{q'}, \, q_{2} \, q_{3}, -q_{4}$$

$$= -\frac{1}{2} \sum_{q''} C_{-q_{1}q', q'', -q'}^{(4)} \left(n_{q''}^{0} + \frac{1}{2} \right) \int_{0}^{\beta} d\tau' \, \mathscr{D}^{0}(q;\tau - \tau') \, \mathscr{D}^{0}(q';\tau')$$

The Fourier transform is

$$\mathscr{D}^{1}(\vec{q};\sigma) = -\frac{\beta}{2} \sum_{q^{*}} C^{(4)}_{-q,q',q'',-q''} \left(n^{0}_{q''} + \frac{1}{2} \right) \mathscr{D}^{0}(q;\sigma) \mathscr{D}^{0}(q';\sigma)$$
(3.43) -

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and corresponds to the diagram of the figure. The next term gives

$$\mathcal{D}^{2}(\vec{q},\tau) = \frac{1}{2} \left(\frac{1}{3!}\right)^{2} \sum_{q_{1} \dots q_{3}} C_{q_{1}q_{2}q_{3}}^{(3)} C_{q_{1}q_{2}q_{3}}^{(3)} C_{q_{1}q_{2}q_{3}}^{(3)} 6 \cdot 3 \cdot 2 \int_{0}^{\beta} d\tau' \int_{0}^{\beta} d\tau''$$

$$\times \left\{ \mathcal{D}^{0}(q;\tau-\tau') \mathcal{D}^{0}(q_{1}^{*};\tau'') \mathcal{D}^{0}(q_{2}^{*};\tau'-\tau'') \mathcal{D}^{0}(q_{3}^{*};\tau'-\tau'') \right.$$

$$\times \delta_{q_{*}} - q_{1}^{\delta} \frac{\delta}{q_{1}'} q_{2}^{\delta} \frac{\delta}{q_{2}'} - q_{3}^{\delta} \frac{\delta}{q_{3}'} - q'$$

$$+ \mathcal{D}^{0}(q;\tau-\tau') \mathcal{D}^{0}(q_{2};\tau') \mathcal{D}^{0}(q_{3}^{*};\tau'-\tau'') \mathcal{D}^{0}(q_{1}^{*};0)$$

$$\times \delta_{q_{*}} - q_{1}^{\delta} \frac{\delta}{q_{*}'} q_{*}^{*} \delta_{q_{*}'} - q_{3}^{*} \frac{\delta}{q_{1}'} - q'_{2} \right\}$$

The two corresponding diagrams are





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Now the second term involves a factor $C_{q'_1, -q'_1, q'_3}^{(3)}$ so that from crystal momentum conservation $\vec{q'_3} = 0$ and this term vanishes (compare Eq.(3.20)). After Fourier transformation we then have

$$\mathcal{D}^{2}(\mathbf{q};\sigma) = \frac{\beta^{2}}{2} \sum_{\mathbf{q}^{\mathsf{n}} \mathbf{q}^{\mathsf{m}}} C_{-\mathbf{q}\mathbf{q}^{\mathsf{n}} \mathbf{q}^{\mathsf{m}}}^{(3)} C_{\mathbf{q}^{\mathsf{n}}, -\mathbf{q}^{\mathsf{n}}, -\mathbf{q}^{\mathsf{m}}}^{(3)} \times \mathcal{D}^{0}(\mathbf{q}^{\mathsf{i}};\sigma) \mathcal{D}^{0}(\mathbf{q}^{\mathsf{i}};\sigma) \sum_{\sigma'} \mathcal{D}^{0}(\mathbf{q}^{\mathsf{n}};\sigma) \mathcal{D}^{0}(\mathbf{q}^{\mathsf{m}};\sigma - \sigma^{\mathsf{i}}) \quad (3.44)$$

From Eqs (3.43) and (3.44) we see that to this order the Fourier transform of (3.42) can be written in the form of the first two terms of the expansion (3.30), so that the self energy is, up to this order,

$$\Pi = \Pi^1 + \Pi^2 \tag{3.45a}$$

where

$$\Pi^{1}(\vec{q};\sigma) = -\frac{\beta}{2} \sum_{q^{"}} C^{4}_{-q,q',q^{"},-q^{"}}\left(n^{0}_{q^{"}}+\frac{1}{2}\right)$$
(3.45b)

$$\Pi^{2}(\mathbf{q};\sigma) = \frac{\beta^{2}}{2} \sum_{\mathbf{q}^{"} \mathbf{q}^{"}} C^{(3)}_{\mathbf{q}\mathbf{q}^{"} \mathbf{q}^{"}} C^{(3)}_{\mathbf{q}\mathbf{q}^{"},\mathbf{q}^{"},\mathbf{q}^{"},\mathbf{q}^{"},\mathbf{q}^{"}} \sum_{\sigma'} \mathcal{D}^{0}(\mathbf{q}^{"};\sigma') \mathcal{D}^{0}(\mathbf{q}^{"};\sigma-\sigma') \qquad (3.45c)$$

corresponding to the diagrams



The diagonal part $\Pi_q(i\sigma)$ defined in Eq.(3.32) is particularly simple since then q' = q,

$$\Pi_{q}^{1}(i\sigma) = -\frac{\beta}{2} \sum_{q^{*}} C_{-q, q, q^{*}, -q^{*}}^{(4)} \left(n_{q^{*}}^{0} + \frac{1}{2} \right)$$
(3.46)

$$\Pi_{\mathbf{q}}^{2}(\mathbf{i}\sigma) = \frac{\beta^{2}}{2} \sum_{\mathbf{q}^{\mathbf{r}} \mathbf{q}^{\mathbf{m}}} \left| C_{-\mathbf{q} \mathbf{q}^{\mathbf{r}} \mathbf{q}^{\mathbf{m}}}^{(3)} \right|^{2} \sum_{\sigma'} \mathcal{D}^{0}(\mathbf{q}^{\mathbf{m}};\sigma') \mathcal{D}^{0}(\mathbf{q}^{\mathbf{m}};\sigma-\sigma')$$
(3.47)

Here we have made use of hermiticity, Eq.(1.31), which also implies that $C^{(4)}_{-q,q,q^n,-q^n}$ is real. This shows that (we have to continue analytically $i \sigma \rightarrow \omega$)

$$\operatorname{Im} \Pi_{\alpha}^{1}(\omega) = 0 \qquad (3.48)$$

so that this term does not contribute to the decay rate (or width). In order to do the analytic continuation of expression (3.47) we have to insert the σ' sum which is given by Eq.(3.22). Here a more convenient form is the following, which is easily obtained by using partial fractions:

$$4\beta \sum_{\sigma'} \mathscr{D}^{0}(q;\sigma') \mathscr{D}^{0}(q';\sigma-\sigma')$$

$$= \frac{n_{q}^{0} + n_{q'}^{0} + 1}{i\sigma + \omega_{q}^{0} + \omega_{q'}^{0}} - \frac{n_{q}^{0} + n_{q'}^{0} + 1}{i\sigma - \omega_{q}^{0} - \omega_{q'}^{0}}$$

$$+ \frac{n_{q}^{0} - n_{q'}^{0}}{i\sigma - \omega_{q}^{0} + \omega_{q'}^{0}} - \frac{n_{q}^{0} - n_{q'}^{0}}{i\sigma + \omega_{q}^{0} - \omega_{q'}^{0}}$$
(3.49)

If now we analytically continue $i\sigma \rightarrow \omega - i\delta$ we find for (3.47)

$$\operatorname{Re} \Pi_{q}^{2}(\omega) = \frac{\beta}{8} \sum_{q' q''} \left| C_{-q q' q''}^{(3)} \right|^{2} \operatorname{P} \left\{ \frac{n_{q'}^{0} + n_{q''}^{0} + 1}{\omega + \omega_{q'}^{0} + \omega_{q''}^{0}} - \frac{n_{q''}^{0} - n_{q''}^{0}}{\omega - \omega_{q'}^{0} + \omega_{q''}^{0}} - \frac{n_{q''}^{0} - n_{q''}^{0}}{\omega + \omega_{q'}^{0} - \omega_{q''}^{0}} \right\}$$

$$\operatorname{Im} \Pi_{q}^{2}(\omega) = \frac{\beta\pi}{8} \sum_{q' q''} \left| C_{-q q' q''}^{(3)} \right|^{2}$$

$$\times \left\{ \left(n_{q'}^{0} + n_{q''}^{0} + 1 \right) \left(\delta \left(\omega + \omega_{q'}^{0} + \omega_{q''}^{0} \right) - \delta \left(\omega - \omega_{q'}^{0} - \omega_{q''}^{0} \right) \right) \right\}$$

$$\left. + \left(n_{q'}^{0} - n_{q''}^{0} \right) \left(\delta \left(\omega - \omega_{q'}^{0} + \omega_{q''}^{0} \right) - \delta \left(\omega + \omega_{q'}^{0} - \omega_{q''}^{0} \right) \right) \right\}$$

$$(3.51)$$

From these expressions the quasiparticle formulas (3.36) to (3.40) are readily constructed. A considerable improvement of the approximation is achieved by replacing n_q^0 and $\mathscr{Q}^0(q;\sigma)$ in Eqs (3.46), (3.47) by the exact quantities n_q , $\mathscr{D}_{\mu\mu'}(\vec{q};\sigma)$. This is the analogue of Migdal's theorem of section 2 in the sense that again the vertices $C^{(n)}$ are taken in their non-renormalized form whereas the phonon lines are calculated rigorously. In the approximation by the first term of (3.34) this means that in Eqs (3.50), (3.51) the renormalized frequencies are to be taken. If this is done Γ_q as given by Eqs (3.36b), (3.51) represents quite well the decay rate of phonons of quantum numbers $q = (\vec{q}; \mu)$. For phonons of sufficiently long wavelength this quantity is directly measurable by ultrasonic attenuation (see Ref. [30]).

3.4. Heat propagation and second sound

Heat propagation has become an increasingly important domain of investigation of insulators. This is due on the one hand to the technique of heat pulses which has been used for a long time for liquid helium but which is new in solid-state physics. On the other hand it is due to a new mode of heat propagation discovered last year (see Ref. [31]), namely second sound, which again was well known in liquid helium. While ordinary heat conduction (i.e. phonon diffusion) and heat convection (i.e. phonon drift) obey the diffusion equation, second sound is a wave propagation of heat and hence does not produce entropy. Here we give a unified phenomenological description of these phenomena. The same description can be formulated in terms of purely microscopic quantities (correlation functions) and in this form gives a rather direct connection of heat propagation with the anharmonic interaction \mathcal{H}^{*}_{anh} (see Ref. [32]).

Heat propagation is governed by two local balance equations, first the energy balance

$$\dot{\mathbf{h}} + \nabla \vec{\mathbf{s}} = \beta^{-1} \sigma \qquad (3.52)$$

where $h(\vec{r}, t)$ is the energy density and $\vec{s}(\vec{r}, t)$ the energy flux. The entropy production $\sigma(\vec{r}, t)$ is negligible so that energy is not dissipated but is conserved. The second balance equation is that of momentum

$$\vec{j} + \nabla \mathbf{IP} = \vec{f}_{ph}$$
 (3.53)

Here $\vec{j}(\vec{r}, t)$ is the momentum density and $\mathbf{P}(\vec{r}, t)$ the momentum flux tensor. $\vec{f}_{ph}(\vec{r}, t)$ is the density of the lattice force introduced in Eq.(1.60) and gives rise to momentum dissipation. Now a heat pulse injected from outside will induce a local temperature variation $\delta T(\vec{r}, t)$ and a local phonon drift velocity $\vec{u}(\vec{r}, t)$. This causes local variations of the quantities in Eqs (3.52), (3.53), the Fourier transforms which have the form

$$\delta \mathbf{h}(\vec{q}, \omega) = \mathbf{C} \, \delta \, \mathbf{T} - i \vec{q} \cdot \boldsymbol{\alpha} \cdot \vec{u}$$

$$\delta \vec{s}(\vec{q}, \omega) = -\kappa \, i \vec{q} \, \delta \, \mathbf{T} + \beta \vec{u}$$

$$\delta \vec{j}(\vec{q}, \omega) = -\lambda \, i \vec{q} \, \delta \, \mathbf{T} + \rho \, \vec{u}$$

$$i \vec{q} \cdot \delta \mathbf{IP}(\vec{q}, \omega) - \delta \vec{f}_{ph}(\vec{q}, \omega) = \mu \, i \vec{q} \, \delta \, \mathbf{T} + \gamma \, \vec{u} \qquad (3.54)$$

Here C is the heat capacity per unit volume, κ the heat conductivity tensor, ρ the excitation mass density tensor (see Ref.[32]). The coefficients $\alpha, \beta, \lambda, \mu, \gamma$ have a somewhat less obvious intuitive meaning $(\beta, \lambda, \mu, \gamma)$ are in general tensors). Introducing expressions (3.54) in the Fourier transform of Eqs (3.52), (3.53) we find

$$(-i\omega C + \vec{q} \cdot \kappa \cdot \vec{q}) \delta T + i\vec{q} \cdot (i\omega\alpha + \beta) \cdot \vec{u} = 0 \qquad (3.55)$$

$$(i\omega\lambda + \mu) \cdot i\vec{q}\,\delta\,T - (i\omega\rho - \gamma) \cdot \vec{u} = 0 \qquad (3.56)$$

Solving Eq. (3.56) for \vec{u} ,

$$\vec{u} = (i\omega\rho + \gamma)^{-1}(i\omega\lambda + \mu) \cdot i\vec{q}\,\delta\,T$$

and inserting into Eq. (3.55), we find

$$-i\omega C + \vec{q} \cdot \kappa \cdot \vec{q} - \vec{q} \cdot (i\omega \alpha + \beta) (i\omega \rho - \gamma)^{-1} \cdot (i\omega \lambda + \mu) \cdot \vec{q} = 0$$

This can also be written, in the limit $q \rightarrow 0, \mbox{ as }$

$$\frac{\omega^2}{q^2} = -\frac{i\omega}{C} \hat{q} \cdot \left(\kappa (\omega) + \varphi (\omega)\right) \cdot \hat{q} \qquad (3.57)$$

where \hat{q} is the unit vector \vec{q}/q and

$$\varphi(\omega) = -(i\omega\alpha + \beta)(i\omega\rho - \gamma)^{-1}(i\omega\lambda + \mu)$$
(3.58)

is the convectivity tensor since it comes from the term proportional in \vec{u} in the energy conservation Eq.(3.55). For cubic crystals all tensors are numbers and the \hat{q} may be dropped. Two frequency regions are now of interest.

In the diffusion range $\omega \ll (|\mu/\lambda|, |\beta/\alpha|, |\gamma/\rho|)$ we have

$$\frac{\omega^2}{q^2} = -\frac{i\omega}{C} \left(\kappa (0) + \varphi (0) \right)$$
(3.59)

which is the dispersion relation of the diffusion equation. We may relate the static conductivity κ (0) and convectivity ϕ (0) to the "umklapp" relaxation time τ_u and "normal" relaxation time τ_N , respectively, in the conventional way

$$\kappa(0) \equiv \operatorname{Cv}_{\mathrm{II}}^{2} \left(\tau_{\mathrm{N}} + \frac{\alpha}{\beta} + \frac{\lambda}{\mu} \right)$$
$$\varphi(0) = \frac{\beta\mu}{\gamma} \equiv \operatorname{Cv}_{\mathrm{II}}^{2} \tau_{\mathrm{u}}$$
(3.60)

where $v_{II} \equiv \sqrt{\beta \mu / C \rho}$ is the "second" sound velocity. In the second-sound range

$$\left(q^{2}\frac{\kappa(\omega)}{C}, |\gamma/\rho|\right) \ll \omega \ll (|\mu/\lambda|, |\beta/\alpha|)$$

we have to the first order

$$\omega^2/q^2 = v_{II}^2 \left\{ 1 - i\omega \tau_N + \frac{1}{i\omega \tau_u} \right\}$$
(3.61)

In particular if, as for fluids,

$$\vec{s} = v_I^2 \vec{j}$$
; $IP = \frac{1}{3} \delta h \cdot 1$; $f_{ph} = \omega$

 $v_{\rm I}$ being the first sound velocity, one finds

$$\beta = \rho v_1^2; \quad \gamma = \frac{\alpha q^2}{3}; \quad \lambda = \frac{\kappa}{v_1^2}; \quad \mu = \frac{C}{3}$$

and (3.61) takes the usual value

$$v_{II} = \frac{v_I}{\sqrt{3}}$$
(3.61a)

This excitation (3.16) exists in the "frequency window" $\tau_N^{-1} \gg \omega > \tau_u^{-1}$. It has been found in solid He⁴ at temperature $T \approx 0.5 \,^{\circ}$ K and high pressure ($\gtrsim 50$ atm.). Up to now it has not been found in other crystals. The balance Eqs (3.52), (3.53) can be obtained from a transport equation (see Ref. [34]). They are typical hydrodynamic equations. Therefore, the problem of deriving a transport equation in a way analogous to section 2.4 is of great interest for the problem of heat propagation in insulators (see Ref. [35]). Second sound as described above is then to be understood as a hydrodynamical excitation. However, it might be that in the limit $\omega \rightarrow \infty$ the hydrodynamic mode (as given by the ladder solution discussed in section 2.4) disappears in favour of a collective mode (as given by the chain solution) [11].

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THE FERMI SURFACE

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Abstract

 Introduction.
 Energy bands and the Fermi surface.
 Conduction electrons in magnetic fields.
 The De Haas-Van Alphen effect.
 Transport properties.
 Galvanomagnetic effects.
 Electromagnetic absorption.
 Cyclotron resonance.
 The R.F. size effect.
 The magnetoacoustic effect.
 Positron annihilation.
 The Kohn effect.
 Electron interactions.
 The Fermi surface in metals.
 Prospects in Fermi surface studies.

1. INTRODUCTION

The purpose of these lectures is to discuss the concept of the Fermi surface (FS), to explain its importance in understanding the detailed properties of metals, and to show how it can be studied experimentally. Much of the material is standard and is contained in reviews and books. notably Chapter 9 of "Principles of the Theory of Solids" by J.M. Ziman (PTS) to which frequent reference will be made. I shall, however, refer to more recent developments where appropriate, and these will be covered in somewhat more detail in these notes. There will be considerable overlap with other courses at the School, but I think that no harm will be done by repeating some of the material from other lectures. perhaps from a slightly different viewpoint. At the end of the notes I shall give a list of references for further reading for those students who are particularly interested in electrons in metals. It is, however, intended that these lectures should form a self-contained course at a fairly elementary level, and I will therefore try to cover most of those aspects of FS studies which seem to me to be most relevant in the understanding of the properties of metals.

A knowledge of the form of the FS and the behaviour of the electrons on it constitutes only a small fraction of the information required to calculate most properties of metals, of course. A number of properties, such as the electronic heat capacity, the Pauli paramagnetism and most transport properties are completely determined from such a knowledge. but many more, including optical properties, lattice dynamics and magnetic interactions, involve the complete band structure. The primary importance of FS measurements is that they allow an extremely accurate determination of the band structure at one energy, the Fermi energy μ , and it is not at present possible to measure the energy levels of the electrons away from the Fermi level with anything like the same accuracy. This means that FS studies provide a unique method for checking the results of band structure calculations, which in turn are fundamental for understanding all electronic properties of metals. They can also be used to check the extent to which the band structure, based on an independent particle model, is a useful concept in the strongly interacting electron system.

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The electronic band structure, particularly those aspects which are related to the form of the FS, will be discussed in the first section. The next few sections will deal with the standard methods of FS determination, all of which require very pure metals and low temperatures. The FS in alloys, and methods of obtaining experimental information on it, will then be discussed. The corrections to the single particle model due to electron interactions, and particularly their effect on FS properties will then be described, with emphasis on the physical principles involved. Finally, the knowledge which has been obtained by experiments and calculations on the FS of real metals will be summarized, and likely future developments in FS studies will be speculated upon.

2. ENERGY BANDS AND THE FERMI SURFACE

In this section, we will summarize briefly some of the important results of energy band theory, which have been discussed in detail in other lectures, and show how to derive the FS from a general set of energy bands.

The single-particle Schrödinger equation for an electron moving in the crystal lattice is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{\mathbf{r}}) + V(\vec{\mathbf{r}})\psi(\vec{\mathbf{r}}) = \epsilon\psi(\vec{\mathbf{r}})$$
(1)

where the potential $V(\vec{r})$ is composed of the lattice potential and the self-consistent potential of the conduction electrons. It therefore has the periodicity of the crystal lattice, so that

$$V(\vec{r} + \vec{R}_{n}) = V(\vec{r} + n_{1}\vec{a}_{1} + n_{2}\vec{a}_{2} + n_{3}\vec{a}_{3}) = V(\vec{r})$$
(2)

where \vec{a}_1 , \vec{a}_2 and \vec{a}_3 are the primitive translation vectors of the lattice and the n are integers. This important symmetry property of the lattice leads to Bloch's theorem, which states that the electron eigenfunctions may be written in the form

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$
(3)

where $u_{\vec{k}}(\vec{r})$ also has the periodicity of the lattice.

The primitive translation vectors of the reciprocal lattice are defined by the equations

$$\vec{\mathbf{b}}_{i} = \frac{2\pi \vec{\mathbf{a}}_{j} \times \vec{\mathbf{a}}_{k}}{\vec{\mathbf{a}}_{i} \cdot (\vec{\mathbf{a}}_{j} \times \vec{\mathbf{a}}_{k})}$$
(4)

so that

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \,\delta_{ij} \tag{5}$$

A general reciprocal lattice vector is

$$\vec{g}_{m} = m_{1}\vec{b}_{1} + m_{2}\vec{b}_{2} + m_{3}\vec{b}_{3}$$
 (6)

so that

$$\vec{g}_{\rm m} \cdot \vec{R}_{\rm n} = 2\pi \ell \tag{7}$$

where *l* is an integer, and therefore

$$e^{i\vec{g}_{m}\cdot\vec{R}_{n}} = 1$$
(8)

It is this relation which makes the reciprocal lattice such an important concept in solid state physics.

The choice of \vec{k} in expression (3) is not unique, since we can write

$$u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}} = \left[u_{\vec{k}}(\vec{r}) e^{-i\vec{g}\cdot\vec{r}} \right] e^{i(\vec{k}+\vec{g})\cdot\vec{r}}$$
$$= v_{\vec{k}+\vec{g}}(\vec{r}) e^{i(\vec{k}+\vec{g})\cdot\vec{r}}$$
(9)

where, from Eq.(8), $v(\vec{r})$ also has the lattice periodicity. \vec{k} is therefore arbitrary to the addition of any reciprocal lattice vector, and a single unit cell in reciprocal space contains all non-equivalent \vec{k} vectors. A convenient choice for this cell is the primitive Brillouin Zone (BZ), which is the volume in reciprocal space nearest the origin, bounded by planes which perpendicularly bisect reciprocal lattice vectors. The BZ for the three common metallic structures are shown in Fig.1.

If we describe the energy eigenvalues by using \vec{k} values within the primitive BZ only – the reduced zone scheme – the energy is a multiple valued function of \vec{k} , and the energy band structure is defined by this function $\epsilon_j(\vec{k})$ throughout the zone. j is a band index which is defined so that, for any \vec{k} , a lower j always corresponds to a lower energy. A part of a typical transition metal band structure is shown in Fig. 2.

It is often convenient to describe the band structure in a scheme in which all points $\vec{k} + \vec{g}$ are considered equivalent — the periodic zone scheme. In this case

$$\epsilon(\vec{k} + \vec{g}) = \epsilon(\vec{k}) \tag{10}$$

so that $\epsilon(\vec{k})$ has the full translational symmetry of the reciprocal lattice. The rotational symmetry of the Hamiltonian is also reflected in $\epsilon(\vec{k})$ and hence in the form of the FS. $\epsilon(\vec{k})$ has the full point symmetry of the crystal, and is a continuous function within the primitive BZ. If we take into account the electron spin, Kramers' theorem states that

$$\epsilon(\dot{\mathbf{k}},\uparrow) = \epsilon(-\dot{\mathbf{k}},\downarrow) \tag{11}$$

If, in addition, there is a centre of inversion symmetry,

$$\epsilon(\vec{k},\uparrow) = \epsilon(-\vec{k},\uparrow) = \epsilon(\vec{k},\downarrow) \tag{12}$$

and all \vec{k} states are at least doubly degenerate. Further degeneracies may occur in symmetry planes of the BZ and may also be reflected in







FIG. 1. Brillouin zones for the fcc, bcc and hcp structures.

FIG. 2. A part of the energy band structure of Pt.

the FS. Spin-orbit coupling, which is important for heavy metals may lift some of these degeneracies.

The \vec{k} value for which $\epsilon(\vec{k})$ is constant in a particular band fall on a surface in reciprocal space, and variation of $\epsilon_j(\vec{k})$ produces a family of constant energy surfaces. The independent electrons are distributed in energy according to the Fermi-Dirac law

$$f(\epsilon) = (e^{(\epsilon - \mu)/kT} + 1)^{-1}$$
(13)

The constant energy surface in \vec{k} space on which $\epsilon(\vec{k}) = \mu$ is called the FS, and at absolute zero it separates occupied from empty states. When the energy bands are known in detail, the FS may readily be determined. The Fermi energy is fixed by requiring that the number of states beneath it is equal to the number of valence electrons. To do this, we need to know that the number of states in a volume $\delta \vec{k}$ in reciprocal space is, including spin,

$$\delta n = \frac{\Omega}{4\pi^3} \ \delta \vec{k} \tag{14}$$

where Ω is the volume of the crystal. The number of states in a single band is therefore two for each unit cell of the crystal lattice. For a particular direction in \vec{k} space, the positions at which the Fermi level cuts the various bands determine the extension of the various sheets of the FS in that direction. In three dimensions, the FS is traced out by observing the variation of k_F with the direction of \vec{k} .



FIG. 3. Sections through the Fermi surface corresponding to the bands of Fig. 2, in the periodic zone scheme.

The FS corresponding to the energy bands of Fig. 2 is shown in Fig. 3. It has three sheets, of which two are closed and enclose filled and empty states respectively. These are called electron and hole surfaces. There is also an open surface, unbounded in the [100] directions. Open surfaces are very common in real metals, and an understanding of their properties is fundamental to FS studies.

3. CONDUCTION ELECTRONS IN MAGNETIC FIELDS

Before going on to discuss the various methods of measuring FS dimensions, we will first review the dynamics of conduction electrons in magnetic fields.

We shall make use of the relation

$$\vec{\nabla}_{\vec{k}} = \frac{1}{\hbar} \frac{\partial \epsilon}{\partial \vec{k}}$$
(15)

and the Lorentz force equation

$$\vec{\mathbf{h}}\vec{\mathbf{k}} = \mathbf{e}\left(\vec{\mathbf{E}} + \frac{1}{c}\vec{\mathbf{v}}\times\vec{\mathbf{B}}\right)$$
(16)

which are discussed in PTS, Chapter 6.



FIG. 4. The motion in \vec{k} space of an electron in a magnetic field.

If the electron is acted on by a magnetic field only, Eq.(16) shows that the component of \vec{k} along \vec{B} is constant, while the component in the plane normal to \vec{B} moves around a constant energy contour, called the orbit in \vec{k} space, as in Fig.4. If we introduce co-ordinates $\vec{\kappa}$ and $\vec{\rho}$ in the plane perpendicular to \vec{B} , Eq.(16) can be integrated to give

$$\mathbf{h}\vec{k} = \frac{\mathbf{e}}{\mathbf{c}}\vec{\rho}\times\vec{\mathbf{B}} \tag{17}$$

The orbit in the metal is therefore related to the \vec{k} space orbit by a rotation through 90° and a scaling such that

$$\Delta \rho = \frac{c \hbar}{eB} \Delta \kappa \tag{18}$$

The types of orbit which occur in a magnetic field in a metal depend on the FS topology, and may be classified as follows:

(a) <u>Closed orbits</u> are characterized by the fact that $\vec{v} = 0$ in any direction normal to \vec{B} , where the average is taken around the orbit. The frequency with which the electron goes around its orbit, known as the cyclotron frequency ω_c , may be calculated by introducing co-ordinates κ_t and κ_n tangential and normal to the orbit, as illustrated in Fig.4. From Eq.(16) we then have

$$\hbar \frac{d\kappa_t}{dt} = \frac{eB}{c\hbar} \frac{\partial \epsilon}{\partial \kappa_n}$$
(19)

or

$$dt = \frac{c\hbar^2}{eB} \frac{d\kappa_n d\kappa_t}{d\epsilon}$$
(20)

Integrating around the orbit

$$\tau_{\rm c} = \oint dt = \frac{c\hbar^2}{eB} \left(\frac{\partial\alpha}{\partial\epsilon}\right)_{\rm k_{\rm Z}}$$
(21)

where α is the area enclosed by the orbit, and we have taken the field to be in the z direction. We then have

$$\omega_{\rm c} = \frac{2\pi}{\tau_{\rm c}} = \frac{\rm eB}{\rm m*c} \tag{22}$$

where the effective mass m* is given by

$$m^* = \frac{\hbar^2}{2\pi} \left(\frac{\partial \alpha}{\partial \epsilon} \right)_{k_z}$$
(23)

For an electron orbit, which encloses states of lower energy, m* is positive, while a hole orbit, which encloses states of higher energy, corresponds to a negative value of m*.

Because of the Bohr-Sommerfeld quantization condition

$$\oint \vec{\mathbf{p}} \cdot d\vec{\mathbf{q}} = (n + \frac{1}{2})h \tag{24}$$

the areas enclosed by the orbits are quantized. In a magnetic field, the canonical conjugate to \vec{r} is $h\vec{k}+(e/c)\vec{A}$, so that

$$(n + \frac{1}{2})h = \oint \left(h\vec{\kappa} + \frac{e\vec{A}}{c}\right) \cdot d\vec{\rho}$$
$$= \frac{e\vec{B}}{c} \cdot \oint \vec{\rho} \times d\vec{\rho} + \frac{e}{c} \oint \vec{A} \cdot d\vec{\rho}$$
$$= \frac{e}{c} B\alpha \vec{r} = \frac{eB}{c} \left(\frac{c\hbar}{eB}\right)^2 \alpha \vec{k}$$

Hence the area enclosed by the orbits in \vec{k} space can take only the values

$$\alpha_{\vec{k}} = (n + \frac{1}{2}) \frac{2\pi eB}{\hbar c}$$
(25)

This is the Onsager-Lifshits quantization condition, which will be the basis of our discussion of the de Haas-van Alphen (HA) effect.

(b) <u>Open orbits</u> are characterized by the fact that $\overline{\vec{v}}$ is generally non-zero in directions normal to \vec{B} . In the periodic zone scheme, such orbits extend indefinitely through \vec{k} space, without closing.



FIG. 5. The Fermi surface of the noble metals in the periodic zone scheme and sections through it, corresponding to orbits in a magnetic field.

In Fig.5 is shown the FS of the noble metals in the periodic zone scheme. It is essentially a bcc array of spheres joined by necks along [111]. Also shown are sections through the FS, normal to [001], and

hence the \vec{k} space orbits which result when a magnetic field is applied in the [001] direction. As the section is moved up the zone, the character of the closed orbits changes from electron to hole and back to electron. If the field is tilted towards [100], a single section contains both electron and hole orbits, and between them there is an open orbit running along [010] in \vec{k} space, and hence along [100] in the crystal. Such an open orbit is periodic and exists for a one-dimensional line of magnetic field directions.



FIG. 6. An aperiodic open orbit and an extended orbit in the noble metals.

If the field is tilted away from [001] in an arbitrary direction, we get the situation depicted in Fig.6. There are still electron and hole orbits in the same section but they are now separated by an open orbit which is not generally periodic. Such open orbits run, in \vec{k} space, in the direction defined by the intersection of the plane normal to the field and a reciprocal lattice plane, and exist over a two-dimensional region of field directions. The directions of magnetic field for which open orbits exist in the noble metals are plotted stereographically in Fig.7.

(c) Extended orbits are closed orbits which cannot be contained in a single unit cell of the reciprocal lattice. An example of an extended orbit, produced by tilting the field away from [001] beyond the region in which aperiodic open orbits exist, is shown in Fig.6. The effective mass for an extended orbit is defined by Eq.(23), and clearly is generally large.

If the energy separation ϵ_g between two bands is small enough, it is possible for an electron in a magnetic field to make a transition between them, by a tunnelling process. This phenomenon is called magnetic breakdown, and it occurs when the field is sufficiently large that $\hbar\omega_c\mu$ becomes comparable with $(\epsilon_g)^2$, which may happen in a field of a few kilogauss. In this case, the electron may move from one sheet

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of the FS to another, so that a closed orbit becomes open, or vice-versa. As the magnetic field is increased therefore, the type of orbit present in the metal may change as breakdown begins to occur, and at intermediate fields a complicated pattern of coupled orbits may result. At high fields, when breakdown is complete, the situation becomes relatively simple again, but the effective FS topology may be quite different from that at low fields. This phenomenon may profoundly affect all of the experiments which we shall discuss which involve high magnetic fields.



FIG. 7. One- and two-dimensional regions of field directions giving open orbits in Au, deduced from magnetoresistance measurements by Gaidukov, Yu., Soviet Phys. JETP 10 (1960)913.

4. THE DE HAAS-VAN ALPHEN EFFECT

It is appropriate to begin our review of methods of FS determination with the HA effect, because it is incomparably the most important experiment in FS studies. Almost all of the most accurate measurements of FS dimensions have been made with this technique, to an accuracy as high as 1 in 10^4 . The experiment consists of measuring the oscillations with field of the low temperature magnetic susceptibility of a single crystal, as a function of the field direction. The principle of the steady field method, which is normally used for the most accurate measurements, is shown in Fig.8. The sample is placed in a high steady field and a small modulating field of frequency ω is applied by means of a A second coil is used to detect the oscillating moment of small coil. the sample at 2ω , which is proportional to the second derivative d^2M/dB^2 of the sample moment. The period of the HA oscillations may be measured by slowly sweeping the steady field, and its dependence on field direction by rotating the sample in a fixed field.

The magnetic moment of a system is related to the free energy by the thermodynamic relation

$$M(B) = -\frac{\partial F}{\partial B} = -\frac{\partial E}{\partial B} \quad (T = 0)$$
 (26)

The HA oscillations are therefore a manifestation of the oscillations of the energy of the metal with field, which in turn are due to the





FIG. 8. Schematic diagram of apparatus for measuring the De Haas-Van Alphen effects, with some typical results.

FIG. 9. Quantized orbits in \vec{k} space in a magnetic field.

quantization of the \vec{k} space orbits. In a magnetic field the electron distribution in \vec{k} space has the form shown in Fig. 9, with the allowed states falling on irregular tubes of area

$$\alpha_{\vec{k}} = (n + \frac{1}{2}) \frac{2\pi eB}{\hbar c}$$
(25)

whose axes run along the field direction. The energy of such quantized levels has been discussed elsewhere in the School, and is

$$\epsilon_{n,k_z} = (n + \frac{1}{2})\hbar\omega_c + \epsilon(k_z) = (n + \frac{1}{2})\frac{\hbar eB}{mc} + \frac{\hbar^2 k_z^2}{2m} \quad \text{(free electrons)} \quad (27)$$

The degeneracy of these quantized levels is $eBdk_z/2\pi^2\hbar c$, so that they can accommodate all the states which would lie between them in zero field. In practice, the number of occupied levels is several thousand, and under these conditions, the Fermi level μ can be taken as effectively constant. The physical reason for the oscillations in E can then be seen from Fig.9. As B is increased, the area of the tubes in-



creases, and, as the area of the outermost filled level approaches the extremal area α_0 of the FS, it abruptly empties when

$$\alpha_0 = (n + \frac{1}{2}) \frac{2\pi eB}{\hbar c}$$
(28)

This occurs for successive values of n, and the resulting oscillations in the energy and moment are periodic in 1/B, with a period

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar c \alpha_0}$$
(29)

In order to calculate the moment at a finite temperature, we must use the expression for the free energy of a system of non-interacting Fermions

$$F = N\mu - kT \sum_{i}^{\infty} \log (1 + e^{(\mu - \epsilon_{i})/kT})$$

$$= N\mu - kT \int_{-\infty}^{\infty} \frac{eB}{2\pi^{2}\hbar c} \sum_{n=0}^{\infty} \log (1 + \exp[((\mu - \epsilon_{n,k_{z}})/kT])) dk_{z}$$
(30)

The evaluation of this integral is performed in PTS, p.275, and we shall not reproduce the details here. Differentiation of F to give the moment yields the result

$$\sum_{\substack{\text{spacing of Landau of } \alpha \text{ near levels extremum}}} \sum_{\substack{\text{spacing of Landau of } \alpha \text{ near levels extremum}}} M = (\pi^2 \sqrt{2\pi\hbar})^{-1} \left(\frac{e}{c}\right)^5 \sqrt{B} \left(\frac{\partial \log \alpha}{\partial \epsilon}\right)^{-1}_0 \left(\frac{\partial^2 \alpha}{\partial k_z^2}\right)^{-\frac{1}{2}}_0$$

$$\times \sum_{\substack{y=1 \\ y=1}}^{\infty} \frac{1}{y^{3/2}} \left[\left(\frac{\pi^2 \text{ ykT}}{\hbar\omega_c}\right) / \sinh \frac{\pi^2 \text{ ykT}}{\hbar\omega_c} \right] e^{-\frac{2\pi y}{\omega_c \tau}}$$
thermal broadening collisions
$$\times \cos \left(\frac{\pi \text{ ygm}^*}{m}\right) \sin \left[\frac{\hbar c y}{eB} \alpha_0 \pm \frac{\pi}{4} - \pi y\right]$$
(31)

spin splitting

In this expression τ is the relaxation time and g the Landé factor for the conduction electrons. The + and - signs are to be taken if α_0 is a minimum or maximum, respectively. The origin of each term in this expression is briefly indicated.

There is clearly an enormous amount of information about the conduction electrons contained in the dependence of the HA oscillations on the magnitude and orientation of the field, and the temperature. Specifically: FERMI SURFACE

(a) The period gives the extremal area of the FS normal to the field direction. Because the phase of the oscillations is so high, the measured area is very exactly the extremal value. If a number of extrema are present, as frequently occurs, a corresponding number of periods is observed. By careful measurement of these periods as a function of the direction of \vec{B} relative to the crystal axes, the shape of the FS may be determined in great detail and with extreme precision.

(b) The temperature dependence of the amplitude of the oscillations gives the effective mass of the extremal orbit. At low temperatures, the amplitude is proportional to $\exp(-kT/\hbar\omega_c)$, which emphasizes the need for low temperatures and high magnetic fields in this experiment.

(c) The field dependence of the amplitude gives, in principle, the mean relaxation time around the extremal orbit. The collision broadening term emphasizes the need for pure crystals and correspondingly long electron free paths, although the requirements in this respect are not so great as in some of the other experiments which we shall discuss.

5. TRANSPORT PROPERTIES

The other experiments which have been used to obtain precise information on the FS of pure metals all involve transport currents in the metal, and we must therefore consider the response of the electron system to external fields. To do this, we will make use of the Chambers path integral method, which gives an integral solution of the Boltzmann equation, provided that a relaxation time describes the scattering of the electrons adequately. This method is particularly useful for considering transport properties in a magnetic field, or when boundary scattering is important.

We wish to determine the distribution function $f(\vec{k}, \vec{r}, t)$, defined so that $f(\vec{k}, \vec{r}, t)d\vec{k} d\vec{r}$ is the probability that an electron has a wavevector in $d\vec{k}$ and is in the volume $d\vec{r}$ at time t. The path integral method is based on the fact that all electrons with a particular \vec{k} and ϵ at a certain position \vec{r} at time t must have followed the same path since their last collision. We can therefore determine $f(\vec{k}, \vec{r}, t)$ by integrating along the path, as in Fig.10. If the energy acquired from the field between $\vec{r'}$ and \vec{r} is $\Delta \epsilon$, we have

$$(\vec{k}, \vec{r}, t) = \int_{-\infty}^{t} \frac{dt!}{\tau} \times f_0(\epsilon - \Delta \epsilon) \times e^{-(t-t')/\tau}$$
(32)
probability probability probability of

of scattering in dt'

of having

correct energy

f

probability of surviving to r without scattering

FIG. 10. Illustrating the path integral method.



We now expand

 $\mathbf{f}_0(\boldsymbol{\epsilon} - \Delta \boldsymbol{\epsilon}) = \mathbf{f}_0(\boldsymbol{\epsilon}) - \Delta \boldsymbol{\epsilon} \frac{\partial \mathbf{f}_0}{\partial \boldsymbol{\epsilon}}$

so that

$$\delta f(\vec{k}, \vec{r}, t) = f(\vec{k}, \vec{r}, t) - f_0(\vec{k}, \vec{r}, t)$$
$$= -\frac{\partial f_0}{\partial \epsilon} \int_{-\infty}^{t} \Delta \epsilon e^{-(t-t')/\tau} \frac{dt'}{\tau}$$

Integrating by parts

$$\delta f = \frac{\partial f_0}{\partial \epsilon} \int_{-\infty}^{t} \frac{d(\Delta \epsilon)}{dt} e^{-(t-t')/\tau} dt'$$

$$\Delta \epsilon = \int_{t'}^{t} \vec{F}(\vec{r'}, t') \cdot \vec{v}(\vec{r'}, t') dt'$$

so that

$$\frac{\mathrm{d}(\Delta\epsilon)}{\mathrm{dt}} = -\vec{\mathrm{F}}\cdot\vec{\mathrm{v}}$$

Hence, we have

$$\delta f(\vec{k}, \vec{r}, t) = -\frac{\partial f_0}{\partial \epsilon} \int_{-\infty}^{t} \vec{F}(\vec{r'}, t') \cdot \vec{v}(\vec{r'}, t') e^{-(t-t')/\tau} dt'$$
(33)

where the integral is taken over the path of the electron. If the relaxation time depends on \vec{k} , $e^{-(t-t')/\tau}$ must be replaced by $exp\left(-\int_{t'} \frac{ds}{\tau(\vec{k})}\right)$.

6. GALVANOMAGNETIC EFFECTS

We shall now use Eq.(33) to calculate the current density in the metal in a d.c. electric field \vec{E} . From Eq.(14) we have

$$\vec{J}(\vec{r},t) = \frac{e}{4\pi^3} \int \vec{v} \,\delta f(\vec{k},\vec{r},t) \,d\vec{k}$$
(34)

The force on an electron in an electric field is \vec{eE} , so that from Eqs (33) and (34)

$$\vec{J}(\vec{r},0) = \frac{e}{4\pi^3} \int \vec{v} \left(-\frac{\partial f_0}{\partial \epsilon}\right) d\vec{k} \int_{-\infty}^{0} e\vec{E} \cdot \vec{v} \exp\left(-\int_{t}^{0} \frac{ds}{\tau}\right) dt$$
(35)

and the conductivity tensor, defined by

$$J_i = \sigma_{ij} E_j \tag{36}$$

is given by

$$\sigma_{ij} = \frac{e^2}{4\pi^3} \int v_i \left(-\frac{\partial f_0}{\partial \epsilon}\right) d\vec{k} \int_{-\infty}^{0} v_j \exp\left(-\int_{t}^{0} \frac{ds}{\tau}\right) dt$$
(37)

In the absence of a magnetic field, \vec{v} and τ are, to first order, constant along the path. We can write the integral over \vec{k} in the form

$$d\vec{k} = \frac{dS \, d\epsilon}{|\nabla_{\vec{k}} \, \epsilon|} = \frac{dS \, d\epsilon}{\hbar v}$$

where dS is an element of constant energy surface, as in Fig.11. Using the δ -function character of $\partial f_0/\partial \varepsilon$

$$\int \mathbf{g}(\boldsymbol{\epsilon}) \left(-\frac{\partial f_0}{\partial \boldsymbol{\epsilon}}\right) d\boldsymbol{\epsilon} = \mathbf{g}(\boldsymbol{\mu}) \tag{38}$$

we find for the d.c. conductivity tensor

$$\sigma_{ij} = \frac{e^2}{4\pi^3\hbar} \int_{\mu} \tau v_j dS_i$$
(39)

where the integral is taken over the FS.

The magnetic field dependence of the conductivity is determined by the variation of the path integral

$$\Delta = \int_{-\infty}^{0} \mathbf{v}_{j} (\mathbf{t}) e^{+\mathbf{t} \tau^{-1}} d\mathbf{t}$$
(40)

as the electron orbits are modified by the field. We will consider the high field limit, such that $\omega_c \tau \gg 1$ for all closed orbits. In the case where only closed orbits are present, v_j (t) is periodic and we may write it as a Fourier expansion

$$\mathbf{v}_{j}(t) = \sum_{n} \mathbf{s}_{n} \sin n \omega_{c} t + \sum_{n} \mathbf{c}_{n} \cos n \omega_{c} t$$
(41)

Substituting in (40) and integrating, we find

$$\Delta = \sum_{n} \frac{n s_{n} \omega_{c} \tau^{2}}{1 + n^{2} \omega_{c}^{2} \tau^{2}} + \sum_{n} \frac{c_{n} \tau}{1 + n^{2} \omega_{c}^{2} \tau^{2}}$$
(42)

If \vec{B} is in the z direction

$$\overline{v}_x = \overline{v}_y = 0, \quad \overline{v}_z \neq 0$$
 (43)



FIG. 11. Volume integration in \vec{k} space.

Since we are interested in the high-field limit of the conductivity tensor, we retain only leading terms in 1/B. Remembering that ω_c is proportional to B, and using the Onsager reciprocal relation

$$\sigma_{ii} (\vec{B}) = \sigma_{ii} (-\vec{B})$$
(44)

we find

$$\lim_{B \to \infty} \sigma_{ij} = \begin{vmatrix} \frac{\alpha}{B^2 \tau} & \frac{\beta}{B} + \frac{\gamma}{B^2 \tau} & \frac{\delta}{B} \\ -\frac{\beta}{B} + \frac{\gamma}{B^2 \tau} & \frac{\epsilon}{B^2 \tau} & \frac{\phi}{B} \\ -\frac{\delta}{B} & -\frac{\phi}{B} & \theta\tau \end{vmatrix}$$
(45)

The only multiplying factor whose value we need to know explicitly is β , which is shown in PTS, p.258 to be given by

$$\beta = ec(n_e - n_h)$$

where n_e and n_h are the number of states enclosed by electron and hole Fermi surfaces, respectively.

If there are open orbits running in the k_x direction, both \overline{v}_y and \overline{v}_z may be non-zero. In this case

	$\frac{\alpha}{\mathrm{B}^{2}\tau}$	$\frac{\beta}{B}$	$\frac{\delta}{B}$	
$\lim_{B\to\infty} \sigma_{ij} =$	$-\frac{\beta}{B}$	μau	u au	(46)
	$-\frac{\delta}{B}$	ντ	heta au	

If there are two sets of open orbits running in different directions, all components of σ have a constant high-field limit.

Experimental studies of galvanomagnetic effects involve the measurement not of the conductivity tensor but of the resistivity tensor. A current is passed through a sample, and the components of the resistivity tensor are measured as a function of a transverse or longitudinal magnetic field, as shown schematically in Fig. 12. Very pure samples and low tempera-



FIG. 12. Measurement of galvanomagnetic effects.

tures are required, so that the high-field limit may be attained. Specifically we normally measure

- ρ_{xx} the transverse magnetoresistance
- ρ_{xy} the Hall voltage (~B) or transverse even voltage (~B²)
- ρ_{zz} the longitudinal magnetoresistance

The resistivity tensor is obtained by inverting σ_{ij} , giving

$$\rho_{ii} = \frac{\sigma_{jj} \sigma_{kk} - \sigma_{jk} \sigma_{kj}}{|\sigma|}, \qquad \rho_{ij} = \frac{\sigma_{kk} \sigma_{ij} - \sigma_{ik} \sigma_{kj}}{|\sigma|}$$
(47)

where

$$|\sigma| = \sigma_{ii} \sigma_{jj} \sigma_{kk} + \sigma_{ii} \sigma_{jk}^2 + \sigma_{jj} \sigma_{ik}^2 + \sigma_{kk} \sigma_{ij}^2$$
(48)

The high field behaviour depends on the FS topology and the number of electron and hole carriers. If there are an even number of conduction electrons per unit cell and all sheets of the FS are closed, the fact that each band contains two electrons per unit cell requires that $n_e = n_h$ and the metal is said to be compensated. On the other hand, if the number of conduction electrons per unit cell is odd, or if the field direction is such that open orbits exist, the metal is uncompensated. In general, a FS sheet has electron/hole character if every orbit is an electron/hole orbit when \vec{B} is applied in a non-symmetry direction giving no open orbits.

We may distinguish the following cases:

(a) Closed orbits, $n_e \neq n_h$. In the high-field limit ρ_{xx} is proportional to $1/\tau$, so that the transverse magnetoresistance saturates and the magnetoresistance ratio

$$R = \frac{\rho_{XX}(\infty)}{\rho_{XX}(0)}$$

is almost independent of τ , having a value of typically around 10. The Hall field is given by

$$\rho_{xy} = \frac{B}{ec(n_e - n_h)}$$
(49)

which is independent of the direction of \vec{B} relative to the crystal axes. The longitudinal magnetoresistance saturates, as it does in all cases.

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(b) Closed orbits, $n_e = n_h$. For a compensated metal ρ_{xx} varies as $B^2 \tau$, so that R is proportional to $B^2 \tau^2$. For a pure metal in high fields, R can be as high as $10^4 - 10^5$. There is no Hall field, but $\rho_{xy} \sim B^2 \tau$ and there is a transverse even voltage.

(c) Open orbits running along k_x . In this case $\rho_{xx} \sim B^2 \tau$ while $\rho_{yy} \sim 1/\tau$. If the current flows in the xy plane making an angle ϕ with the y axis, the resistance has the form

$$\rho(\phi) = \rho_{vv} \sin^2 \phi + \rho_{vv} \cos^2 \phi \tag{50}$$

By studying the transverse magnetoresistance as a function of current and field direction, the presence of open orbits can be detected and their direction in \vec{k} space determined. This allows the FS topology to be studied in detail and may also give FS dimensions. For instance, the magnetoresistance data of Fig. 7 gives the radius of the necks in Au. There is also in this case an anisotropic Hall field and a transverse even voltage proportional to $B^2 \sin \phi \cos \phi$.

(d) Open orbits in two directions. In this case, all components of the resistivity tensor approach constant values in high fields.

7. ELECTROMAGNETIC ABSORPTION

We now consider the transport of electrons in electric fields which vary in space and time, which may be studied experimentally by measuring the microwave absorption of a crystal, using the type of apparatus shown schematically in Fig.13. The absorption coefficient A, which is the ratio of the absorbed to incident power, may be measured by the increase in the sample temperature, the amplitude of the reflected signal, or the change in Q of the cavity.



If a microwave field varying as $exp(i\omega t)$ is applied to the metal surface, with the coordinate system of Fig. 14, Maxwell's equations give

$$\frac{\partial \mathbf{E}_{\mathbf{x}}}{\partial z} = \frac{\mathrm{i}\omega}{\mathrm{c}} \mathbf{H}_{\mathbf{y}}, \quad \frac{\partial \mathbf{H}_{\mathbf{y}}}{\partial z} = \frac{4\pi}{\mathrm{c}} \mathbf{J}_{\mathbf{x}}$$
(51)

where the displacement current has been neglected, since ω is much less than the plasma frequency.



FIG. 14. Specular reflection at the sample surface.

The surface impedance is defined by

$$Z = R + iX = \frac{4\pi}{c} \left(\frac{E_x}{H_y} \right)_0 = \frac{(E_x)_0}{\int_0^{\infty} J(z) dz}$$
(52)

and the absorption coefficient is

$$A = \frac{cR}{\pi}$$
(53)

If the local relation

$$\vec{J} = \sigma \vec{E}$$
 (54)

can be used, Eq. (51) may be written

$$\frac{\partial^2 \mathbf{E}_x}{\partial z^2} = \frac{4\pi i \omega}{c^2} \mathbf{J}_x = \frac{4\pi i \omega \sigma}{c^2} \mathbf{E}_x$$
(55)

which has the solution

$$E_{x} = (E_{x})_{0} e^{-\gamma z}, \quad \gamma = (1+i) \left(\frac{2\pi\omega\sigma}{c^{2}}\right)^{\frac{1}{2}}$$
(56)

The wave therefore decays exponentially with an extinction distance

$$\delta = \left(\frac{c^2}{2\pi\omega\sigma}\right)^{\frac{1}{2}}$$
(57)

This is the normal skin effect, which occurs under such conditions that the mean free path ℓ is much less than the skin depth δ , so that the local relation (54) may be used. At low temperatures in pure metals, at typical microwave frequencies of about 10^{10} c/s, δ is about 10^{-6} while ℓ may be as large as 10^{-2} cm, so this condition is not generally satisfied, and it is necessary to consider explicitly the Fourier components $\sigma(\vec{q}, \omega)$ of the conductivity, to calculate the surface impedance under anomalous skin effect conditions.

Accordingly, we Fourier transform the field, writing

$$E(z) = \int_{-\infty}^{\infty} E(q) e^{-iqz} dq, \quad E(q) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(z) e^{iqz} dz$$
 (58)

From Eq. (55) therefore

$$q^{2}E(q) + \frac{4\pi i\omega}{c^{2}} J^{t}(q) = 0$$
 (59)

where $J^{t}(q)$ is the Fourier component of the total current. The solution of this problem for general boundary conditions is complicated, but if we make the simplifying assumption of specular reflection at the surface as in Fig. 14, the boundary condition can be replaced by considering an infinite sample and putting E(z) = E(-z). Such a field distribution requires a current sheet I at z = 0 with Fourier components $I/2\pi$. Equations (59) can then be written

$$q^{2}E(q) + \frac{4\pi i\omega}{c^{2}} \left(\frac{I}{2\pi} + \sigma(q) E(q) \right) = 0$$
(60)

so that

$$E(q) = \frac{-2i\omega I}{c^2 q^2 + 4\pi i \omega \sigma(q)}$$
$$E(z) = -4Ii\omega \int_{0}^{\infty} \frac{\cos qz}{c^2 q^2 + 4\pi i \omega \sigma(q)} dq$$
(61)

Since the fields and therefore the total current are confined to the $\dot{}$ skin layer

$$\int_{0}^{\infty} J(z) dz = -\frac{I}{2}$$
 (62)

so that

$$Z = \frac{8i\omega}{c^2} \int_0^{\infty} \frac{dq}{q^2 + \frac{4\pi i\omega}{c^2} \sigma(q)}$$
(63)

From Eqs (33) and (34)

$$\sigma_{ij}(\mathbf{q}) = \frac{\mathbf{e}^2}{4\pi^3} \int \mathbf{v}_i \left(-\frac{\partial f_0}{\partial \epsilon}\right) d\vec{k} \int_{-\infty}^{0} \mathbf{v}_j \, \mathbf{e}^{i(\omega \mathbf{t} - \vec{\mathbf{q}} \cdot \vec{\mathbf{r}})} \, \mathbf{e}^{\frac{\mathbf{t}}{\tau}} \, d\mathbf{t}$$
(64)

In the limit when $q\ell \gg 1$, it may be shown (Ref. [2], p.52) that

$$\sigma_{xx}(q) = \frac{e^2}{4\pi^2 \hbar q} \int_{\mu} \left[\rho_y \right] dk_y$$
(65)

where ρ_y is the radius of curvature of the FS in a section normal to k_y and the integral is restricted to the zone on which the electron velocity



FIG. 15. The effective zone on the Fermi surface for electromagnetic absorption.

is normal to \vec{q} , as in Fig.15. From expression (64), it is clear that these are the only electrons which contribute to the conductivity, since the path integral vanishes for the others when ℓ is large. $\sigma(q)$ is independent of ℓ in this limit. If we define

$$S^{3} = \frac{\omega e^{2}}{\pi \hbar c^{2}} \int_{\mu} \left| \rho_{y} \right| dk_{y}$$
(66)

we may write the surface impedance in the anomalous limit

$$Z_{\infty} = \frac{8i\omega}{c^2} \int_{0}^{\infty} \frac{dq}{q^2 + iS^3/q} = \frac{8\pi\omega}{3^{3/2}Sc^2} (1 + \sqrt{3}i)$$
(67)

For the more realistic condition of diffuse surface reflection, this expression is multiplied by a factor 9/8.

From a study of the anisotropy of the surface impedance, it is therefore possible to determine information about the curvature of the FS. This method is of great historical importance since Pippard used it for his pioneering work on Cu. The difficulties of interpretation for all but the most simple surfaces are so great, however, that it has now been rendered obsolete by more powerful techniques.

8. CYCLOTRON RESONANCE

If a steady magnetic field is applied parallel to the surface of the metal, as in Fig.16, the electrons spiral about the field direction and may make periodic excursions into the skin layer. If the field is such that

$$\omega = n\omega_c \tag{68}$$

for a particular electron, it will always experience the same field as it passes through the skin layer and hence absorb energy strongly from it. In one cyclotron period the exponential terms in the path integral in Eq. (64) change by

$$W \doteq \frac{2\pi}{\omega_{c}} \left(\frac{1}{\tau} + i\omega \right)$$
(69)

FIG. 16. Azbel-Kaner cyclotron resonance.

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so that the path integral may be written in the form

$$\Delta = \Delta_0 (1 + e^{-W} + e^{-2W} \dots) = \Delta_0 \left(1 - e^{\frac{2\pi}{\omega_c \tau} (1 + i\omega\tau)} \right)^{-1} = F\Delta_0$$
(70)

Provided the $\omega \tau > 1$, the factor F is oscillatory and gives rise to the resonance oscillations. As in the anomalous skin effect, the distortion of the FS is limited to an effective zone where the electron velocity is parallel to the surface, and detailed calculation shows that, in strong fields, the contribution from a section normal to \vec{B} is approximately

$$d\sigma_{xx}(q) = F(B) \frac{e^2 |\rho_y| dk_y}{2\pi^2 \hbar q}$$
(71)

which, apart from the factor F(B), is similar to the zero field result. If ω_c is constant over the FS, the surface impedance is

$$Z_{\infty}(B) = \alpha Z_{\infty}(0) F^{-\frac{1}{3}} (B)$$
(72)

where α varies slowly with B. Fig. 17 shows the theoretical value of dR/dB compared with experimental results on Cu.



FIG. 17. Experimental and theoretical cyclotron resonance signals, from Kip, A.F., Langenberg, D.N., Moore, T.W., Phys. Rev. 124 (1961) 359.

If ω_c varies over the FS, the extremal value will generally dominate the resonance. If the field is tilted slightly out of the plane of the surface, only those electrons for which the mean velocity in the direction of the field vanishes will return to the skin layer, and these will dominate the resonance. If the r.f. electric field is along the magnetic field

$$d\sigma_{yy}(q) \approx F(B) \frac{e^2 |\rho_x| dk_x}{2\pi^2 \hbar q}$$
(73)

and the limiting points L in Fig. 15 may dominate.

A careful study of cyclotron resonance for many different field orientations will therefore give information about the FS topology, from the angles over which the various orbits are observed to exist, and more importantly, allows the velocity at all points on the FS to be deduced. Fig. 18 shows some of the effective masses observed in the (110) plane of Cu, together with the orbits to which they correspond.

9. THE R.F. SIZE EFFECT

This technique, in common with the magneto-acoustic effect which will be discussed next, depends on the relation (18) between the orbit sizes in \vec{r} and \vec{k} space. From the dimensions in the crystal of the orbits of electrons on the FS, it is possible to infer the dimensions of the FS itself. In the RFSE the orbit dimensions are compared with the dimensions of a very thin crystal plate. Once again, the surface impedance of the sample is measured, but this time at relatively low frequencies, typically 1-5 Mc/s. The sample may be placed within the inductance of the tank circuit of an oscillator, as in Fig. 19, in which case the change of frequency with field is given by

$$\frac{\partial f}{\partial B} = -\gamma \frac{\partial x}{\partial B}$$
(74)

where γ is approximately constant. Alternatively, standard NMR techniques may be used to measure $\partial R/\partial B$.

At the frequencies used, the skin depth δ is about 10⁻³ cm, so that the fields are effectively confined to the surface of the samples, which are generally somewhat less than 1 mm in thickness. Since $\omega \ll \omega_c$, the fields experienced by the electrons are effectively static. If the metal is sufficiently pure that ℓ is comparable with the thickness d, there will be a field B₀, below which the dominant orbit just scatters from the bottom surface, as shown in Fig.20. This will cause a sudden change in the path integral in Eq.(64) and a consequent anomaly in $\partial Z/\partial B$, an example of which is shown in Fig.21. From Eq.(18) the extension of the orbit in \vec{k} space normal to \vec{B} and the metal surface is

$$\Delta \mathbf{k} = \frac{\mathbf{e}\mathbf{B}_0}{\mathbf{c}\hbar} \,\mathbf{d} \tag{75}$$

When ℓ is long, the electrons in a magnetic field can set up current and field sheets within the metal, so that an anomaly also occurs at nB₀, or when two orbits from different FS sheets have a total extension d, as shown in Fig.20. It is therefore possible to trace out the linear dimensions of the FS by using different crystal and field orientations, and the results are accurate to approximately the ratio δ/d , or typically about 1%. This method is probably second only to the HA effect for determining FS dimensions and, in addition, it can give valuable information on electronic mean free paths.



FIG. 18. a) Orbits in Cu giving rise to cyclotron resonance oscillations. b) Cyclotron resonance effective masses in the (110) plane of Cu, observed by Koch, J.F., Stradling, R.A., Kip, A.F., Phys. Rev. 133 A (1964) 240. The numbers correspond to the orbits in Fig. 18 (a).



b)



FIG. 21. R.F. size effect signals observed in K by Koch, J.F., Wagner, T.K., Phys. Rev. 151 (1966)467.



FIG. 22. Principle of magnetoacoustic measurements.

10. THE MAGNETOACOUSTIC EFFECT

This method also traces out the linear dimensions of the FS by measuring the sizes of the orbits in the crystal. The reference length in this case is not the dimension of the sample, but the wavelength of a high frequency acoustic wave propagating in it. A schematic diagram of the apparatus used for such measurements is shown in Fig.22. A short r.f. pulse is applied to a piezoelectric quartz plate and generates an ultrasonic pulse. Successive acoustic reflections from the end of FERMI SURFACE

the single-crystal sample are reconverted by the transducer into r.f. signals, which are displayed on an oscilloscope, or measured otherwise. The attenuation coefficient α is thereby determined as a function of the applied magnetic field.

We first consider the ultrasonic absorption by a free electron gas, in which are embedded N positive ions per unit volume. The energy flows from the acoustic wave, via the electric fields which it sets up, to the electrons, whence it returns to the lattice in a random form through collisions. The energy flow from the acoustic wave to the electrons is given by the Joule heating

$$Q = Re(\vec{J}_e^* \cdot \vec{E})$$
(76)

where \vec{J}_e is the electron current.

The ionic velocity is

$$\vec{u} = \vec{u}_0 e^{i(\omega t - \vec{q} \cdot \vec{y})}$$
(77)

and we consider only longitudinal waves, for which \vec{u} and \vec{q} are parallel. The attenuation coefficient is then

$$\alpha = \frac{2Q}{\rho u^2 s}$$
(78)

where ρ is the density and s the sound wave velocity. For frequencies well below the plasma frequency, the electronic and ionic currents cancel, so that

$$\vec{J}_e = Ne\vec{u}$$
 (79)

We now use the path integral method to calculate the electric field which self-consistently produces an electronic current which just balances the ionic current. As in Eq.(32), we therefore have

$$f(\vec{k}, \vec{r}, t) = \int_{-\infty}^{t} f_0(\vec{k'}, \vec{r'}, t') e^{-(t-t')/\tau} \frac{dt'}{\tau}$$
(80)

where $f_0\left(\vec{r}^{\prime}\right)$ is the Fermi distribution in the strained moving lattice, which is

$$f_0(\epsilon^{\prime}, \vec{r}^{\prime}) = \left[\exp\left(\frac{\epsilon^{\prime} - \mu^{\prime}}{kT}\right) + 1 \right]^{-1}$$
(81)

where

$$\mu' = \mu \left(1 + \frac{2}{3} \frac{\delta N}{N} \right) = \mu \left(1 + \frac{2}{3} \frac{\vec{u} \cdot \vec{q}}{\omega} \right)$$
(82)

and

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If we now expand to first order in \vec{u} and proceed as in the derivation of Eq.(35), we find

$$\vec{\mathbf{J}}_{e}(\vec{\mathbf{r}},t) = \frac{e}{4\pi^{3}} \int \vec{\mathbf{v}} \left(-\frac{\partial f_{0}}{\partial \epsilon}\right) d\vec{\mathbf{k}} \int \left[\left(e\vec{\mathbf{E}}' + \frac{m\vec{\mathbf{u}}'}{\tau}\right) \cdot \vec{\mathbf{v}}' + \frac{2}{3}\mu \frac{\vec{\mathbf{u}}' \cdot \vec{\mathbf{q}}}{\omega\tau} \right] e^{-\frac{(t-t')}{\tau}} dt'$$
(84)

For longitudinal waves propagating in the y direction, with a field B in the z direction, we may write this formally as

$$J_{x} = \sigma_{xx} E_{x} + \sigma_{xy} \left(E_{y} + \frac{mu_{y}}{e\tau} \left[1 + \frac{iav_{0}}{s} \right] \right) = 0$$

$$J_{y} = \sigma_{yx} E_{x} + \sigma_{yy} \left(E_{y} + \frac{mu_{y}}{e\tau} \left[1 + \frac{iav_{0}}{s} \right] \right) = Neu_{y}$$
(85)

where v_0 is the Fermi velocity and $a = q\ell/(1 + i\omega\tau)$. From Eqs (76), (78) and (85), we therefore have

$$\alpha = \frac{\mathrm{Nm}}{\rho_{\mathrm{ST}}} \left(\frac{\sigma \sigma_{\mathrm{XX}}}{\sigma_{\mathrm{XX}} \sigma_{\mathrm{yy}} - \sigma_{\mathrm{Xy}}^2} - 1 - \frac{(\mathrm{q}\ell)^2}{3} \right)$$
(86)

where the d.c. conductivity σ is given by

$$\sigma = \frac{\mathrm{Ne}^2 \tau}{\mathrm{m}}$$
(87)

and we have used the fact that $\omega \tau \ll 1$ at acoustic frequencies. In zero magnetic field \vec{v} and τ are constant along the path and

$$\sigma_{yy}(q) = \frac{3\sigma}{(q\ell)^3} (q\ell - \tan^{-1} q\ell), \quad \sigma_{xy} = 0$$
 (88)

so that

$$\alpha = \frac{\mathrm{Nm}}{\rho \, \mathrm{s}\tau} \left[\frac{(q\ell)^2 \, \tan^{-1} q\ell}{3(q\ell - \tan^{-1} q\ell)} - 1 \right] \tag{89}$$

In a magnetic field, \vec{v} varies along the path and the conductivity depends on B. We may write

$$\sigma_{ij} (q, B) = \sigma_{ij} (\beta)$$
(90)

where

$$\beta = \frac{2q\dot{v}_0}{\omega_c} = 2\pi \frac{D}{\lambda}$$
(91)

and D is the diameter of the largest orbit in the crystal in the field B. Integration of the sinusoidally varying forces around the circular electron orbits may cause the components of the conductivity tensor to oscillate



FIG.23. a) Theoretical magnetoacoustic oscillations for the free electron model, from Kjeldaas, T., Holstein, T., Phys. Rev. Lett. 2 (1959) 340. b) Magnetoacoustic oscillations in the noble metals, observed by Morse, R.W. and coworkers (see The Fermi Surface, John Wiley and Sons, New York (1960)).



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if $q\ell$ is sufficiently large, and these oscillations are reflected in the attenuation coefficient, as shown in Fig.23.

In a real metal, the attenuation coefficient may be written as an integral over the FS of the form

$$\alpha = (2\pi^{3} \hbar \rho \operatorname{su}^{2})^{-1} \int_{\mu} \frac{\mathrm{dS}}{\ell} \left| \int_{-\infty}^{0} \vec{F} \cdot \vec{v} \exp\left(-\int_{t}^{0} \frac{\mathrm{ds}}{\tau}\right) \mathrm{dt} \right|^{2}$$
(92)

where \vec{F} is an effective force on the electron which, as in Eq.(84), represents the effect of electric fields and the lattice strain and motion. This force has the spatial periodicity of the acoustic wave and, again, the variation of the path integral with \vec{B} results in magnetoacoustic oscillations. For an orbit of the type shown in Fig.24, for instance, the path integral will clearly be maximum when

$$(n + \frac{1}{2})\lambda = D = \frac{\hbar c}{eB}\Delta k$$
 (93)

where Δk is the extension of the \vec{k} space orbit normal to \vec{B} and \vec{q} . For more complicated orbits this relation will not be so simple, and the factor $\frac{1}{2}$ in Eq.(93) will be replaced by another value, but in general a set or sets of oscillations in the absorption will be observed, with a period in 1/B given by

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{c \hbar q \,\Delta k} \tag{94}$$

where Δk is the extension in \vec{k} space normal to \vec{B} and \vec{q} of the dominant orbit or orbits. The linear dimensions of the FS can then be deduced from measurements with a variety of crystal orientations and field directions, just as in the R.F. Size Effect. The Magnetoacoustic Effect is somewhat less satisfactory however, because the oscillations from different sheets of the FS may be difficult to disentangle, and it is not always quite sure which orbit is dominant in a particular set of oscillations.

11. POSITRON ANNIHILATION

The experiments which have been discussed so far all require long electronic mean free paths and are therefore restricted to very pure metals or ordered alloys at low temperatures. We shall now discuss two techniques which, though substantially less powerful than those previously mentioned, do not suffer from this limitation and may therefore be applied to metals at elevated temperatures, or alloys. In a disordered alloy, Bloch's theorem is no longer strictly valid, and the scattering of the conduction electrons by the disordered potential produces a reduction in the free path which is reflected in a smearing out of the FS by, typically, a few percent of k_F . Within this limitation, however, the FS of an alloy is a valid concept. The electronic structure of disordered alloys is a topic of great current interest.





The first method which we shall discuss for studying such systems uses the momentum distribution of the photons emitted when electrons and positrons annihilate, to study the momentum distribution of the electrons. The type of apparatus most commonly used is shown schematically in Fig. 25. Positrons from a radioactive source are absorbed by the monocrystalline sample and thermalize in about 10^{-12} s, so that they have essentially zero momentum when they annihilate after about 10^{-10} s. Because of the momentum of the annihilating electron, there is a small angle θ between the photon paths, and the experiment consists of measuring the number of photon coincidences as a function of θ . A typical photon distribution is shown in Fig. 26.

With the long slit geometry of Fig. 27, a coincident pair of photons can only enter the counters if they have a total momentum $\hbar \vec{p}$ such that

$$\theta = \frac{\hbar p_z}{mc}$$
(95)

If we neglect the Coulomb correlation between the electrons and positrons, the number of coincidences at an angle θ is proportional to

$$N(\theta) = N\left(\frac{\hbar p_z}{mc}\right) = \iint_{-\infty}^{\infty} dp_x dp_y \sum_{\vec{k}} \Gamma(\vec{p}, \vec{k})$$
(96)

where the sum is over all occupied electron states, and the probability of producing a photon pair of momentum \vec{p} by the annihilation of a positron with an electron of wavevector \vec{k} is proportional to

$$\Gamma(\vec{p},\vec{k}) = \left| \int \psi_{\vec{k}}(\vec{r}) \psi_{+}(\vec{r}) e^{-i\vec{p}\cdot\vec{r}} d\vec{r} \right|^{2}$$
(97)

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FIG. 26. Experimental and theoretical angular distribution of photons from positron annihilation in a c-axis Y crystal, from Williams, R. W., Loucks, T. L., Mackintosh, A. R., Phys. Rev. Lett. <u>16</u> (1966) 168.



For the free electron model, the positron wavefunction is constant and the electron wavefunction is a plane wave, so

$$\Gamma(\vec{p}, \vec{k}) = \delta(\vec{p} - \vec{k})$$
(98)

and the photons carry off the electron momentum, as expected. The integral (96) is now just the area of a slice through the spherical FS at

a distance k_z = $\theta mc/\hbar$ from the origin, as in Fig.27, so that the photon distribution has the form

where

$$N(\theta) \sim \left(1 - \left(\theta/\theta_{\rm F}\right)^2\right) \tag{99}$$

$$\theta_{\rm F} = \frac{\hbar k_{\rm F}}{\rm mc} \tag{100}$$

For Bloch electrons, we have

$$\Gamma(\vec{p},\vec{k}) = \left| \int \psi_{+}(\vec{r}) u_{\vec{k}}(\vec{r}) e^{i(\vec{k}-\vec{p})\cdot\vec{r}} d\vec{r} \right|^{2} = \sum_{\vec{g}} c_{\vec{g}}\delta(\vec{p}-\vec{k}-\vec{g})$$
(101)

so that the photons have momentum $\hbar(\vec{k} + \vec{g})$, where \vec{g} is any reciprocal lattice vector. The components with $\vec{g} \neq 0$ in (101) are generally small, because the nuclear repulsion keeps the positron out of the ion cores, where most of the oscillations in $u_{\vec{k}}(\vec{r})$ occur.

In a real metal, there will be discontinuities in the slope of $N(\theta)$ at those angles at which Eq. (100) is satisfied for any k_F in the periodic zone scheme. These will generally be too small to detect however, and it is usually necessary to compare the measured distribution with that calculated using Eqs (96) and (97), and thereby to determine whether the calculated electronic structure is correct. Such a comparison is made for Y in Fig.26, from which it may be seen that the theory reproduces the qualitative features of the experimental results, but that some of the predicted structure in the distribution is smeared out, probably due to correlation effects not taken into account in the independent particle model.

It is possible to increase the amount of information derived from this experiment by using another pair of slits at right angles to the first, and thus to accept photons emanating from annihilations with electrons in a line, rather than a slice, through \vec{k} space. This causes a severe decrease in the coincidence counting rate, but the method has been successfully applied to the determination of the neck radius in concentrated disordered alloys of Cu.

12. THE KOHN EFFECT

The phonon spectrum of a metal can readily be measured by inelastic neutron scattering, as has been extensively discussed in other courses, and it contains implicitly a great deal of information about the conduction electrons. We shall here be concerned only with the anomalies which may occur due to the discontinuities in the occupation of the electron states in \vec{k} space, and which therefore provide an image of the FS, as first pointed out by Kohn.

In the adiabatic approximation, the frequencies $\omega(\vec{q})$ and displacements $\vec{u}(\vec{q})$ of the lattice waves in a metal of ionic mass M are determined by the equations

$$M\omega^{2}(\vec{q}) u_{i}(\vec{q}) = \sum_{j} M_{ij}(\vec{q}) u_{j}(\vec{q})$$
(102)

where $M_{ij}(\vec{q})$ is the dynamical matrix, defined by

$$M_{ij}(\vec{q}) = \frac{1}{\Omega_c} \sum_{\vec{g}} \left[(\vec{q} + \vec{g})_i (\vec{q} + \vec{g})_j \phi(\vec{q} + \vec{g}) - \vec{g}_i \vec{g}_j \phi(\vec{q}) \right]$$
(103)

 Ω_c is the volume of the unit cell and $\sigma(\vec{q})$ is the Fourier transform of the interionic potential. This potential is screened by the conduction electrons, and the screening is expressed in terms of a \vec{q} dependent dielectric function $\kappa(\vec{q})$. The anomalies in the dielectric function are therefore reflected in the phonon spectrum.

For a free electron gas, as shown in PTS, p. 126,

$$\kappa(\vec{q}) = 1 + \frac{4\pi e^2}{q^2} \sum_{\vec{k}} \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon(\vec{k} + \vec{q}) - \epsilon(\vec{k})}$$

$$= 1 + \frac{4\pi e^2}{q^2} N(\mu) \left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \log \left|\frac{2k_F + q}{2k_F - q}\right|\right)$$
(104)

where $N(\mu)$ is the density of electron states at the Fermi level. The Fermi distribution functions in the numerator ensure that, at absolute zero, only states for which \vec{k} is occupied and $\vec{k} + \vec{q}$ unoccupied, or viceversa, contribute to the sum. The strongest contribution to the sum is made by terms with small energy denominators, which come from states \vec{k} lying just inside the FS, such that the addition of \vec{q} takes them just outside. The rapid disappearance of such states as q approaches $2k_F$ produces a rapid drop in $\kappa(\vec{q})$ at this value, and this means that the screening of the interionic potential drops, so that, from Eq.(103), the frequencies suddenly increase.

For a real metal, the dielectric function may be written in the form

$$\kappa(\vec{q}) = 1 + \frac{4\pi e^2}{q^2} \sum_{j, j', \vec{k}} \frac{F_{jj'}(\vec{k}, \vec{k} + \vec{q}) [f_0(\epsilon_j(\vec{k})) - f_0(\epsilon_{j'}(\vec{k} + \vec{q}))]}{\epsilon_{j'}(\vec{k} + \vec{q}) - \epsilon_{j}(\vec{k})}$$
(105)

where j and j' are band indices, $F_{jj'}$ is a slowly varying function which depends on the electron wavefunctions, and the electron states are described in the periodic zone scheme. The weak singularities in the free electron dielectric function may be considerably enhanced in some circumstances, especially when the FS has large flat regions, as often occurs in transition metals, for instance that shown in Fig. 28, and many small energy denominators therefore occur for some critical \vec{q} .

The anomalies in $\kappa(\vec{q})$ can be translated into anomalies in the phonon spectrum by using Eqs (102) and (103) and remembering that $\phi(\vec{q} + \vec{g})$ is screened by $\kappa(\vec{q} + \vec{g})$. If a sharp decrease in $\kappa(\vec{q})$ occurs in the primitive BZ, an increase in the interionic force results, and the frequencies abruptly increase. If the anomaly in $\kappa(\vec{q})$ occurs outside the primitive BZ, the simplest method of determining the effect on the frequencies is to use the periodic zone scheme for the phonons, which is equivalent to considering the different terms in Eq. (103).



FIG. 28. - Cross section of the Fermi surface in paramagnetic Cr, in the periodic zone scheme.



FIG. 29. Kohn anomaly in lead, observed by Brockhouse, B.N., Arase, T., Caglioti, G., Rao, K.R., Woods, A.D.B., Phys. Rev. 128 (1962) 1099.

An example of an experimentally observed Kohn anomaly in a phonon dispersion curve is shown in Fig.29. As a method of tracing out the FS of a pure metal, the Kohn effect suffers from the limitation that the anomalies tend to be rather broad and the derived dimensions there-
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fore imprecise. Furthermore, clear anomalies are rather rare, so only a few FS dimensions may be determined. However, the anomalies may be as well defined in disordered alloys as in pure metals, so that the effect of solute concentration on some FS dimension may be studied systematically. The Kohn effect may also be observed in magnon spectra, since the Fourier transform of the exchange interaction between magnetic ions has a form very similar to Eq. (105).

This completes our brief survey of the main methods of FS determination. The De Haas - Van Alphen effect remains supreme in this field, although the other techniques may give valuable supplementary information. The information which each experiment provides is summarized pictorially in Fig. 30.



FIG. 30. Methods of Fermi surface determination.

13. ELECTRON INTERACTIONS

The discussion so far has proceeded entirely within the framework of the independent particle model, and it is now appropriate to discuss briefly the extent to which the results which we have derived remain valid when electron interactions are taken into account. Many body effects in metals have been treated in detail elsewhere in the School, and we shall merely review those aspects which are relevant to FS studies.

In the Landau Fermi liquid theory, the interactions are taken into account by writing the excitation energy of the electron system as

$$\delta \mathbf{E} = \sum_{\vec{k}} \epsilon_0(\vec{k}) \, \delta n_{\vec{k}} + \frac{1}{2} \sum_{\vec{k}, \vec{k}'} f(\vec{k}, \vec{k}') \, \delta n_{\vec{k}} \delta n_{\vec{k}'}. \tag{106}$$

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where $\delta n_{\vec{k}}$ is the number of excited quasielectrons in state \vec{k} , in which the spin is implicitly included, and $f(\vec{k}, \vec{k}')$ is a quasiparticle interaction energy. The interactions among the electrons and phonons therefore have two effects. Firstly they modify the single quasiparticle energy $\epsilon_0(\vec{k})$, so that it is different from the $\epsilon(\vec{k})$ which would be given by an accurate band calculation based on the independent particle model, and secondly they cause an interaction between quasiparticles. The quasiparticle energy in the presence of other excited quasiparticles is given from Eq. (106) as

$$\widetilde{\epsilon}(\vec{k}) = \epsilon_0(\vec{k}) + \sum_{\vec{k}'} f(\vec{k}, \vec{k}') \delta n_{\vec{k}'}$$
(107)

and the equilibrium distribution function is

$$n_{\vec{k}} = (e^{(\tilde{\epsilon}(\vec{k}) - \mu)/kT} + 1)^{-1}$$
 (108)

The FS at absolute zero is that surface in \vec{k} space on which $\epsilon_0(\vec{k}) = \mu$, and the volume which it encloses is independent of the interactions, although they may affect its shape. Because of the electron-electron interactions an excited quasiparticle has a finite lifetime, which is inversely proportional to $(\tilde{\epsilon}(\vec{k}) - \mu)^2 + (\pi kT)^2$, and a state with a single quasiparticle is therefore only an eigenstate of the system as the quasiparticle energy approaches μ at T = 0.

A transport equation, analogous to the Boltzmann equation, can be written for the quasiparticle distribution $n_{\vec{k}}$, and from this it may be deduced that transport properties which are independent of time are unaffected by the quasiparticle interactions. The galvanomagnetic effects are therefore still determined by the FS topology, and the magnetoacoustic and R.F. size effects, for which the fields are effectively static, measure the caliper dimension of the FS. Time dependent properties generally depend on $f(\vec{k}, \vec{k}')$, but not the surface impedance in the anomalous limit, so that the anomalous skin effect still measures the FS curvature, and Azbel-Kaner cyclotron resonance the effective mass.

Although Bloch states are not eigenstates of the system, the ground state wave function can be expended in terms of them and an occupation number for the Bloch states thereby defined. This occupation probability does not fall from one to zero at the FS, as it would in the non-interacting system, but it does have a discontinuity when $\vec{k} = \vec{k}_F$, and this is sufficient to ensure that the Kohn effect still measures the FS extension. The photon distribution from positron annihilation still has a kink at an angle determined by Eq. (100), although the general form of the distribution may be considerably affected by the interactions. Most importantly, these discontinuities also determine the oscillations in the magnetic susceptibility, so that the HA effect measures the extremal area of the FS, and its temperature dependence, the effective mass.

It is therefore fortunately true that all of the experiments which we have discussed are essentially unaffected by the quasiparticle interaction $f(\vec{k}, \vec{k}')$, and measure the FS and the effective mass in the interacting system. This is true both for electron-electron and for electron-phonon interactions. This is not to say that the FS itself is unaffected by the

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interactions, of course. $\epsilon_0(\vec{k})$ will generally differ from $\epsilon(\vec{k})$, so that the FS geometry and the Fermi velocity may differ from that predicted by the independent particle model. The change in the FS itself appears to be generally small, but the effective mass may be considerably altered, especially by the electron-phonon interaction, and we will discuss this with reference to the electronic heat capacity. This is given in the independent particle model by

$$C_{v} = \frac{\pi^{2}}{3} k^{2} N(\mu) T$$
 (109)

From Eq. (14) the density of states is given by

$$N(\mu) = \frac{\Omega}{4\pi^3} \int_{\mu} \frac{dS}{|\partial \epsilon / \partial \vec{k}|} = \frac{\Omega S}{4\pi^3 \hbar} \left(\frac{1}{v_0} \right)$$
(110)

where the average is taken over the FS.

Eq.(109) remains valid in the interacting system, but $N(\mu)$ must be that deduced from $\epsilon_0(\vec{k})$. The effect of the electron-phonon interaction on $\epsilon_0(\vec{k})$ may be expressed by a relation of the form

$$\epsilon_{0}(\vec{k}) = \epsilon_{e}(k) + \frac{1}{2\pi^{3}} \int d\vec{q} \left| M_{\vec{k},\vec{k}-\vec{q}} \right|^{2} \left[\frac{1 - n\vec{k} - \vec{q}}{\epsilon_{e}(\vec{k}) - \epsilon_{e}(\vec{k}-\vec{q}) - \hbar\omega_{\vec{q}}} + \frac{n\vec{k} - \vec{q}}{\epsilon_{e}(\vec{k}) - \epsilon_{e}(\vec{k}-\vec{q}) + \hbar\omega_{\vec{q}}} \right]$$
(111)

where $\epsilon_{e}(\vec{k})$ is the quasiparticle energy without the electron-phonon interaction, and $M_{\vec{k},\vec{k}'\cdot\vec{q}}$ is the matrix element for scattering by a phonon of energy $\hbar\omega_{\vec{d}}$ from \vec{k} to $\vec{k} \cdot \vec{q}$.



FIG. 31. The effect of the electron-phonon interaction on the energy bands near the Fermi level.

The phonon correction is only large at low temperatures for energies differing from μ by an amount less than about the maximum $\hbar\omega$. The band structure near μ in the interacting system therefore looks as shown in Fig.31, and the effective mass may be considerably enhanced. For instance, in Pb the electron-phonon interaction is believed to cause about a twofold enhancement in the density of states, whereas the electron-electron interaction produces only a 10% increase. As the temperature is increased above the Debye temperature, the two terms in the integral in Eq.(111) tend to cancel and the phonon enhancement disappears.

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An important property which is affected by the quasiparticle interaction is the Pauli paramagnetism of the conduction electrons. In the independent particle model

$$\chi = \mu_{\rm B}^2 \,\mathrm{N}(\mu) \tag{112}$$

Because of the spin dependence of the quasiparticle interaction, this value is enhanced to

$$\chi_{0} = \frac{\mu_{\rm B}^2 \, {\rm N}(\mu)}{1 - \nu} \tag{113}$$

where, writing the spin dependence of f explicitly

$$\nu = \frac{2}{(2\pi)^6 \operatorname{N}(\mu) \operatorname{M}^2} \int_{\mu} [f(\vec{k}\uparrow, \vec{k}\downarrow) - f(\vec{k}\uparrow, \vec{k}\downarrow\uparrow)] \frac{\mathrm{d}S_{\vec{k}}}{v_{\vec{k}}} \frac{\mathrm{d}S_{\vec{k}\downarrow}}{v_{\vec{k}\downarrow}}$$
(114)

Because of the exchange correlation, ν is always positive, and for Na the enhancement of the paramagnetism is about 30%. For transition metals the exchange correlation is large and $v_{\vec{k}}$ small, so that ν is generally large. If it exceeds 1, ferromagnetism results, as in Fe, Co and Ni.

Such a magnetic instability need not occur for a uniform magnetization. The response of the system to a sinusoidally varying static magnetic field of wavevector \vec{q} may be written in terms of a \vec{q} -dependent susceptibility, which is given in the Hartree approximation by

$$\chi_{\rm H}(\vec{q}) = \mu_{\rm B}^2 \chi_0(\vec{q})$$

= $\mu_{\rm B}^2 \sum_{j,j',\vec{k}} \frac{I_{jj'}(\vec{k},\vec{k}+\vec{q})[f_0(\epsilon_j(\vec{k})) - f_0(\epsilon_j'(\vec{k}+\vec{q}))]}{\epsilon_j'(\vec{k}+\vec{q}) - \epsilon_j(\vec{k})}$ (115)

where $I_{jj^\prime}\,$ is determined by the wavefunctions. This is again enhanced by the electron interactions and, in the self-consistent field approximation, the susceptibility in the interacting system has the form

$$\chi(\vec{q}) = \frac{\mu_{B}^{2} \chi_{0}(\vec{q})}{1 - V(\vec{q}) \chi_{0}(\vec{q})}$$
(116)

where $V(\vec{q})$ is the Fourier transform of the exchange interaction between the conduction electrons. If $\chi(\vec{q})$ diverges for some non-zero \vec{q} , a spindensity wave will be formed in the conduction electron gas. Because of the form of Eq. (115), which is similar to Eq. (106), this is likely to happen at some \vec{q} which spans a dimension of the FS. In Cr, for instance, the \vec{q} of the spin density wave is believed to be determined by the separation between the parallel electron and hole sheets of the FS, shown in Fig.28.

14. THE FERMI SURFACE IN METALS

The experimental techniques which we have reviewed, together with band structure calculation's, which have been discussed elsewhere, have revealed an enormous amount of information about the FS in metals. A fairly comprehensive list of references to this work has been assembled (Ref. [14]) and should be referred to for detailed information. In this section we will present a brief summary of the salient features of the band structures of the different classes of metals, which have resulted from these investigations.

(a) <u>Simple metals</u>. The conduction electron states are derived from atomic s and p states and, because of the cancellation between the core potential and the kinetic energy associated with the oscillations of the conduction electron wavefunctions in the core, the energy levels are very close to the free electron, or empty lattice, values

$$\epsilon_{\vec{g}}(\vec{k}) = \frac{\hbar^2}{2m} |\vec{k} + \vec{g}|^2 \qquad (117)$$

The empty lattice energy bands for the fcc structure are shown in Fig.32, together with the calculated energy bands for Al and Pb. The spin-orbit splitting is significant for the latter. The empty lattice FS may readily be constructed by noting that a state \vec{k} is filled in the nth band if it lies less than the free electron k_F from at least n reciprocal lattice points.

The band structure and FS of a simple metal can generally be described quite well in terms of a few Fourier coefficients $v_{\vec{g}}$ of a weak local pseudopotential, although for the highest accuracy a non-local pseudopotential may be necessary, and spin-orbit coupling must be included, especially for heavier metals.

The remarkable sphericity of the K FS is illustrated in Fig.33, while the close resemblance between the FS of Pb and the empty lattice model is shown in Fig.34.

(b) <u>Semi-metals</u>. These metals (As, Sb, Bi) are really a subgroup of the simple metals, since their energy bands are close to the free electron bands. However, they have an unusual structure and a very small number of carriers. They each have three electron pockets and a compensating number of holes. The form of the hole surfaces is very dependent on the spin-orbit coupling, and different in the three metals.

(c) <u>Transition metals</u>. The atomic d-levels contribute to the conduction bands, which bear no resemblance to the empty lattice model. A typical transition metal band structure, with d-bands intersecting and hybridizing with the parabolic s-p bands, is shown in Fig. 2. This interaction with the d-bands is the reason for the necks in the [111] directions of the noble metals.

Although the pseudopotential method is of no use for describing transition metal band structures, and more complicated interpolation schemes must be used, there are certain simplifying features. The rigid band approximation works rather well, so that the band structures

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FIG. 32. Energy bands in the fcc structure. (a) The empty lattice model. (b) Al. (c) Pb.

X

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FIG. 33. The Fermi surface of k measured by Shoenberg, D., Stiles, P.J., Proc. R. Soc. <u>A 281</u> (1964) 62, using the De Haas-Van Alphen effect. The contours show departures from sphericity in parts in 10^5 .

of all transition metals of a particular structure are rather similar, especially if they are in the same period. The band structures of, for instance, Rh, Pd and Ag are very similar and, in practice, a common band structure may be used to determine the FS, by allowing μ to vary



FIG. 34. Cross sections of the Fermi surface in Pb compared with the empty lattice model. From Anderson, J. R., Gold, A. V., Phys. Rev. 139 A (1965) 1459.

according to the number of conduction electrons. Descending a column in the periodic table, for instance the series Cr, Mo, W, one finds that the d-bands become broader and spin-orbit splitting becomes progressively larger.

On the right side of the 3d transition series, where the bands are narrow and the electron interactions large, magnetically ordered states are common and the band structures may be considerably modified by the interaction between the conduction electrons and the ordered moment. In the ferromagnetic metals, Kramers' theorem is no longer valid and the energy bands for up and down spin electrons split. The Fermi surfaces for the two spin states must then be considered individually in discussing, for instance, the galvanomagnetic properties. In antiferromagnetic metals the periodicity of the total potential is modified, so that new energy gaps will appear in the band structure and the FS will generally be considerably modified.

(d) Lanthanides and actinides. Very little experimental work has been carried out on the FS of these complex metals, which are characterized by having unfilled f shells. Band structure calculations have been performed for many of them, and for hcp rare earth metals are in qualitative agreement with positron annihilation experiments. Many of these metals are magnetic and their complex magnetic structures are known to be intimately related to the conduction electron band structure.

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15. PROSPECTS IN FERMI SURFACE STUDIES

In these notes, we have emphasized the determination of the geometrical shape of the FS, and so much work has been carried out in the last ten years that this aspect of FS studies may reasonably be considered to be drawing to a close. It is true that there remain many metals for which the FS has not been measured in detail, notably the alkaline earth metals and magnetic metals, but these problems are being actively pursued and will probably be solved fairly soon. Much less is known about the velocity and relaxation time. The variation of the velocity over the FS is known in detail only for the noble metals and it is an important parameter for many phenomena, notably transport properties. The comparison between the measured velocity and that derived from band structure calculations gives an estimate of the many body enhancements of the effective mass, and its variation over the FS. Very little is known about the relaxation time and its k dependence, and indeed it is clear that the relaxation time approximation is not, in many cases, an adequate method of describing the scattering process. We may anticipate that there will be a careful study of scattering mechanisms in metals in the future.

FS studies have had a very important effect in increasing confidence in band structure calculations, even for complex metals. The emphasis in these calculations will probably now shift towards the application of the calculated band structures and wavefunctions to more complicated phenomena, such as the optical absorption, the phonon spectrum, magnetic interactions, the properties of defects, and many others. The experimental emphasis may be expected to shift at the same time towards the study of the electrons away from the FS, and the effect of the interactions in modifying the band structure. In this programme, the information which has been accumulated about the electrons on the FS will provide invaluable assistance to future research.

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POSITRON ANNIHILATION IN LIQUIDS AND SOLIDS

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Abstract

1. Introduction. 2. Selection rules of annihilation. 3. Experiments in condensed matter. 3.1. Lifetime measurements. 3.2. Angular correlation studies. 3.3. Polarization of electrons in ferromagnets. 4. Theory of positron annihilation in metals. 5. The effective mass of the positron. 5.1. Definition of the effective mass m_{+}^{*} . 5.2. Theoretical computation of m_{+}^{*} . 5.3. Experimental data. 5.4. Thermalization time. 6. Theory of paramagnetic quenching.

1. INTRODUCTION

The existence of the positron as the antiparticle of the electron is a fundamental consequence of the Dirac electron theory. After the discovery of the positron, early work [1] was devoted to testing the implications of this theory experimentally, for example the equality of the rest masses of the electron and the positron, and the annihilation of an electron-positron pair to produce two γ -rays, each of energy mc² = 511 keV, travelling in opposite directions. With the development of quantum electrodynamics, the electron-positron system again became the centre of interest. Selection rules for the dematerialization of the particles into photons were formulated. Experiments were successfully performed to vindicate these and other predicted polarization properties of the annihilation γ -rays. From the fact that a component of the annihilation was independent of pressure in certain gases, an interesting discovery was made: namely, an electron-positron pair could exist in a bound state, the positronium.

In this paper we shall not consider the fundamental aspects of quantum electrodynamics, but concentrate on the phenomena that occur when positrons are injected into bulk matter, particularly solids and liquids. The emphasis will be more on quantitative understanding of the complicated processes that occur.

2. SELECTION RULES OF ANNIHILATION [2]

An electron-positron pair can annihilate by emitting one, two, three, or more γ -quanta. The higher quantum yields are negligible. For energy-momentum conservation, one quantum annihilation occurs in the presence of a third particle, and, because of its rarity, it is not of much interest to us [3]. Annihilation into two γ -rays of equal wavelength, travelling in opposite directions from a bound electron-positron pair at rest, happens with a lifetime $\sim 10^{-10}$ s. The three γ -annihilation takes a longer time, $\sim 10^{-7}$ s, since it is a process of higher order.

Consider two photons of equal wavelength λ propagating in opposite directions along the z axis. There are four such states which we shall denote by Ψ^{RR} , Ψ^{RL} , Ψ^{LR} and Ψ^{LL} . The first index refers to the circular polarization state of the γ -ray propagating in the +z direction, the second to the other photon. Thus Ψ^{RL} would represent a state with a right-circularly polarized photon proceeding along the z axis and a left-circularly polarized photon proceeding the -z axis.

To investigate the behaviour of these four states under a space rotation or an inversion, let us first write down the electric field for a rightcircularly polarized electromagnetic wave moving along the z axis:

$$(E_{x})_{+}^{R} = E_{0} \cos (kz - \omega t + \delta_{+}^{R})$$

$$(E_{y})_{+}^{R} = E_{0} \sin (kz - \omega t + \delta_{+}^{R})$$
(1)

For a right-circularly polarized wave moving in the opposite direction

$$(\mathbf{E}_{\mathbf{x}})_{-}^{\mathbf{R}} = \mathbf{E}_{0} \cos \left(-\mathbf{k}\mathbf{z} - \omega \mathbf{t} + \boldsymbol{\delta}_{-}^{\mathbf{R}}\right)$$
$$(\mathbf{E}_{\mathbf{y}})_{-}^{\mathbf{R}} = -\mathbf{E}_{0} \sin \left(-\mathbf{k}\mathbf{z} - \omega \mathbf{t} + \boldsymbol{\delta}_{-}^{\mathbf{R}}\right)$$
(2)

Under a rotation through an angle ϕ around the z axis

D.

$$x = x' \cos \varphi + y' \sin \varphi$$
$$y = -x' \sin \varphi + y' \cos \varphi$$
$$z = z'$$
(3)

we have

$$(\mathbf{E}_{\mathbf{x}})_{+}^{\mathbf{K}} = \mathbf{E}_{0} \cos (\mathbf{k} \mathbf{z} - \omega \mathbf{t} + \delta_{+}^{\mathbf{R}} + \varphi)$$

$$(\mathbf{E}_{\mathbf{y}})_{+}^{\mathbf{R}'} = \mathbf{E}_{0} \sin (\mathbf{k} \mathbf{z} - \omega \mathbf{t} + \delta_{+}^{\mathbf{R}} + \varphi)$$
(4)

and

$$(\mathbf{E}_{\mathbf{x}})_{-}^{\mathbf{R}'} = \mathbf{E}_{0} \cos \left(-\mathbf{k}\mathbf{z} - \omega \mathbf{t} + \delta_{-}^{\mathbf{R}} - \varphi\right)$$

$$(\mathbf{E}_{\mathbf{y}})_{-}^{\mathbf{R}'} = -\mathbf{E}_{0} \sin \left(-\mathbf{k}\mathbf{z} - \omega \mathbf{t} + \delta_{-}^{\mathbf{R}} - \varphi\right)$$
(5)

Thus the phase of a right-circularly polarized wave along the z axis changes by $+\varphi$, while that of a right-circularly polarized wave along the -z axis changes by $-\varphi$ under the rotation. For the quantum state Ψ^{RR} the total phase factor is the product of the two phase factors of the two photons. Hence we conclude that the state Ψ^{RR} is an eigenstate of the rotation (3) with eigenvalue 1. Mathematically the states are changed under the rotation (3) by a unitary transformation which we shall call R_{φ} . We conclude that

$$R_{\varphi} \Psi^{RR} = \Psi^{RR}$$
 (6)

Similar conclusions are reached for the rotation around the x axis through an angle $180^{\circ}(R_{\xi})$ and for an inversion (P). More complete derivations, including the polarization properties, follow from field theoretic considerations. The results are summarized in Tables I, II and III.

Now it is well known that opposite parities are assigned to particle and antiparticle (fermions), so that the intrinsic parity of an electronpositron pair is odd, with the convention that vacuum has even parity. Therefore both ${}^{1}S_{0}$ and ${}^{3}S_{1}$ states have odd parity. Hence from the above tables the ${}^{3}S_{1}$ state cannot decay by two photons, while the ${}^{1}S_{0}$ state can. The ${}^{3}S_{1}$ state can decay into three or more photons, through higher order interaction, and thus lives longer. The experiments checking the various predictions of Tables I, II, and III are described by DeBenedetti [1].

TABLE I. EIGENVALUES OF ROTATION $\mathbf{R}_{\varphi},\ \mathbf{R}_{\xi}$ AND INVERSION FOR THE TWO PHOTON STATES

	_Ψ RR _{÷ Ψ} LL	$\Psi^{RR} - \Psi^{LL}$	Ψ^{RL}	Ψ^{LR}
R _φ	1	1	e ^{2i φ}	$e^{-2i\varphi}$
Rg	1	1		
Р	1	-1	1	1

 R_{φ} = Rotation around the z axis through φ .

 R_{ξ} = Rotation around the x axis through 180°.

P = Inversion.

TABLE II. ANGULAR MOMENTUM (J) AND PARITY OF THE TWO PHOTON STATES

0	1	2, 4, 6	3, 5, 7
$\Psi^{RR} + \Psi^{LL}$	Forbidden	$_{\Psi}$ RR + $_{\Psi}$ LL, $_{\Psi}$ RL, $_{\Psi}$ LR	Ψ ^{RL} , Ψ ^{LR}
$\Psi^{RR} - \Psi^{LL}$	Forbidden	$\Psi^{RR} - \Psi^{LL}$	Forbidden
	0 ¥ ^{RR} + ¥LL ¥ ^{RR} - ¥LL	0 1 $\psi^{RR} + \psi^{LL}$ Forbidden $\psi^{RR} - \psi^{LL}$ Forbidden	0 1 2, 4, 6 $\psi^{RR} + \psi^{LL}$ Forbidden $\psi^{RR} + \psi^{LL} + \psi^{RL} + \psi^{LR}$ $\psi^{RR} - \psi^{LL}$ Forbidden $\psi^{RR} - \psi^{LL}$

TABLE III. CORRELATION OF THE PLANES OF POLARIZATION OF DISINTEGRATION PHOTONS

J Parity	o 1	2, 4, 6	3, 5, 7,	
Even		∫ ≥ 50%	= 50%	
	Forbidden	1 1≤ 50%	= 50%	
Odd	Forbidden	Ţ	Forbidden	

Let us now turn to the bound state 'positronium'. Except for finer details originating from quantum electrodynamics, the energy levels E_n of positronium are similar to the hydrogen atom, the reduced mass being only half the electron mass in the Schrödinger equation. So

$$E_n = -\frac{me^4}{4\,\tilde{n}^2 n^2} \tag{7}$$

The ionization potential is 6.8 electron volts; the energy of the first excited state is 5.1 eV and the Lyman α line has a wavelength 2400 Å. But, for an increase of the radii the internal wave functions are the same as for hydrogen. The lifetimes of the excited states against optical de-excitation are twice as great as those of the corresponding hydrogen states.

The 1S ground state is split into a lower singlet (para) and higher triplet (ortho) level by the magnetic and radiative interactions. The splitting is

$$\Delta W = 2.0337 \times 10^5 \text{ Mc/s} = 8.35 \times 10^{-4} \text{ eV}$$

Radiative transitions between these states are very slow, since they are of magnetic dipole character. The singlet state $({}^{1}S_{0})$ decay rate λ_{s} entirely by two-quantum annihilation is (τ_{s} = singlet lifetime)

$$\lambda_{\rm s} = 0.804 \times 10^{10} \, {\rm s}^{-1}, \ \tau_{\rm s} = 1.25 \times 10^{-10} \, {\rm s}$$

For the triplet state $({}^{3}S_{1})$ decay by three-quantum annihilation, the decay rate is $(\tau_{+} = \text{triplet lifetime})$

$$\lambda_{\star} = 7.2 \times 10^6 \text{ s}^{-1}, \quad \tau_{\star} = 1.4 \times 10^{-7} \text{ s}$$

The states of positronium show no first order (linear) Zeeman effect. There is, however, a second-order effect due to mixing of singlet and triplet components in a magnetic field. Owing to this admixture the triplet state can now decay by two-quantum annihilation. The experimental aspect is summarized by Deutsch [1].

3. EXPERIMENTS IN CONDENSED MATTER [4]

Fundamentally there are two types of measurements done with positrons interacting with matter. One may measure the lifetime of positrons, or one may study the angular correlation of the annihilation γ -rays.

The lifetime measurements are done with standard delayed coincidence techniques. The sample may be a pure substance or may contain certain impurities, for instance doped semiconductors or liquids with magnetic ions. The dependence of lifetime on temperature and pressure has also been observed in many cases. In metals, lifetime measurements reveal information about the interaction of the positron with the electrons. In other substances we get information about the collision processes, for example exchange scattering cross-section of positronium, or sometimes the average scattering cross-section of the positron against atoms. The strong Coulomb interaction of the positron distorts the electronic wavefunctions in condensed systems, and this is a limitation of the method of positron annihilation to explore the electronic properties.

The angular correlation measurements may be done for two or three annihilation quanta. The three-quantum annihilation has been studied particularly to check predictions of quantum electrodynamics [1], but is not of any great interest to us. Two-quantum annihilation yields information about the momentum distribution of electrons in matter, so it is of direct interest in the study of the Fermi surface of metals. For other materials, as the exact state of the positron may not be clearly established, the data are difficult to interpret, but some progress has been made.

The two-photon angular correlation has been studied at different temperatures to observe the motion of positrons in metals. This is a measurement of the effective mass of the positron in a metallic environment. In addition, information can be obtained about the rate of energy loss and thermalization of positrons in metals. It is now known that positrons in metals annihilate before thermalization at very low temperatures. There is thus a natural limit of resolution.

Some studies of angular correlation have been made in magnetic metals to derive information about the polarization of magnetic electrons.

We shall now look at the experimental data in more detail.

3.1. Lifetime measurements

Materials in which the lifetime has been measured can be divided into two classes. The first class consists of metals and heavily doped semiconductors which show essentially one lifetime (Fig. 1). The second class comprises materials in which evidence for at least two lifetimes is known (Fig. 2). The short lifetime, called τ_1 , is roughly $\sim 2 \times 10^{-10}$ s. The longer lifetime, τ_2 , varies more, from about 5×10^{-10} s to about 10^{-8} s in various substances.

Table IV represents the lifetime data of metals and semiconductors [5-11]. τ_1 is characteristic of homogeneous metal. The second longlived component, τ_2 , present with a small intensity, I_2 , is now generally regarded as due to annihilation in the surface as well as lattice defects in metals [6]. The decay rates for the 'nearly free electron' metals Li, Na, K, Rb, Cs, Mg and Al fall on a smooth curve (Fig. 3) which approaches the spin averaged positronium rate at low densities or large r_s . In standard many-body theory, densities are often referred to in r_s units defined as follows. If n be the number of valence electrons per cm³, and a_0 the Bohr radius, we write

$$n = \left[\frac{4\pi}{3} a_0^3 r_s^3\right]^{-1}$$
(8)

The rates for Be and Bi and the semiconductors Si and Ge are below the nearly free electron curve; the rates for the transition metals and Cd are above it, but we should remember the difficulty of defining the exact number n of valence electrons in transition metals. For the rare earths, Eu ($r_s \sim 3.24$) and Yb ($r_s \sim 2.9$) appear to contribute 2 valence electrons while the rest contribute 3 ($r_s \sim 2.47$), and the rates fall accordingly. Recalling that the density of electrons varies as r_s^{-3} , the variation of lifetime with r_s is rather small; clearly the density of electrons at the



FIG.1. Measured decay curve for sodium, after Weisberg, H., Berko, S., Phys. Rev. <u>154</u> (1967) 249, showing essentially one life-component.



FIG.2. Typical lifetime curve with two components. 1 channel= 1.41×10^{-10} s; (a) benzene, (b) chlorobenzene, (c) bromobenzene, (d) prompt coincidence curve. (After Germagnoli, E., Poletti, G., Randone, G., Phys. Rev. <u>141</u> (1966) 419...

positron position is quite different from the average density and the Coulomb interaction between the electrons and the positron is important.

On the other hand, it is not possible to interpret the lifetime data in terms of positronium formation. The fact that singlet positronium would be formed only one quarter of the time would lead to an unobserved long lifetime, or, if triplet-to-singlet conversion were rapid, to a lifetime four times that of singlet positronium, 5×10^{-10} s. In fact one can show that a positronium-like bound state does not exist at metallic densities, and the concept of the bound state cannot be defined properly [12, 13].

The long lifetime τ_2 is shown by most other solids, liquids, and gases. The problem logically separates into two parts: the explanation of the intensity I_2 and the origin of τ_2 . In most cases triplet positronium

is formed. Sometimes, as in alkali halides, a more complicated longlived compound state may form. The mechanism and probability of the positronium or complex formation will explain I_2 . Then its transition to the singlet state with subsequent decay gives rise to the τ_2 component.



FIG.3. Measured annihilation rates plotted against r_s (after Weisberg, H., Berko, S., Phys. Rev. 154 (1967) 249). Theoretical values indicated are: λ_{pos} , the spin-averaged positronium annihilation rate; λ_{ps}^{-} the rate for positronium negative ion; 'Sommerfeld', the rate for a non-interacting electron gas: "RPA" the rate calculated in the random-phase approximation by Kahana [29] and 'Kahana', the full many-body calculation of Kahana and Carbotte [29].

The problem of formation of positronium is not quantitatively understood¹. The intensity I_2 varies a great deal, from 20% to 60%. Ore [16] has discussed the energetics of positronium formation in gases, and his treatment can be adapted to the molecular solids. Let us designate the binding energy of positronium by W_{ps}. This may be somewhat smaller than 6.8 eV inside a solid. Suppose that the ionization potential of a molecule of the material is I (for most materials this is about 10 eV). If the initial energy of the positron is E, positronium formation is possible provided $E > I - W_{ps}$. As long as E is greater than the lowest electronic excitation energy of the molecule, however, inelastic scattering will compete. At energies above the ionization threshold, inelastic scattering with ionization will generally have a larger cross-section associated with the presence of two free particles in the final configuration. Thus there exists a limited range of energy over which positronium formation will take place. This range is called the 'Ore gap'.

¹ The formation of positronium in the scattering of a positron in atomic hydrogen has been investigated by Massey and Mohr [14] in the Born approximation. They also allow for the fact that a slow positron is repelled by the nucleus of the hydrogen atom, such that the wave-function for its motion relative to the atom has a considerably smaller amplitude in the region of the atom than a plane wave. The positronium formation cross-section is zero below 6.8 eV, but rises quite rapidly to a maximum $4.5 \pi a_0^2$ at ~14 eV and then falls off. Allowance for the repulsion cuts down the maximum by almost 2, and makes the curve flatter. The inelastic cross-section becomes important above 10.2 eV. Hence the region 6.8 to 10.2 eV roughly corresponds to the Ore gap. A recent calculation is due to Cheshire [15].

Z	Material	τ ₁ [ns]	$ au_{2}$ [ns]	I 2[%]	Referenc
3	Li	0.29 ± 0.02	0.59	6.5	[5]
		0.291 ± 0.006	2.78 ± 0.25	0.6 ± 0.1	[6]
4	Ве	0.213 ± 0.005	0.44	18	[6]
5	В	0.35 ± 0.05	1.9 ± 0.05	2.8 ± 0.5	[10]
11	Na	0.315 ± 0.02	0.57	4.3	[5]
		0.338 ± 0.007			[6]
12	Mg	0.232		0	[6]
13	A1	0.1	1.0 ± 0.2	30	[7]
		0.193 ± 0.02	0.39	6.5	[5]
		0.187	0.324	6	[8]
		0.21 ± 0.01			[9]
		0.201 ± 0.005^{a}	0.32	30	[6]
14	Si	0.222 ± 0.005	0.508 ± 0.094	1.0 ± 0.7	[6]
		0.26 ± 0.03	1.2 ± 0.05	2.6 ± 0.5	[10]
19	K	0.40 ± 0.02			[5]
		0.397 ± 0.010		0	[6]
21	Sc	0.238 ± 0.009			[8]
2 6	Fe	0.160 ± 0.005	0.38	15	[6]
27	Co	0.162 ± 0.014	0.577 ± 0.051	1.2 ± 0.2	[6]
28	Ni	0.172 ± 0.005	0.465 ± 0.080	1.8 ± 0.9	[7]
29	Cu	0.1	0.7 ± 0.06	20	[7]
		0.181 ± 0.005	0.445 ± 0.055	2.5 ± 1.0	[6]
31	Ga	0.194 ± 0.004	0.426 ± 0.048	3.1 ± 1.2	[6]
32	Ge	0.226 ± 0.005	0.480 ± 0.063	2.2 ± 1.1	[6]
		0.24 ± 0.05	1.9 ± 0.05	1.6 ± 0.5	[10]
37	Rb	0.401 ± 0.010			[6]
39	Y	0.252			[8]
4 7	Ag	0.15 ± 0.06			[11]
4 8	Cd	0.185 ± 0.004	0.526 ± 0.041	1.6 ± 0.4	[6]
50	Sn	0.202 ± 0.005	0.521 ± 0.050	2.0 ± 0.6	[6]
55	Cs	0.43 ± 0.02			[5]
		0.418 ± 0.010		0	[6]

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TABLE IV. LIFETIME DATA OF METALS AND SEMICONDUCTORS

Table	IV	(cont.)
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Z	Material	$ au_1$ [ns]	$ au_2$ [ns]	I 2[%]	Reference
57	La	0.251			[8]
58	Ce	0.244			[8]
59	Pr	0.239			[8]
60	Nd	0.244			[8]
62	Sm	0.246			[8]
63	Eu	0.278			[8]
64	Gd	0.248			[8]
65	Tb	0.247	,		[8]
66	Ďу	0.241			[8]
67	Но	0.243			[8]
68	Er	0.242			[8]
69	Tm	0.246			[8]
70	Yb	0.263 ± 0.009			[8]
71	Lu	0.247		•	[8]
79	Au	0.1	0.66 ± 0.03	30	[7]
80	Hg	0.220 ± 0.007	0.426 ± 0.065	4.4 ± 2.9	[6]
82	Pb	0.201 ± 0.005	0.477 ± 0.048	2.7 ± 1.0	[6]
83	Bi	0.243 ± 0.008 ^a	0.34	20	[6]
	GaS	0.28 ± 0.05	2.1 ± 0.05	2.3 ± 0.5	[10]
	SiC	0.22 ± 0.05	1.8 ± 0.05	1.3 ± 0.5	[10]

^a With I_2 constrained to be 5‰.

The application of an electric field should cause an increase in the amount of positroniums formed, because of the acceleration of any free low-energy positrons present back into the Ore gap. This has been found to be true [17]. Several polyatomic gases failed to show any increase in yield, probably as a result of large inelastic scattering crosssections with excitations of low-lying molecular levels. In other words, here positrons have a short mean free path. Hence the average scattering cross-section of positrons in some gases can be estimated, for example, for He, Ne and A we have $\sigma = .023\pi a_0^2$, $0.12\pi a_0^2$ and $1.5\pi a_0^2$ respectively.

In alkali halides positrons appear to decay through at least two different processes [18]. The first component $\tau_1 \sim 2 \times 10^{-10}$ s is conceivably due to positrons which annihilate when free. The second component which occurs with an intensity I₂ between 25% and 85% is characterized by a mean life $\tau_2 \sim 4$ to 8×10^{-10} s. The annihilation rate λ_2 is connected with the molecular density n within each halide series according to the relation $\lambda_2 = \lambda_0 + on$. λ_0 decreases on passing from fluorides to bromides

and α turns out to be simply proportional to the square of the radius of the negative ion. The τ_2 component is sensitive to the application of a static magnetic field; the magnetic quenching, however, is appreciably lower than what would be expected if one attributed this component to the decay of free triplet positronium atoms. Theoretical arguments against positronium formation in alkali halides have been advanced [19]. It has been suggested that the τ_2 component is due to the formation of compounds such as Cl (e⁻ e⁺). Table V represents some data on alkali halides. Various other data can be found in the article of Wallace [4]. Sometimes in these decays a third component is seen. The decay in liquid He has also three components, but is very little understood [20].

Let us now turn to the origin of the τ_2 component. Any process whereby the two-photon annihilation replaces the longer-lived three-photon annihilation and contributes to the τ_2 component is called 'quenching' [21]. Here various mechanisms operate: unpaired electron exchange, angular momentum reorientation, chemical compound formation, pick-off and spin reversal by internal magnetic fields. One can also induce quenching by applying external magnetic and electric fields.

The quenching effect was discovered quite early [1]. Addition of small amounts of paramagnetic gases like NO, NO₂ or O₂ in inert gases argon and freon, or alkali metals in ammonia solution, or paramagnetic ions in aqueous solution shows a large change in τ_2 from that charac-

Halide	n × 10 ⁻²²	$ au_1 imes 10^{10} ext{ s}$	$ au_2 imes 10^{10} ext{ s}$	I ₂ [%]	$ au_3 imes 10^9 ext{ s}$	I ₃ [%]
LiF	6.04		4.02 ± 0.21	70 ± 15	2.7	0.8
NaF	4.00		5.05 ± 0.35	49 ± 5	2. 5	1.4
KF	2.57		6.20 ± 0.40	33 ± 7	2.7	0.4
CsF	1.42		7.60 ± 0.21	46 ± 5		
Li Ce	2.94	1.8 ± 0.6	4.25 ± 0.25	30 ± 10		
NaCl	2.23	1.6 ± 0.8	4.96 ± 0.24	52 ± 15	2.0	0.9
KCl	1.60	2.2 ± 0.9	6.07 ± 0.12	50 ± 15		
RbC1	1.37	2.2 ± 0.9	6.27 ± 0.19	31 ± 10		
CsCl	1. 42	1.6 ± 0.5	6.39 ± 0.18	25 ± 4		••
LiBr	2.40		4.58 ± 0.20	55 ± 10	3.6	1.0
NaBr	1.87		5.56 ± 0.20	34 ± 7	3.6	0.8
KBr	1.39		6.73 ± 0.22	37 ± 7		
CsBr	1.26		6.54 ± 0.38	31 ± 4		
NaI	1.48		5.11 ± 0.18	61 ± 9	3.3	1.2
КI	1.13		6.40 ± 0.21	43 ± 7		
RbI	1.00		6.36 ± 0.18	56 ± 15	3.9	0.2
CsI	1.05		6.36 ± 0.29	25 ± 4	3.9	0.8

TABLE V. LIFETIME DATA ON ALKALI HALIDES [18]

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teristic of pure argon, freon, ammonia or water, respectively. The free unpaired paramagnetic electron can quite easily be exchanged with the electron in positronium, converting the triplet into the singlet state. The cross-sections are large, $\sim 10^{-16}$ or 10^{-15} cm². In O₂ both the outer electrons of the ${}^{3}\Sigma_{g}$ ground state can be exchanged, the molecule remaining in the triplet state but with a changed orientation in space. The quenching cross-section of Cl₂ is also high, about 10^{-16} cm², probably owing to a compound formation, as shown by the absence of any effect of an external magnetic field. The similarity with the alkali halides may be noted.

In most other substances, particularly with all their spins paired up, the τ_2 decay occurs through pick-off. During collisions of orthopositronium with atoms and molecules, the positron finds itself in a region of high density of electrons, and picks up one electron of the correct spin to form a singlet combination, which annihilates. This mode of decay accounts for the τ_2 component in inert gases and other molecular substances. The cross-sections are about 10^{-20} to 10^{-19} cm². Spin reversal may also occur because of internal magnetic fields or spin-spin interaction, but the cross-section is quite small compared with those of the other processes.

3.2. Angular correlation studies

If the electron-positron system were at rest, the two γ -rays would come out exactly opposite and could be detected by two counters in a line on the horizontal plane. The positron in the solids has very low momentum during annihilation. However, electrons in atoms will generally have momenta $\sim mc/137$. Electrons in metals have all monenta up to the Fermi momentum. Hence the annihilating pair will have generally a finite momentum, and the two γ -rays will come out at a certain angle. One of the counters can be moved up or down from the horizontal plane and the coincidence curve will measure the number of pairs having a certain component of momentum along the vertical z axis.

The angular distribution curves for metals can be divided into two types [22]. The first type consists of simple metals like Li, Na, K, Cs, Ca and Al. Here the curve is almost, but not quite, an inverted parabola with a sharp cut-off at the Fermi momentum k_F and a small tail beyond it. Now, according to the Sommerfeld theory, the angular correlation curve will be a simple inverted parabola. If $P(\vec{k})$ denotes the probability of an electron of momentum \vec{k} (neglect positron momentum), the observed curve is

$$\mathbf{P}(\mathbf{k}_{z}) = \iint \mathbf{P}(\vec{\mathbf{k}}) \, d\mathbf{k}_{x} \, d\mathbf{k}_{y} = \frac{2\pi \left(\mathbf{k}_{F}^{2} - \mathbf{k}_{z}^{2}\right) \, \text{for } \mathbf{k}_{z} \leq \mathbf{k}_{F}}{0 \qquad \text{for } \mathbf{k}_{z} \geq \mathbf{k}_{F}} \tag{9}$$

The tail is attributed to the annihilation with the core electrons and in part to the electron-positron interaction. The surprising feature is that the angular correlation curves seem to follow the prediction of the free electron theory so well, while the lifetime measurements manifestly require the consideration of the electron-positron Coulomb interaction.

Since this experiment measures the momentum component along a definite direction, any anisotropy of the electron momentum distribution due to the Bloch character of the metallic electron should show up [23]. Metallic single crystals have been studied to detect these anisotropies in the Fermi surface (Fig. 4). These measurements may sometimes be used to make estimates of the band gaps at the Brillouin zone boundary.

The angular correlation curves of the second type of metals comprising Cu, Ag, Au, the transition and rare earth metals, start off at the centre like a parabola, but have a relatively large tail. A substantial fraction of the annihilation must be occurring with the d-electrons and the core electrons (Fig. 5).



FIG.4. The angular distribution of photons arising from annihilation with electrons in Be single crystals for three different crystallographic orientations. Also shown is the angular correlation curve for Na metal and the estimated instrument resolution (after Stewart, A.T., Shand, J.B., Donaghy, J.J., Kusmiss, J.H., Phys. Rev. 128 (1962) 118).

Another method of presenting the data is to plot the slope of the angular distribution curve [24]. This, by Eq. (9), should be a straight line with a sharp discontinuity at the Fermi momentum; above k_F , the slope vanishes. Actually, at finite temperatures the triangular shape is somewhat smeared out. The results of the first category of metals, however, show a fairly sharp fall-off at k_F , while the metals of the second type do not show the fall-off so clearly (Fig. 6).



FIG.5. Decomposition of $N_1(\theta)$ in Fe into a conduction band (1) and a 3d band (2) contribution. The predicted $p(\theta)$ and the experimentally observed $p(\theta)$ (cross points) are shown (Berko, S., Zuckerman, J., Phys. Rev. Letters 13 (1964) 339a)).



FIG.6. Effective temperature of positrons in Na, Rb. Assuming thermalization (linear portion), the slope gives the effective mass m_{\pm}^{*} . At low temperature, thermalization does not occur (Stewart, A.T., Shand, J.B., Kim, S.M., Proc. phys. Soc. London <u>88</u> (1965) 1001 and Kim, S.M., Stewart, A.T., Carbotte, J.P., Phys. Rev. Letters <u>18</u> (1967) 385)).

Angular correlation in alkali metals and mercury has also been obtained in the liquid state [24, 25]. This is a convenient method for studying momentum distribution of electrons in liquid metals. At high temperatures, however, the motion of positrons should be considered.

In Si and Ge, the angular correlation curves show similar anisotropies and can be understood roughly by taking into account the Bloch character of the electrons [26]. Data also exist for alkali halides [27]; the effect of the positive ion is found to be rather small, and there are characteristic variations with the halogen ions. The interpretation of these curves is rather difficult, since the exact nature of the positron-halogen binding is not clearly understood.

3.3. Polarization of electrons in ferromagnets [28]

Since positrons from β -decay are longitudinally polarized and retain most of the polarization while slowing down in metals, they can be used to probe the polarization of electrons in ferromagnetic materials. Several such measurements have been performed. Positrons are collimated by circular apertures before they strike the ferromagnetic sample. A strong magnetic field is used to saturate the sample parallel (†) or antiparallel (↓) to the incident positron momentum. Because of polarization, the probability of singlet overlap is changed from 1/4 to $\frac{1}{4}$ (1 \mp P_e P_p). P_e and P_p are the electron and the positron polarization, respectively. Similarly, the triplet overlap is changed to $\frac{1}{4}$ (3 \pm P_e P_p). The experiment now measures

 $\mathbf{p}(\boldsymbol{\theta}) = \frac{\mathbf{N} \boldsymbol{\uparrow}(\boldsymbol{\theta}) - \mathbf{N} \boldsymbol{\downarrow}(\boldsymbol{\theta})}{\mathbf{N} \boldsymbol{\uparrow}(\boldsymbol{\theta}) + \mathbf{N} \boldsymbol{\downarrow}(\boldsymbol{\theta})}$

The explanation of these measurements is unfortunately somewhat model dependent, particularly because of the poor status of the theory of ferro-magnetic metals. However, the shape of $p(\theta)$ in Fe can be interpreted to imply a conduction band polarization opposite to that of the d-electrons.

4. THEORY OF POSITRON ANNIHILATION IN METALS [29]

We have noted the failure of the Sommerfeld theory of free electrons to explain the lifetime in metals. To incorporate the electron-positron interaction, Ferrell [19] computed the first-order correction to the wavefunction of the annihilating pair, using the perturbation method on a screened Coulomb interaction. His results indicated a correction in the right direction. Since then the entire theory has been worked out in detail with the techniques of the many-body theory by Kahana, Carbotte and others. Some progress in real metals has been achieved. The results are in good agreement with the experimental observation.

To understand Kahana's work, consider the positron interacting with the electron gas. First we want to treat the two-body correlations of an electron and the positron accurately. One must, however, take into account the effect of the Pauli principle and the screening of the Coulomb interaction, because of the other electrons. So we write down the Schrödinger equation for the pair, but in momentum space, where the above restrictions can be conveniently handled. Since the positron has negligible momentum, the entire momentum comes from the electron; put $\vec{k_p} = 2 \vec{a}$. The equation reads

$$(k^{2} - a^{2}) \Phi(k) = \frac{4\pi}{(2\pi)^{3} a_{0}} \int \frac{d^{3}k'}{|\vec{k} - \vec{k}'|^{2}} \Phi(k')$$
(10)

The prime on the integration sign indicates the restrictions of screening and the Pauli principle. The latter demands that the electron go outside the Fermi sea before interacting in an intermediate state with the positron. Momentum consideration gives

$$\left|\vec{k}' + \vec{a}\right| \ge k_{\rm F} \tag{11a}$$

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k' = a (forward scattering) (11b)

The screening can be accounted for by demanding that the relative momentum transferred in the pair collision satisfy

$$\left|\vec{\mathbf{k}} - \vec{\mathbf{k}}\right| \ge k_{\rm c} \tag{12}$$

where

 \mathbf{or}

$$k_c = 0.470 r_s^{\frac{1}{2}} k_F$$
 (13)

Eq. (10) is now brought into a more manageable form by concentrating on the distorted part $u(\vec{k})$ of the wave function. Write

$$\Phi(\vec{k}) = \delta(\vec{k} - \vec{a}) + fu(\vec{k})$$
(14)

The δ -function represents an initial plane wave of relative momentum $\vec{a} = \frac{1}{2} \vec{k}_{e}$, and $f = 4\pi (2\pi)^{-3} a_{e}^{-1}$. Equations (14) and (10) give

$$u(k) = \frac{1}{(k^{2} - a^{2})} \frac{1}{|\vec{k} - \vec{a}|^{2}} + \frac{f}{k^{2} - a^{2}}, \int d^{3}k' \frac{u(k')}{|\vec{k} - \vec{k'}|^{2}}$$
(15)
$$|\vec{k'} + \vec{a}| \ge k_{F}$$
$$|\vec{k'} - \vec{a}| \ge k_{C}$$
$$|\vec{k'} - \vec{k'}| \ge k_{C}$$

The denominator is non-singular because of the restrictions on momenta. Eq. (15) is valid for $|\vec{k} - \vec{a}| \ge k_c$. When $|\vec{k} - \vec{a}| \le k_c$, u(k) = 0.

As the restrictions on the momenta are quite complicated, Kahana had to carry out a good deal of numerical work. However, some features are easy to see. For $\vec{a} = 0$,

$$u(\mathbf{k}) = \frac{1}{\mathbf{k}4} + \frac{f}{\mathbf{k}2} \int d^{3}\mathbf{k'} \frac{u(\mathbf{k'})}{|\vec{k} - \vec{k'}|^{2}}$$

$$(16)$$

$$k' \ge k_{F}$$

$$|\vec{k'} - \vec{k}| > k_{C}$$

The perturbation solution consists of iteration in Eq. (16). So to the first approximation $u = 1/k^4$. The configuration space wave function is then

$$\Psi(\vec{\mathbf{r}}) = \int \Phi(\mathbf{k}) e^{i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}} d^3\mathbf{k} = 1 + \frac{4\pi f}{r} \int_{\mathbf{k}_F}^{\infty} \frac{d\mathbf{k}}{\mathbf{k}^3} \sin \mathbf{k}\mathbf{r}$$
(17)

The second term represents a concentration of electrons about the position of the positron. If we now assume that the annihilation rate does not vary very much with the electron momentum, one can compute the enhancement over the Sommerfeld rate given by Eq. (14).

$$|\Psi(0)|^2 = \left(1 + \frac{2}{\pi a_0 k_F}\right)^2 = \left(1 + \frac{2r_s}{6.02}\right)^2$$
 (18)

This was, in fact, the result of Ferrell [19].

The above approach overlooks an important aspect of the pair interaction. Actually the force between the positron and the electrons is

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crudely represented by a static potential. One ought to include the retardation effects in interaction, and the way to do it is to consider the dynamical dielectric constant of the electron gas.

We shall only give the outline of the Kahana-Carbotte approach. The calculation of the annihilation rate reduces to an estimation of the electron density at the positron averaged over all the positron positions, that is, to

$$n = \int \langle \psi^{\dagger}(\vec{x}) \psi(\vec{x}) \varphi^{\dagger}(\vec{x}) \varphi(\vec{x}) \rangle d^{3}\vec{x}$$
(19)

 $\varphi(\vec{x},t)$ is the Heisenberg field operator for the positron at time t and position \vec{x} , while $\psi(\vec{x},t)$ is the corresponding electron field. The expectation value is taken in the fully interacting ground state for the system of electrons and positrons. Once Eq. (19) is known we get the annihilation rate R by comparison with the known density and rate in positronium

$$R = \frac{1}{4} R_{\text{Positronium}} (n/n_{\text{Positronium}}) = \lambda n$$
 (20)

$$A = \frac{1}{4} R_{\text{Positronium}} / n_{\text{Positronium}}$$
(21)

The factor $\frac{1}{4}$ arises from the spin averaging, when we remember that annihilation into two γ -quanta takes place from the singlet state.

The quantity (19) is related to the electron-positron Green's function

$$G_{ep}(xy; x'y') = (-i)^{2} \langle T(\psi(x)\varphi(y)\varphi^{\dagger}(y)\psi^{\dagger}(x)) \rangle$$
(22)

Then

$$n = (-i)^2 \int d^3 x \lim_{t' \to t^+ 0} G_{ep}(\vec{x}, t, \vec{x}, t; \vec{x}, t' \vec{x}, t') \qquad (23)$$

If the positron were uncorrelated with the electrons (Sommerfeld theory), we would have

$$G_{ep}(xy; x'y') = G_e(xx')G_p(yy')$$
 (24)

where

$$G_{e} (\mathbf{x} \mathbf{x}') = (-\mathbf{i}) \langle \mathbf{T} (\psi (\mathbf{x}) \psi^{\dagger} (\mathbf{x}')) \rangle$$

$$G_{p} (\mathbf{x}, \mathbf{x}') = (-\mathbf{i}) \langle \mathbf{T} (\varphi (\mathbf{x}) \varphi^{\dagger} (\mathbf{x}')) \rangle$$
(25)

In the presence of interaction, we have an integral equation for $G_{ep}(xy; x'y')$

$$G_{ep}(xy; x'y') = G_{e}(xx') G_{p}(yy') + (-i) \int d\xi \, d\eta \, d\xi' \, d\eta'$$
$$\times G_{e}(x\xi) G_{p}(y\eta) I(\xi\eta; \xi'\eta') G_{ep}(\xi'\eta'; x'y')$$
(26)

The interaction I will contain the polarization part, so we can, to start with, put I = u(x-y) where u satisfies another integral equation:

$$u(x-y) = v_{ep} (x-y) + (-i) \int dz dz' v_{ep} (x-z) G_e(zz') G_p(zz') u(z'-y)$$
(27)

 $v_{ep} (x-y) = -v_{ee}$, where v_{ee} is the Coulomb interaction between the electrons. We may neglect the self-energy parts on the propagators here, and solve Fig. (27) by using Fourier transform

$$u(\mathbf{x}) = \frac{1}{(2\pi)^4} \int d\vec{\mathbf{k}} d\omega \ \mathbf{e}^{i\vec{\mathbf{k}}\cdot\vec{\mathbf{x}}-i\omega t} u_k(\omega)$$
(28a)

$$\mathbf{v}_{ee} = \frac{1}{(2\pi)^4} \int d\vec{\mathbf{k}} d\omega \, e^{\vec{\mathbf{k}}\cdot\vec{\mathbf{x}}\cdot\vec{\mathbf{u}}\cdot\vec{\mathbf{k}}} \, \mathbf{v}_k \,, \, \mathbf{v}_k = \frac{4\pi e^2}{k^2} \,\delta \, (\omega)$$
(28b)

$$G_{e}^{0}(\mathbf{x}) = \frac{1}{(2\pi)^{4}} \int d\vec{\mathbf{k}} d\omega \frac{\vec{\mathbf{e}} \cdot \vec{\mathbf{k}} \cdot \vec{\mathbf{x}} \cdot i\omega t}{-\omega + \epsilon_{\mathbf{k}} + i\eta} + \frac{1}{(2\pi)^{4}} \int d\vec{\mathbf{k}} d\omega \frac{\vec{\mathbf{e}} \cdot \vec{\mathbf{k}} \cdot \vec{\mathbf{x}} \cdot i\omega t}{-\omega + \epsilon_{\mathbf{k}} - i\eta}$$
(28c)

We obtain

$$u_{k}(\omega) = v_{k} / \epsilon (\vec{k}, \omega), \qquad \epsilon (\vec{k}, \omega) = 1 + 2v_{k} Q_{k}(\omega)$$
$$Q_{k}(\omega) = \frac{1}{(2\pi)^{4}} \int d\vec{q} d\epsilon \quad G^{0}_{\vec{q} + \vec{k}} (\omega + \epsilon) \quad G^{0}_{\vec{q}}(\epsilon) \qquad (29)$$

 $\epsilon(\vec{k},\omega)$ is the frequency dependent dielectric constant of the electron gas. In the limit of high density the correlation correction becomes

$$n^{h.d.} = \frac{2i\lambda}{(2\pi)^6} \int d\vec{k} d\vec{p} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{u_k(\omega)}{\epsilon_k - \omega - i\eta} \left[\frac{\theta(\vec{p} - \vec{k} - k_F)\theta(k_F - p)}{\epsilon_p - \epsilon_{p-k} - \omega + i\eta} - \frac{\theta(k_F - |\vec{p} - \vec{k}|)\theta(p - k_F)}{\epsilon_p - \epsilon_{p-k} - \omega - i\eta} \right], \qquad \eta = 0^{\dagger}$$
(30)

The calculation now proceeds numerically. Various other corrections, such as self-energy effects, have been investigated. On the whole, the rates calculated by Carbotte and Kahana agree with the experimental results.

If we omit the \vec{p} -integration in Eq. (30) we get the momentumdependent annihilation rate, that is, this is the probability of annihilation with a total momentum \vec{p} . From this, the angular correlation can be computed. The positron's Coulomb force leaves the break at the Fermi surface unaltered [33] but has other subtle effects. The angular correlation curve bulges out significantly from the free electron parabola, and there is a small residual tail.

Annihilation with the core electrons has been estimated for simple metals. Since the positron is repelled by the nucleus, its wave function in the core region is small, and its Coulomb force is counteracted by the nuclear Coulomb force. Hence the core annihilation is small. This remark does not apply to the d electrons in the transition metals.

The total charge attracted by the positron must be unity [30]; Carbotte has calculated the charge distribution around the positron. It has a smaller amplitude at the centre than at a heavy impurity, but it extends further, with weaker Friedel oscillations. Annihilation in real metals is now under study by Carbotte and collaborators. For metallic sodium, the crystal field has a small effect.

5. THE EFFECTIVE MASS OF THE POSITRON

The problem of the determination of the effective mass of the positron has not been completely cleared up yet, but much progress has been achieved on the experimental side.

5.1. Definition of the effective mass m_{+}^{*} [31]

The operational definition of the effective mass m_{+}^{*} is based on an analysis of the temperature dependence of the angular correlation curve of the two- γ -annihilation. Theoretical calculations show that the positrons are thermalized before annihilation, if the temperature of the metal is not very low [32]. In practice the temperature above which thermalization occurs is roughly the Debye temperature. We shall discuss the problem later but assume thermalization now. Since the annihilation rate is practically velocity independent, the final momentum distribution $g(\vec{p})$ for low concentration of positrons can be taken to be a Maxwellian characteristic of the temperature T of the solid:

$$g(\vec{p}) = \exp(-\vec{p}^2/2m_+^*k_BT)/(2\pi m_+^*k_BT)^{2/2}$$
 (31)

where k_B is the Boltzmann constant. This equation defines m_{\pm}^{*} .

For simple normal metals the angular correlation curve for two- γ -ray annihilation manifests a sharp break at the Fermi momentum in the limit of zero temperature. Despite strong Coulomb interaction of the positron and the electrons this break can be shown to persist, at least to all orders of the perturbation theory [33]. At non-zero temperatures, when the diffuseness of the Fermi surface due to electronic momenta is still negligible, the finite momentum of the positron will cause the intensity of the γ -rays to rise at the Fermi momentum above that expected at zero temperature. This rate of rise is proportional to $T^{\frac{1}{2}}$ and is quite different from that due to other effects, such as mean free path or thermal expansion, which will be proportional to T or higher powers of T.

The probability that the γ -rays have a momentum K_z in the z direction is given by (see Eq. (9))

$$P(K_z) = \lambda \int \int dK_x dK_y \int d\vec{p} \frac{1}{(2\pi m_+^{\kappa} k_B T)^{\frac{3}{2}}} \cdot \frac{e}{e^{(E_p - \mu)/k_B T + 1}}$$
(32)

where μ is the Fermi energy of the electrons, and λ is a constant depending on experimental conditions, source strength, etc. We assume a free electron model and a spherical Fermi surface, so $E_p = p^2/2m$. Eliminate λ by taking the values of $P(K_z)$ at $K_z = k_F$ where the positron effect is maximum and $K_z = 0$, where the geometry is well-defined and

the intensity large. This gives

$$P(k_{\rm F})/P(0) = \frac{1}{\pi^{\frac{1}{2}}} \left(\frac{m_{\rm F}^{*}T}{mT_{\rm F}}\right)^{\frac{1}{2}} - \frac{1}{4} \frac{m_{\rm F}^{*}T}{mT_{\rm F}} + 0 \ (T^{\frac{3}{2}})$$
(33)

Consider next extraneous effects of the mean free path and thermal expansion. The mean free path contribution is calculated by determining the momentum distribution of the electrons in the presence of a small concentration of impurities and finding $P(k_F)/P(0)$ for zero momentum positrons. The effect of thermal expansion is easy to estimate for spherical Fermi surfaces, where the expansion simply causes a decrease in the Fermi momentum. Putting these corrections together, we obtain

$$\frac{P(k_F)}{P(0)} = \frac{1}{\pi^2} \left(\frac{m_F^* T}{m_F} \right)^{\frac{1}{2}} - \frac{1}{4} \frac{m_F^* T}{m_F} + \frac{\hbar u_F}{\pi k_B T_F 1} + \frac{T}{T_F} \ln 2 - \int_0^1 \alpha(T') dT'$$
(34)

т

 u_F and l are the Fermi velocity and the mean free path, respectively, of the electron, and α is the linear expansion coefficient. Since l varies inversely as T and α is constant or varies with higher powers of T, the correction terms are small at low temperature. A good check on the assumption of complete thermalization of the positron will be obtained by actually noting the $T^{\frac{1}{2}}$ behaviour.

The experimental requirements are as follows. To avoid complications in thermal expansion, the Fermi surface should be nearly spherical. The metal should have high T_M/T_F and Θ_D/T_F to maximize the positron effect and minimize thermal expansion (T_M is the meeting point, ε_D is the Debye temperature), but ($T_M - \Theta_D$) should be large so that thermalization of the positron occurs over a large range of temperature. Finally, it should be a good conductor. The metals suggested are

	Т _М °К	⊙ _D ° K	T_F/T_M	$\Theta_{\rm D}/{\rm T_F}$
Li	459	363	120	$0.62 imes 10^{-2}$
Na	371	150	100	0.41×10^{-2}
K	337	100	71	$0.42 imes 10^{-2}$
$\mathbf{R}\mathbf{b}$	312	58	67	$0.28 imes 10^{-2}$
Cs	301	42	60	$0.23 imes10^{-2}$
Caª	1124 (740)	230	49 (73)	$0.42 imes 10^{-2}$

(Ca has a transition at 740°K, which limits the temperature range)

5.2. Theoretical computation of m^{*}[34]

The effective mass of the positron will be changed from the bare value because of two effects. First, the positron moves in a periodic potential of the solid; this we call the 'band effective mass'. Secondly, it interacts with electrons and phonons in solids; these may together be subsumed under the 'many-body effective mass'. The phonon part is small: the electronic part is the major contribution to m^{*}₄ as measured by the experiment. The positron forms a dressed complex with electrons that screen out its long-range Coulomb field. In thermal equilibrium with the solid at temperature T, it has the same momentum distribution

as a classical particle of mass m^{*}. The band effective mass is of indirect significance. The above picture regards the positron and the electrons in metals as free particles. While for conduction electrons in alkali metals such a picture is justified by both theory and experiment, this is not a priori evident for the positron without an examination of its band structure. If the positron near the bottom of the ground-state band has an effective mass close to unity, our assumption about its free character is justified. This is indeed true, for the band mass in metals turns out to be essentially unity.

For the band effective mass we use the classical Wigner, Seitz, and Bardeen [35] method. The potential V seen by the positron in z unit cell is a weak repulsion, the resultant of a nuclear repulsion screened out over most of the volume of the unit cell by the electron is attraction. The wave function of the positron for the state of wave vector \vec{k} is written as

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \left[u_0(r) + i\vec{k}\cdot\vec{r}v(r)\right]$$
(35)

Writing

$$u_0(r) = R/r,$$
 $v(r) = (P/r^2) - (R/r)$ (36)

the equations satisfied by ${\bf R}$ and ${\bf P}$ are obtained from the Schrödinger equation

$$\frac{d^2 R}{dr^2} + \frac{2m}{\hbar^2} (E_0 - V(r)) R = 0$$
(37)

$$\frac{d^2 P}{dr^2} - \frac{2}{r^2} P + \frac{2m}{\hbar^2} (E_0 - V(r)) P = 0$$
(38)

The boundary condition to determine the ground state energy E_0 is

$$(du_0/dr)_{r_a} = 0$$
 (39)

at the cell boundary r_0 . For P the scale factor for the solution non-singular at the origin is fixed by

$$v(r_0) = 0$$
 $P(r_0) = r_0 R(r_0)$ (40)

We integrate (37) and (38) numerically and the energy obtained is

$$E_{\overrightarrow{k}} = E_0 + \frac{\hbar^2 k^2}{2m_{\overrightarrow{k}}^*}$$
(41)

which gives m^{*} directly. Table VI represents some results.

We may therefore ignore the band structure altogether for calculating the many-body effective mass m_{\star}^* . First take a static model, that is, consider the electron-positron interaction to be a screened, short-

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Metal	rs	Band mass m [*] ₊ /m	Many-body mass m*/m	Experimental value m [*] ₊ /m
Li	3.27		1.13 ^c	1.8
Na	3. 97	1.06 ^a , 1.05 ^b	1.12^{a} 1.6^{d} 1.18^{c}	1.8 ± 0.2
к	4. 95		1. 19 ^C	2.1
Rb	5.30		1.20 ^C	2.3
Cs	5.71		1.21 ^c	2.5 (?)
Ca	3. 25	1.09 ^b	1. 13 [°]	1.8

TABLE VI. EFFECTIVE MASS m_{\star}^* FOR POSITRON IN METAL

(a) Reference [34(a)] and [34(c)]

(b) Reference [37]

(c) Reference [34(b)]

(d) Reference [34(e)]

ranged Yukawa potential. Calculate the second order perturbation energy with a positron of momentum \vec{p} interacting with the Fermi sea of electrons.

$$E^{(2)} = \sum_{\substack{k \leq k_F \\ |\vec{k} + \vec{q}| \geq k_F}} |V(q)|^2 / \left(\frac{p^2}{2m} + \frac{k^2}{2m} - \frac{(\vec{p} - \vec{q})^2}{2m} - \frac{(\vec{k} + \vec{q})^2}{2m}\right)$$
(42)

Here $V(q) = -4\pi e^2 / (k_s^2 + q^2)$. The electron-electron interaction is taken into consideration through the screening wave vector k_s . Using the fact that $|\vec{p}|$ is small, we obtain the terms in p^2 :

r--

$$E^{(2)}(p) = \frac{p^{2}}{2m} \frac{4\alpha^{2}r_{s}^{2}}{3\pi^{2}} \left[-\int_{0}^{2} dq \frac{q\left\{\frac{q+2}{q+1} - \ln(1+q)\right\}}{\left\{q^{2} + \frac{1}{2}k_{FT}^{2}\left[1 + \frac{1}{q}\left(1 - \frac{q^{2}}{4}\right)\ln\frac{2+q}{2-q}\right]\right\}^{2}} + \int_{2}^{\infty} dq \frac{q\left\{\ln\frac{q+1}{q-1} - \frac{2q}{q^{2}-1}\right\}}{\left\{q^{2} + \frac{1}{2}k_{FT}^{2}\left[1 + \frac{1}{q}\left(1 - \frac{q^{2}}{4}\right)\ln\frac{2+q}{2-q}\right]\right\}^{2}}$$
(43)

Here $\alpha = (4/q\pi)^{\frac{1}{3}}$ and k_{FT} is the Fermi-Thomas screening wave vector.

The second-order contribution comes out to be negative, so m^*_+ is larger than one

$$p^2/2m_+^* = p^2/2m + E^{(2)}(\vec{p})$$
 (44)

One ought to point out that the term in p^2 is just the leading term, but there are other non-analytic terms of the type $p^4 \ln p$, so that a series expansion in powers of p is not strictly valid. It is only in an asymptotic sense that the effective mass can be defined. Using Eqs (43) and (44) for $r_s = 3.97$ in Na, one obtains $m_+^* = 1.12m$.

The interaction experienced by the positron, as we have seen above, is not really static, and one should consider the dynamic response of the electron gas. We therefore consider again the bare Green's function of the positron

$$G_{p}^{0}(\vec{k},\omega) = (\omega - \epsilon_{\vec{k}} + i\delta)^{-1}$$
(45)

and the full Green's function with interaction

$$G_{p}(\vec{k},\omega) = \left[\omega - \epsilon_{\vec{k}} - \Sigma(k,\omega)\right]^{-1}$$
(46)

 $\Sigma(\vec{k},\omega)$ is the self-energy of the positron and

$$G_{p}(\vec{k},\omega) = G_{p}^{0}(\vec{k},\omega) + G_{p}^{0}(\vec{k},\omega) \Sigma(\vec{k},\omega) G_{p}(\vec{k},\omega)$$
(47)

The infinitesimal imaginary part δ in Eq. (45) is always positive as the Fermi energy of the free positron may be taken to be vanishingly small. Including the dynamical response function $\epsilon(\vec{k},\omega)$, the self-energy Σ is

$$\Sigma(\vec{k},\omega) = \frac{i}{(2\pi)^4} \int d^3 q \ d\omega' \ G_e^0(\vec{k} - \vec{q},\omega - \omega') \ v(q) \left[\frac{1}{\epsilon(\vec{q},\omega')} - 1\right]$$
(48)

where now $v(q) = 4\pi e^2 / q^2$. We can write

$$v(q)\left(\frac{1}{\epsilon(\vec{q},\omega)}-1\right) = \frac{1}{\pi} \int_{0}^{\infty} dt \left| \operatorname{Im} \frac{v(q)}{\epsilon(\vec{q},t)} \right| \left[\frac{1}{\omega - t + i\delta} - \frac{1}{\omega + t - i\delta} \right]$$
(49)

and after the ω ' integration

=

$$\Sigma(\vec{k},\omega) = \frac{1}{8\pi^4} \int d^3 q \int_0^{\infty} dt \left| \operatorname{Im} \frac{v(q)}{\epsilon(\vec{q},t)} \right| \frac{1}{\omega - \epsilon_{\vec{k}} - \vec{q}} - t + i\delta$$
(50)

The quasiparticle energy, to a first approximation, is given by

$$E_{k} \approx \epsilon_{k} + \operatorname{Re} \Sigma(\vec{k}, \epsilon_{k})$$

$$\epsilon_{k} + \frac{1}{8\pi^{4}} \int d^{3}q P \int_{0}^{\infty} dt \left| \operatorname{Im} \frac{v(q)}{\epsilon(q, t)} \right| \frac{1}{\epsilon_{k} - \epsilon_{k} - q} t$$
(51)

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The calculation from here on requires some care, because of the logarithmic terms we described above. Hamann has carried out the numerical work and finds $m_{\pm}^{*=}$ 1.15 m in Na. Estimating exchange and other corrections in $\epsilon(\vec{k},\omega)$, he maintains that $m_{\pm}^{*}<1.18$ m in Na. Table VI represents the results. Hamada and Nakamura showed that the relativistic effects did not change this result.

Recently Mikeska has studied the positron phonon interaction and found that the momentum distribution of the positron has a part proportional to $1/p^4$, besides the usual Gaussian of Eq. (31). This long-range part dominates for p > 0.2 kp where kp is the characteristic Debye wave vector of the solid, and may raise the effective mass in Na to about 1.6 m.

5.3. Experimental data

The experiments on m^{*} measurements have been carried out by Stewart and Shand [36], and Stewart, Shand and Kim [37]. Actually they find it difficult to verify Eq. (34) and use a different analysis with the assumption that the extraneous effects are small. In the first experiment on sodium Stewart and Shand observed the angular correlation curves with the specimen at temperatures 110°, 300°, 400° and 600°K. These were fitted by a convolution of a free electron momentum distribution with a Gaussian function for resolution (cf. Eq. (32)). The resolution consists of two parts, an optical part determined by the apparatus geometry and a part due to the positron motion. The instrument resolution is separated out. Then the data are plotted in the slope method against temperature, the fitting being done by a variable effective temperature T_{eff} in the Gaussian (with m^{*}₄=m). Assuming complete thermalization T_{eff} is the actual temperature and the slope then gives the effective mass [36] (Fig. 6)

$$m_{+}^{*} = (1.9 \pm 0.4) m.$$

Stewart, Shand, and Kim repeated their experiments in several other metals, and the values quoted in Table VI show that they are quite high compared with the computed values.

Continuing their experiments they discover [39] that positrons are not always termalized before annihilation. At high temperatures, the observed effective temperature is linear with the specimen temperature. The linearity is taken as good evidence of thermalization and then the data can be appropriately characterized by an effective mass. At low temperatures the linearity is lost, and positrons do not appear to thermalize. Assuming as before a Boltzmann distribution (which is, however, not true for unthermalized positrons) the analysis of these measurements yields a positron effective temperature of about 160°K at the lowest temperature for Na. Similar results are given in Table VII.

5.4. Thermalization time [32]

The thermalization time was calculated by Lee-Whiting by assuming an interaction of the form $e^2 \exp(-k_s r)/r$ between the electron and the positron. In recent re-examination of the problem Carbotte and Arora

Metal	T°K	eV	
Li	~ 200 .	~ 0.017	
Na	160 ± 50	0.013 ± 0.004	
К	~ 100	~ 0.008	
Rb	~ 60	~ 0.005	

TABLE VII. MINIMUM POSITRON ENERGY

have derived the same formula for the rate R of energy loss (for $\hbar^2 k^2/2m = E \ll E_F$)

$$R = \frac{1}{3\pi} \frac{me^4}{\hbar^3} E F (k/k_s)$$
(52)

where

$$F(x) = \frac{5}{x^2} - \frac{56}{3} + \left(4 - \frac{6}{x^2}\right) \ln\left(1 + 4x^2\right) + \frac{1}{x} \left(18 - \frac{5}{2x^2}\right) \tan^{-1} 2x$$
(53)

For small k,

$$R \sim \frac{1}{3\pi} \frac{16}{35} \frac{e^4}{\hbar} \frac{k^6}{k_s^4}$$
(54)

An essential difference is that the Thomas-Fermi screening parameter k_{FT} replaces the semi-phenomenological screening length used by Lee-Whiting. The resulting thermalization time increases considerably because of the strong k_s^{-4} dependence. Also R depends sensitively on the temperature through the cube of the positron energy. Numerical estimates show that, while in metals at high temperatures the thermalization time is much shorter than the annihilation time, at low temperatures positrons may annihilate prior to complete thermalization. For example, in Al the positron would fall to 0.01 eV (~120°K) in a time 4×10^{-10} s, which is about twice as long as the annihilation time.

6. THEORY OF PARAMAGNETIC QUENCHING [14]

The long lifetime τ_2 arises by quenching, and we have discussed the various processes involved. Recently we have made some progress in the calculation of paramagnetic quenching, with alkali atoms acting as quenching agents in liquid ammonia [39].

A theoretical calculation of the triplet to singlet conversion in collisions of orthopositronium with atomic hydrogen was given by Massey and Mohr [14], using the Born approximation. Since the alkali atoms are hydrogen-like, we can illustrate the calculation in these systems by this simpler example. The total Hamiltonian describing the collision of positronium and the hydrogen atom is

$$H = \frac{\vec{p}^2}{2m} + \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} + \frac{e^2}{r} - \frac{e^2}{r_1} - \frac{e^2}{r_2} - \frac{e^2}{|\vec{r} - \vec{r}_1|} - \frac{e^2}{|\vec{r} - \vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$
(55)

The subscripts 1 and 2 denote the two electrons; (\vec{r}, \vec{p}) are the coordinate and momentum of the positron. The origin of the co-ordinates is taken at the proton, and recoil effects are neglected. To describe the scattering it is convenient to utilize the formulation described by Goldberger and Watson [40]. We decompose H into the incident channel Hamiltonian when electron 2 is in the hydrogen atom:

 $H = K_{c} + V$ (55')

$$K_{c} = \frac{p_{1}^{2}}{2m} - \frac{e^{2}}{r_{2}} + \frac{p^{2}}{2m} + \frac{p_{1}^{2}}{2m} - \frac{e^{2}}{|\vec{r} - \vec{r}_{1}|}$$
(56)

$$V = -\frac{e^2}{r_1} + \frac{e^2}{r} - \frac{e^2}{|\vec{r} - \vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$
(57)

The incident channel wave-function can be written as

$$\chi_{A[a]} = \frac{e^{i\vec{k}\cdot(\vec{r}+\vec{r}_{1})/2}}{(2\pi)^{\frac{3}{2}}} \tilde{\phi}_{1s}(|\vec{r}-\vec{r}_{1}|)^{3}\chi_{M}(1)\phi_{1s}(r_{2})^{2}\chi_{s}(2)$$
(58)

Here $\tilde{\varphi}_{1s}$ and φ_{1s} denote the ground state of positronium and hydrogen, respectively, ${}^{3}\chi_{M}(1)$ is the triplet spin function of the orthopositronium, and ${}^{2}\chi_{s}$ (2) is the spin function of the electron 2. Since there are two electrons in the problem, we must antisymmetrize the wave-function (58):

 $X_{A[a]} = \frac{1}{\sqrt{2}} [X_a - P_{12} X_a]$ (59)

where P_{12} interchanges particles 1 and 2. Since in the final state the positronium changes into the singlet state, the outgoing channel wave-function is

$$\chi_{b} = \frac{e^{i\vec{k'}\cdot(\vec{r}+\vec{r}_{1})/2}}{(2\pi)^{\frac{5}{2}}} \tilde{\varphi}_{1s} (|\vec{r}-\vec{r}_{1}|)^{1}\chi_{0}(1)\varphi_{1s}(r_{2})^{2}\chi_{s'}(2)$$
(60)

and after antisymmetrization

$$\chi_{A[b]} = \frac{1}{\sqrt{2}} (\chi_b - P_{12} \chi_b)$$
 (61)

The matrix element for the transition in the Born approximation can be written as (A[b] | V | A[a]), which can be reduced to

$$(A[b]|V|A[a]) = \langle x_b|V|x_0 \rangle - \langle P_{12}x_b|V|x_a \rangle$$

$$(62)$$

The first term is the direct term, the second the 'exchange' term. As

$${}^{1}X_{0}^{\dagger}(1){}^{2}X_{s'}^{\dagger}(2){}^{3}X_{M}(1){}^{2}X_{s}(2) = 0$$
(63)
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the direct term vanishes. Thus we have only the exchange term left from Eq. (62). Now

$${}^{1}\chi_{0}^{\dagger}(2){}^{2}\chi_{s}^{\dagger}(1){}^{3}\chi_{M}(1){}^{2}\chi_{s}(2) = \begin{cases} \frac{1}{\sqrt{2}}\delta_{s\downarrow} & \delta_{s'\uparrow} \\ \frac{1}{2}(\delta_{s'\downarrow} & \delta_{s\downarrow} - \delta_{s'\uparrow} & \delta_{s\uparrow} \end{pmatrix} \\ -\frac{1}{\sqrt{2}}\delta_{s\uparrow} & \delta_{s'\downarrow} \end{cases}$$
(64)

corresponding to M = 1, 0, -1. Now define

$$I = \int e^{i\vec{k}\cdot\vec{(r+\vec{r}_{2})}/2} \tilde{\phi}_{1s}(|\vec{r} - \vec{r}_{2}|) \phi_{1s}(r_{1}) V(\vec{r}_{1};\vec{r}_{1},\vec{r}_{2})$$

$$\times e^{i\vec{k}\cdot\vec{(r+\vec{r}_{1})}/2} \tilde{\phi}_{1s}(|\vec{r} - \vec{r}_{1}|) \phi_{1s}(r_{2}) d\vec{r} d\vec{r}_{1} d\vec{r}_{2}$$
(65)

For calculating cross-sections we need the square of the matrix element averaged over the initial spin state and summed over the final ones.

$$\sum_{s'} \frac{1}{2} \sum_{s} \frac{1}{3} \sum_{M} |\langle 0s' | T_{ex} | Ms \rangle|^2 = \frac{1}{4} \cdot \frac{1}{(2\pi)^6} |I|^2$$
(66)

The problem is to calculate I, which is an extremely complicated manycentre integral. However, if we assume that positroniums are thermalized, only s-wave scattering is important, as $ka_0 \ll 1$, $k'a_0 \ll 1$. A good approximation for our purpose may be obtained by calculating I for $\vec{k} = \vec{k'} = 0$. We get

$$I = -2\pi e^2 a_0^2 \times 3.75 \tag{67}$$

The differential cross-section for ortho-para conversion is then

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{(2\pi)^4}{\mathrm{fi}v_i} \int \frac{\mathrm{d}^3 \,\mathrm{k}_{\mathrm{f}}}{\mathrm{d}\Omega} \delta \left(\epsilon_i - \epsilon_{\mathrm{f}}\right) \frac{1}{4} \frac{1}{(2\pi)^6} \left|\mathbf{I}\right|^2$$

$$= 14.1 \,\mathrm{a}_0^2$$
(68)

Here we neglect the triplet-singlet energy difference and put $\vec{k_i} = \vec{k_f} \cdot S_{\sigma}$

$$\sigma_{\rm g} = 56.4 \,\pi \, {\rm a}_0^2 \tag{69}$$

A more exact calculation by Fraser gives $34\pi a_0^2$ and shows how the cross-section falls off with energy.

One can go on to the quenching action of alkali atoms, treating each atom hydrogen-like. Intuitively we should replace the scattering integral I by a corresponding integral involving the outermost alkali orbital $\psi(\mathbf{r})$

$$\mathbf{J} = \int \mathfrak{F}_{1s}\left(\left|\vec{\mathbf{r}} - \vec{\mathbf{r}}_{2}\right|\right) \psi\left(\mathbf{r}_{1}\right) \left[\frac{\mathbf{e}^{2}}{\mathbf{r}} - \frac{\mathbf{e}^{2}}{\mathbf{r}_{1}} + \frac{\mathbf{e}^{2}}{\left|\vec{\mathbf{r}}_{1} - \vec{\mathbf{r}}_{2}\right|} - \frac{\mathbf{e}^{2}}{\left|\vec{\mathbf{r}} - \vec{\mathbf{r}}_{2}\right|}\right] \mathfrak{F}_{1s}\left(\left|\vec{\mathbf{r}} - \vec{\mathbf{r}}_{1}\right|\right) \psi\left(\mathbf{r}_{2}\right) d\vec{\mathbf{r}} d\vec{\mathbf{r}}_{1} d\vec{\mathbf{r}}_{2}$$

$$(70)$$

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POSITRON ANNIHILATION

A more thorough investigation for the problem with the Li atom has been done again in the Born approximation. Besides Eq. (70), which indeed gives the dominant contribution, there are contributions from two kinds of terms. First, the screening of the nuclear charge by the inner electrons has certain exponential terms in the interaction part. Second, there are contributions when some inner electrons are also permuted - the so-called rearrangement terms. These are found to be small. For Li and Na in liquid ammonia we have found the quenching cross-section at zero momentum transfer to be

$$\sigma_q(Li) = 5.9 \times 10^{-14} \text{ cm}^2$$

 $\sigma_q(Na) = 7.2 \times 10^{-14} \text{ cm}^2$
(71)

The quenching process for these systems has not been studied accurately, but the order of magnitude seems to be correct.

We have now also calculated the quenching cross-section for the oxygen molecule [41]. A difficulty here is the enormous complication of the ground state wave-function in the oxygen molecule. Fortunately, by rephrasing the Born approximation as a variational calculation, we can, to first order, avoid the complications of the internal wave-functions, and use quite simple molecular orbitals. The quenching cross-sections for low concentration of O_2 is found to be

$$\sigma_{\rm c}(O_2) = 3.56 \times 10^{-16} \ {\rm cm}^2$$
 (72)

This is in fair agreement with the experimental data. Much still remains to be done in this area of investigation.

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Abstract

A short historical and general introduction is followed by the thermodynamical explanation of the disturbance of superconductivity by high magnetic fields and of the occurrence of an intermediate state. Meissner's effect and London's equations are discussed. The introduction of an order parameter is advocated as well as the Ginsburg-Landau refinement in which such a parameter receives a complex character as well as spatial stiffness. The value of the G-L formalism for interpretation of the mixed superconductors and of the B. C. S. theory has been stressed, a few applications, in particular of type II superconductors in the mixed state, are mentioned.

1. Superconductivity of mercury was discovered by Kamerlingh Onnes in 1911 [1] as a direct consequence of the liquefaction of helium in 1908. The first experiments were carried out on Sn, Pb and Hg, all "soft" superconductors. There is a very sharp transition temperature T_c (Fig. 1). Superconductivity is disturbed by an external magnetic field (see Ref. [2])

$$H_{c} \approx H_{c} (0) (1 - T^{2}/T_{c}^{2}),$$
 (1)

or by an electric current as soon as the magnetic field see (Fig. 2) caused by the current is equal to H_c (Silsbee's rule). In the periodic system of elements there are two separate groups (Fig. 3) of superconductors: nine elements, among which Al, In, Sn, Hg, Pb, the so-called soft superconductors, and sixteen "hard" superconductors, among which V, Nb, La, Te, U. Sometimes different modifications of one element (La, Hg) are superconductors; Bi becomes a superconductor under very high pressures. Many metallic compounds, among which CuS and BiAu₂, are also superconductors. Compounds of the β W structure (Nb₃ Sn, V₃ Ga, Mo₃ Ir) have the highest critical temperatures (up to about 20°K) and can also stand up to the highest magnetic fields.

2. At T_c there is no heat of transformation but merely a jump in the specific heat (transition of the second order). The disturbance of superconductivity in a needle or film by a parallel magnetic field H can be explained by simple thermodynamics (Ref. [3]). The electronic specific heat per unit volume (Figs 4a, 4b, 5a, 5b) in the normal state $C_n = \gamma T$ and in the superconducting state at $T > T_c/3$, is $C_s \approx 3\gamma T^3/T_c^2$. This gives at H = 0 for the difference of the free energies per unit volume:

$$F_{n} - F_{s} \approx F_{n}(0) - \frac{\gamma T^{2}}{2} - F_{s}(0) + \frac{\gamma T^{4}}{4 T_{c}^{2}}$$
 (2)

As a consequence of a longitudinal magnetic field H, G = F + H $^2/8\pi$.

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FIG.1. Specific resistance of superconductors, rather pure p and impure normal conductor ip, as a function of temperature



FIG.2. Critical magnetic field H_c separating superconducting and normal state. The critical field as a function of temperature is approximately a part of a parabola with its top at T = 0

Ia	Πa	Ша	IVa	٧a	<u>v</u> ю	VII0				Iь	пь	шь	ΙΣр	ТР	⊽ть	νīь	M
н																	He
Li	Be											в	с	N	0	F	Ne
Na	Мg											AI	Si	Ρ	s	СІ	A
κ	Ca	Sc	Ti	<u>v</u>	Cr	Мn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	к
Rb	Sr	Y	Zr	мЬ	Мо	<u>Tc</u>	Ru	Rh	Pd	Ag	۲q	<u>In</u>	Sn	SÞ	Te	J	Xe
Cs	Ba	lo	Ha	Ta	w	Re	Os	ir	Pt	Au	Hg	τı	РЬ	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												





FIG.4. a) Electronic entropy S in the normal and superconducting states as a function of temperature
 b) Electronic specific heat C in the normal and superconducting states as a function of temperature



FIG.5. a) Electronic specific heat over temperature as a function of $T^{\,2}$ for the normal and superconducting states

b) Electronic free energy as a function of T^2 for the normal and superconducting states



- FIG.6. a) Gibbs free energy G of a round wire as a function of a longitudinal ______ and a transverse _ _ _ _ magnetic field H
 - b) Induction B and magnetization M in a round wire in a longitudinal magnetic field __________ (superconducting and normal states) and in a transverse field _______ (superconducting, intermediate and normal states)

Consequently, a first-order transition to the normal state occurs at

$$\frac{H_c^2}{8\pi} \approx (F_n(0) - F_s(0)) (1 - T^2/T_c^2)^2$$
(3)

and consequently

$$H_c \approx H_c(0) (1 - T^2/T_c^2)$$
 (4)

3. If the sample has another shape or orientation, the transition starts at a lower field but ends at H_c (Ref. [4]). If the demagnetizing factor is ϵ (= 2π for a transverse cylinder and = $4\pi/3$ for a sphere), $G_s - F_s$ is $H^2/(8\pi - 2\epsilon)$. Thus the magnetic flux enters the body at $H_c(1 - \epsilon/4\pi)$ and the last trace of superconductivity disappears at H_c , the variation of the magnetization M = (B - H)/4 π being linear in H for completely homogeneous samples (Figs, 6a, 6b). At the field $H_c(1 - \epsilon/4\pi)$ the local field at the equator is equal to H_c . Between that field and H_c the body is in the intermediate state consisting of a periodic mixture of normal and superconducting regions.

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The periodicity in this mixture is of the order $(\ell \delta)^{\frac{1}{2}}$ where ℓ is the dimension in the direction of the field, while $\delta H_c^2/8\pi$ is the surface Gibbs free energy of the boundary between the normal and the superconductive state (Fig. 7).



FIG.7. Boundary structure of intermediate superconducting state. Magnetic field perpendicular to the paper

4. The connection between the heat of transition at the transition between the superconductive and the normal phase is simply given by Clapeyron's equation in which $p \rightarrow H$ and $v \rightarrow -M$:

$$\frac{\mathrm{dH}_{\mathrm{c}}}{\mathrm{dT}} = -\frac{4\pi(\mathrm{S}_{\mathrm{n}} - \mathrm{S}_{\mathrm{s}})}{\mathrm{H}} \approx -\frac{2\mathrm{TH}_{\mathrm{c}}(0)}{\mathrm{T}_{\mathrm{c}}^{2}}$$
(5)

while at $T_{\rm c}~{\rm Rutgers}^{\rm I}$ equation

$$\left(\frac{\mathrm{dH}_{\mathrm{c}}}{\mathrm{dT}}\right)^{2} = \frac{4\pi(\mathrm{C}_{\mathrm{n}} - \mathrm{C}_{\mathrm{s}})}{\mathrm{T}_{\mathrm{c}}} \approx \frac{4\mathrm{H}_{\mathrm{c}}^{2}(0)}{\mathrm{T}_{\mathrm{c}}^{2}}$$
(6)

is valid. Both expressions (5) and (6) are in agreement with formula (4). 5. The thermodynamical treatments discussed above assume that the transitions between the superconducting and normal states are reversible. This was confirmed for very homogeneous samples by the Meissner effect (Ref. [5]) according to which, in a transition from the normal to the superconducting state, the magnetic induction is expelled from the interior of the sample; so B = 0. This requires that a thin screening current should run just below the surface of a superconductor in an external field. Supposing that screening currents just below the surface are carried by n electrons with mass m and charge e per unit volume, the current density is $j_0 exp - x/\lambda$, λ being the penetration depth first calculated by Mrs. De Haas-Lorentz (Ref. [6]) and being given by

$$\lambda = \left(\frac{m c^2}{4\pi n e^2}\right)^{\frac{1}{2}}$$
(7)

where λ is of the order of $10^{-6} - 10^{-5}$ cm while the current density may go up to 10^9 amp cm⁻².

6. In 1934 Gorter and Casimir (Ref. [7]) introduced an order parameter 1-x for superconductivity which goes to zero when T approaches T_c . The

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guessed dependence (Fig.8) of the free energy density at $\rm H$ = 0 on x and T was

$$F_{s} = \frac{xH_{c}^{2}(0)}{8\pi} - \frac{1}{2} \gamma x^{\frac{1}{2}} T^{2}$$
(8)

For every T the minimum value of F_s is supposed to be realized and this value decreases and moves to the right when T increases. The dependence on T of 1-x at the minimum is given by

$$\mathbf{x} = \left(\mathbf{T}/\mathbf{T}_{c}\right)^{4} \tag{9}$$

The measured increase of λ near T_c led to a marked proportionality of 1-x and n given in (7), but also other expressions, instead of (8), may do rather well (Fig. 9).



FIG.8. Free energy density as a function of disorder parameter x=1 - y at five different temperatures. The realized equilibrium states are indicated by dot.



FIG.9. Order parameter 1 - x as a function of temperature

7. De Haas and Voogd [8] discovered in 1930 that some alloys can remain superconducting up to quite high magnetic fields. Eqs (3), (2), (5) and (6) would lead to differences in specific heats that are many times higher than those observed. In connection with this it was suggested Ref. [9] that in these superconductors may split up into superconductive regions which are smaller or thinner than λ . So magnetic induction would penetrate into these regions and the magnetic term in G could remain much smaller than $H^2/8\pi$. It remained unclear why in certain alloys (now called type II superconductors) this splitting up is possible and not in pure or almost pure soft metals. Pippard [10] called attention to the range of coherence ζ in superconductivity. In a pure superconductive metal

$$\xi_0 \approx 0.18 \, \frac{\hbar \nu_{Fe}}{k T_c} \tag{10}$$

where $\nu_{\rm Fe}$ is an average velocity of electrons at the Fermi surface, while in a dirty superconductor where the mean free path of the electrons $l < \xi_0$, the range of coherence $\xi_0 \approx l$. It may then be argued that near T_c the surface Gibbs free energy of an s-n boundary should be about $0.74 \xi_0 [T_c / (T_c - T)]^{\frac{1}{2}}$. $H_c^2/8\pi$. The fact that the magnetic field penetrates into the superconductor over a distance $\lambda = \lambda_0 (1 - T^4/T^4)^{-\frac{1}{2}}$ leads to an effective surface free energy term of negative sign of the order of $-\lambda_0(1-T^4/T_c^4)^{-\frac{1}{2}}$. $H_c^2/8\pi$. If the resulting total surface free energy is positive, one has the old-fashioned (type I) superconductors, while if it is negative one has a type II superconductor in which a splitting up into very small regions occurs in high fields. Then this type-II superconductor is in what is now called the mixed state. Schubnikov had been stating that this new phase occurs in a well-defined field range from H_{cl} to H_{c2} . (Figs 10a, 10b, 11a, 11b). Later it was found by Cribier [11] c.s., by interference of monochromatic neutrons, that the splitting occurs in a regular way of quantized vortices in agreement with the Ginsburg-Landau-Abrikosov theory (see Ref. [11]).



FIG.10. a) Induction B and magnetization M in a type II superconductor; b) demagnetization factor $\epsilon = 0$. For H_{C3} see section 12



FIG.11. a) Induction B and magnetization M in a type II superconductor; b) demagnetization factor $\epsilon = 2\pi_{\bullet}$ SUPERCONDUCTIVITY

8. The relation between the magnetic field just below the flat surface of a superconducting region and the screening current is given by one of Maxwell's equations

$$\frac{4\pi}{c}\vec{j} = \operatorname{curl}\vec{h}$$
(11)

together with London's equation (Ref. [12])

$$\operatorname{curl}\vec{j} = -\frac{n \ e^2}{m \ c} \vec{h}$$
(12)

 \vec{h} being the local value of the magnetic field. The latter equation may be found by eliminating \vec{E} from $d\vec{j}/dt = n e(\vec{E}e/m)$ and Maxwell's equation curl $\vec{E} = -(1/c (d\vec{h}/dt))$. One then gets

$$\frac{\mathrm{d}}{\mathrm{dt}} \left(\mathrm{curl}\,\vec{j} \right) = -\frac{\mathrm{n}\,\mathrm{e}^2}{\mathrm{m}\,\mathrm{c}}\,\frac{\mathrm{d}\vec{h}}{\mathrm{dt}} \tag{13}$$

and integrating this, taking the integration constant to be zero, gives the London equation (12). Taking the integration constant zero eliminates the possibility of having a homogeneous magnetic field inside the body of the superconductor (Meissner effect).

From Eqs (11) and (12) one gets, taking the surface of the superconductor in the yz plane and the magnetic field in the y-direction,

$$h_{v} = H_{0} \exp(-x/\lambda)$$
(14)

$$j_{z} = -\frac{cH_{0}}{4\pi\lambda} \exp(-x/\lambda)$$
(15)

where

$$\lambda = \left(\frac{\mathrm{m} \mathrm{c}^2}{4\pi \mathrm{n} \mathrm{e}^2}\right)^{\frac{1}{2}}$$
(7)

The Maxwell pressure P at a distance x below the surface $P = (H_0^2/8\pi) \exp(-2x/\lambda)$ may be transformed with the aid of Eqs (14, (15) and (7) into:

$$P = \frac{1}{2} m j^2 / e^2 n$$
 (16)

which, in view of j = nev, just compensates the Bernouilli pressure $-1/2 \text{ mnv}^2$, connected with the average velocity of the electrons. At the surface itself there is a total pressure jump $H_c^2/8\pi$.

9. Bohr's quantum condition (Fig. 12) for the momentum of an electron in the hydrogen atom is

$$\oint \vec{p}_{s} \cdot d\vec{s} = \oint (\vec{mv}_{s} + \frac{e}{c} \vec{A}) \cdot d\vec{s} = \ell h$$
(17)

where l is an integer. In 1948 F. London [13] proposed an application of this condition to the particles responsible for superconductivity. The main

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term in the expression for the angular momentum is then the magnetic term

$$\int \frac{\mathbf{e}}{\mathbf{c}} \, \vec{\mathbf{A}} \cdot \mathbf{d} \vec{\mathbf{s}} = \frac{\mathbf{e}}{\mathbf{c}} \int \int \vec{\mathbf{B}} \, \mathbf{dO}$$

and thus

$$\int \int BdO + \frac{mc}{e} \oint \vec{v}_{s} \cdot d\vec{s} = \int \int BdO + \frac{mc}{n e^{2}} \oint \vec{j} \cdot d\vec{s}$$
$$= \int \int BdO + \frac{4\pi\lambda^{2}}{c} \oint \vec{j} \cdot d\vec{s}$$
(18)

The expression

 $\int \int BdO + \frac{4\pi\lambda^2}{c} \oint \vec{j} d\vec{s}$

taken round a hole in a superconductor is, according to London's equation, independent of the path chosen round the hole and is called "fluxoid". In analogy with (17), London suggested that the fluxoid should be a multiple of hc/e (Fig. 13).

In 1961, however, the fluxoid through superconducting rings was found by Deaver and Fairbank and by Doll and Näbauer to be a multiple of $hc/2e = 2 \times 10^{-7}$ gauss cm⁻². This indicates that the quantum condition ought to be applied to pairs of electrons with a total charge of 2e (and a mass 2m) which fitted very well into the theoretical concepts of Fröhlich and the B.C.S. theory (see sections 10 and 15).

10. Fröhlich [14] suggested that superconductivity is due to an interaction between conduction electrons by means of virtual phonons and that hence, for a given arrangement in space, T_c should be proportional to the $h\nu$ of conformable lattice oscillators and so to the Debye temperature. Since for an average atomic mass \overline{M} of different isotopic conditions $\theta_{Deb} \propto \overline{M}^{-\frac{1}{2}}$, he predicted $T_c \propto \overline{M}^{-\frac{1}{2}}$. This was found to be in good agreement with the behaviour of almost all isotopic mixtures (exceptions: Ru, Os).





FIG.14. Difference of reflection coefficient in the far infrared by a superconductive and a normal surface



Earlier, Daunt and Mendelssohn [15] had already concluded from the absence of a Thomson heat when a supercurrent runs parallel to a tamperature gradient, that there exists an energy gap 2Δ in the electron spectrum of a superconductor. This was confirmed by the exponential disappearance of the specific heat and of the electronic thermal conductivity below about $T_c/3$.

Clear proofs (Ref. [16]) of this hypothesis were given by the absorption of electromagnetic radiation at frequencies between the infra-red and the microwave region and, most clearly, by the tunnel effects when a current passes an insulating barrier between two superconductors (Fig. 14). In the current voltage diagram sharp kinks are seen when the bottom or the top of the gap in a superconductor passes a bottom (or top) of the metal at the other side of the barrier (Figs 15, 16).

11. One may write for the free energy density given in Eq. (8) if one is in the temperature region just below T_c ,

$$F_{s} = \frac{\gamma T_{c}^{2}}{4} \left[\left\{ -1 + 4 \ \frac{T_{c} - T}{T_{c}} \right\} - 2y \ \frac{T_{c} - T}{T_{c}} + \frac{y^{2}}{4} \right]$$
(19)



FIG.16. Current through a In-Al tunnel junction as a function of voltage, In being positive, at very low temperature T_1 , and somewhat higher temperature T_2 .

where y = 1-x. Ginsburg and Landau in 1950 introduced two essential refinements into this expression. First, they replaced the scalar order parameter y = 1-x by the square $(\psi^0)^2$ of a complex order parameter and, secondly, they described the quasi-elasticity of that parameter and the interaction with a magnetic field \vec{h} by adding a space-dependent expression, taking care of gauge invariance conservation

$$\frac{1}{2m^{x}} \left| -i\hbar \vec{\nabla} \psi^{0} - \frac{e^{x}}{c} \vec{A} \psi^{0} \right|^{2} + \frac{h^{2}}{8\pi}$$

The complex famous G-L guess for the Gibbs free energy (Ref. [17]) density thus became

$$G_{s} = G_{n} + \alpha^{0} |\psi^{0}|^{2} + \frac{\beta^{0}}{2} |\psi^{0}|^{4} + \frac{1}{2m^{x}} |\left(-i\hbar\vec{\nabla} - \frac{e^{x}}{c}\vec{A}\right)\psi^{0}|^{2} + \frac{h^{2}}{8\pi}$$
(20)

where \vec{A} is a vector potential fitting to \vec{h} ; \vec{m}^{x} and e^{x} are the effective mass and charge of the electric particles responsible for superconductivity while the coefficients $\alpha^{0} = -\gamma T_{c}(T_{c} - T)/2$ and $\beta^{0} = \gamma T_{c}^{2}/8\pi$ characterize the slope and curvature as a function of $|\psi^{0}|^{2}$. The dimensionless order parameter ψ^{0} is connected with the original G-L order parameter ψ by $|\psi^{0}|^{2} = |\psi|^{2}/n_{0}$, where n_{0} is the temperature-independent electron density.

In the pure superconductor the penetration depth

$$\lambda = \left(\frac{\mathrm{mc}^{2}}{4\pi \mathrm{n}_{0}|\psi^{0}|^{2}\,\mathrm{e}^{\mathrm{x}2}}\right)^{\frac{1}{2}}$$
(21)

and the coherence length

$$\xi = \hbar (-n_0 / 2m^x \alpha^0)^{\frac{1}{2}}$$
(22)

are the characteristic lengths in characterizing the superconductor.

In particular, the ratio

$$\kappa = \frac{\lambda}{\xi}$$
(23)

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characterizes the nature of the solutions of the G-L equations which we shall discuss. Since both λ and ξ are proportional to $(T_c - T)^{-\frac{1}{2}}$, κ is a constant in the neighbourhood of T_c . Another well-known expression is

$$\kappa = \frac{\sqrt{2} e^{x}}{\hbar c} H_{c} \lambda^{2}$$
(24)

Gorkov's variation [18] of the B.C.S. theory near T permits us to derive the G-L equations for the cases of a "clean" superconductor $\xi_0 \gg \ell$ as well as of the "dirty" case ($\xi_0 \ll \ell$). A very essential conclusion is moreover that $e^x = 2e(see Sec.9)$. The expressions for κ are, near T_c ,

$$\kappa_{c1} = 0.96 \lambda_0 / \xi_0$$
 (25)

$$\kappa_{\rm d} = 0.715 \,\lambda_0/\ell \tag{26}$$

while the expressions for the Gibbs free energy of the surface of an nsboundary are 1.89 $\xi H_c^2/8\pi$ for $\kappa \ll 1$ and $-1.104 \lambda H_c^2/8\pi$ for $\kappa \gg 1$. 12. In order to find the thermodynamical solution based on (20), G_s has to be minimized with respect to variations of ψ and \vec{A} , which leads to the G-L relations in their usual form:

$$\frac{1}{2m^{x}} \left(-i\hbar \vec{\nabla} - \frac{e^{x} \vec{A}}{c} \right)^{2} \psi + \alpha \psi + \beta \psi \left| \psi \right|^{2} = 0$$
(27)

$$\vec{j} = \frac{e^{x}\hbar}{2m^{x}i} \left[\psi^{\dagger} \vec{\nabla} \psi - \psi \vec{\nabla} \psi^{\dagger} \right] - \frac{e^{x^{2}}}{m^{x}c} \left| \psi \right|^{2} \vec{A}$$
(28)

where $\psi = n_0^{\frac{1}{2}} \psi^0$, $\alpha = \alpha^0/n_0$ and $\beta = \beta^0/n_0^2$. It is confirmed that the solution is simple as long as the total Gibbs free surface energy is positive. This occurs if $\kappa < \frac{1}{2}\sqrt{2}$. One then has a type I superconductor and only small complications may occur at the surface of the metal if $1\sqrt{6} < \kappa < \frac{1}{2}\sqrt{2}$.

If $\kappa > \frac{1}{2}\sqrt{2}$ one has (Ref. [19]) a type II superconductor (see section 7) with a fully superconducting state if $0 < H < H_{c1}$, a mixed superconductive state if $H_{c1} < H < H_{c2}$, a normal state at $H > H_{c2}$ with the possibility of a thin surface layer if $H_{c2} < H < H_{c2}\sqrt{3}$ (Fig.17).



FIG.17. Critical magnetic fields as a function of temperature in a type-II superconductor. Superconductive and mixed states are separated by the H_{C1} transitions and mixed state and normal states by the H_{C2} transitions. The dotted line in between is an abstraction indicating direct transitions between superconducting and normal states if it were a type-I superconductor (see Fig. 2)

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13. The mixed state between H_{c1} and H_{c2} presents a few complications. Only for the case $\kappa \gg 1$ there is a simple expression for the value of H_{c1} :

$$H_{c1} = \frac{H_c}{\kappa \sqrt{2}} \ln \kappa = \frac{\varphi_0}{4\pi \lambda^2} \ln \kappa$$
(29)

where ϕ_0 =hc/2e is the fluxoid quantum (see section 9), but for $\rm H_{c2}$ one has the general expression

$$H_{c2} = \kappa \sqrt{2H_c}$$
(30)



FIG.18. Electronic specific heat divided by T for H=0, two magnetic field values below $H_{C1}(0)$ and two field values between $H_{C1}(0)$ and $H_{C2}(0)$ as functions of T^2



FIG.19. Electronic specific heat divided by T extrapolated to T=0. The linear slope near $H_{C2}(0)$ confirms the second-order character of the transition between mixed and normal states

At H_{cl} , quantized flux vortices φ_0 then enter the superconductor, repulsing each other with a force which decreases exponentially with the distance. This transition to the mixed state is accompanied by a steep fall of -M. If one passes into the mixed state by increasing T, keeping H constant, one passes a steep peak in the specific heat (Ref. [20]). If $\kappa \gg 1$ the energy per unit vortex length is $(\hbar c/2e\lambda)^2 \ln \lambda/\xi$ while the central field in the vortices is supposed to be about $2H_c$. The quantized vortices have the tendency to arrange themselves in a regular triangular lattice. This has been verified by means of interference of neutrons (Ref. [11]).

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When H_{c2} is approached, the average value of ψ^2 decreases linearly. The variations become less and less pronounced and, apart from the immediate neighbourhood of the surface, the normal state is reached everywhere at H_{c2} . If $\kappa \gg 1$, dM/dH is almost constant in a wide field range. Then

$$4\pi \frac{\mathrm{dM}}{\mathrm{dH}} \approx \frac{1}{1.16(2\kappa^2 - 1)}$$
(31)

FIG.20. Sketch of moving intermediate state structure in a current-carrying wire in a transverse field below $\rm H_{c}$



FIG. 21. Observed electric resistance for four currents in the case of Fig. 20

At lower κ values the magnetization curve may be remarkably hollow. 14. When intermediate state structures or if quantized vortex lines in the mixed state are moving in a direction perpendicular to the direction of the induction (Ref. [21]) this gives rise to a voltage perpendicular to the two directions mentioned (Fig. 20). This leads to an effective resistance which is usually a fraction of the resistance in the normal state (Fig.22). Hall and Nernst effects also occur. In case of inhomogeneities in the sample, (Ref. [22]), flux pinning may occur; this may lead to lower voltage or even zero voltage and thus to preservation of superconductivity, even at quite high current densities. It also leads to inhomogeneity of flux density and to magnetic hysteresis. If the Lorentz forces lead to flux jumping, this will be accompanied by sudden extra dissipation of heat (Fig.22). Large flux jumps may occur at temperatures much lower than T_c and in the absence of rapid cooling. In specific heat measurements in the presence of an external magnetic field, this may lead to an apparent shift of the specific heat to higher temperatures and thus to entropy production. Also, at the surface of samples and at the boundary between s- and n-regions irreversible processes may occur.



FIG. 22. Magnetization in the first two quadrants of a type-II superconductor with hysteresis ----- indicates a part of the complete hysteresis cycle ----- indicates the magnetization curve in the absence of hysteresis

15. The theory of Bardeen, Cooper and Schrieffer (Ref. [23]) (B.C.S. theory) ascribes the occurrence of an energy gap in superconductors to interaction between pairs of quasiparticle excitations by means of virtual phonons, the mean velocities of the interacting pairs of excitations being the same, or anyhow varying very slowly in space. The energy gap is the energy required to break up a pair. This energy gap at T = 0, (see section 10) is, according to the B.C.S. theory, given by

$$\Delta_0 = 2\hbar \,\omega_{\rm Deb} \, {\rm e}^{-1/N(0)V} \tag{32}$$

where N(0) is the density of states of one electron at the Fermi surface and -V the interaction energy between a pair of quasiparticles. Studying the dependence on temperature one gets $2\Delta_0 \approx 3.52$ k T_c and thus one gets

$$kT_{c} \approx 1.14 \hbar \omega_{\text{Deb}} e^{-1/N(0)V}$$
 (33)

which fits quite well for the cases that N(0)V < 0.4. Then $kT_c \leq 0.1 \hbar \omega_{Deb}$. It is further expected that $(dH_c/dT)_{T_c} \approx 1.74 H_c(0)/T$ and $(C_n - C_s)_{T_c} \approx 1.43 \gamma T_c$. In case of small values of N(0)V this fits better to the data than $(dH_c/dT)_{T_c} = 2H_c(0)/T$ and $(C_n - C_s)_{T_c} = 2\gamma T$ (as follows from sections 2 and 4). In the "strong coupling" cases Pb and Hg, however, the deviations from the formulae of sections 2 and 4 are in the opposite sense (where $kT_c \ge 0.1 \hbar \omega_{Deb}$). For Nb those formulae are rather well obeyed. 16. A most interesting field of research was opened in 1962 and the following years by the investigations on quantum interference (Ref. [24]). There was no time available to embody this topic, which has fascinating connections with the anomalous flow properties of liquid helium II, in the present introductory lectures.

17. In the course of time a number of applications of superconductivity have been proposed and developed, e.g., in bolometers functioning at T_c ,

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memories and switches for computors and different measuring equipment. Since the development of type II superconducting compounds with H_{c2} values of the order of 200000 ϕ , the obtaining of permanent very high magnetic fields with no or little energy dissipation belongs to the direct possibilities. Such fields may be of great use in magnetic research, in constructing particle accelerators and perhaps for thermomagnetic generation of electric energy. Fields of 140 000 ϕ have been reached (Ref. [25]) by using Nb₃Sn bands. The reduction of microwave losses in cavities (Ref. [26]) e.g., made of Pb or Nb, is another near possibility but this is not an application of type II superconductivity.

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SEMICONDUCTORS

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Abstract

Introduction. 2. The band structure of semiconductors. 2.1. Free-electron model.
 2.2. The band structure of Ge and Si. 2.3. Semiconducting compounds with zinc-blende structure.
 2.4. Energy levels in a magnetic field. 2.5. Effect of homogeneous deformation on energy levels.
 3. The optical properties of semiconductors. 3.1. Optical constants. 3.2. Optical transitions.
 3.2.1. Direct (vertical) interband transitions. 3.2.2. Indirect interband transitions. 3.2.3. Direct intraband transitions. 3.2.4. Interband transitions in a magnetic field. 4. Electrical conductivity in semiconductors. 4.1. Electrical con activity. 4.1.1. Simple parabolic band. 4.1.2. Simple ellipsoidal band. 4.3.3. Magnetoresistance.
 4.3.1. Simple parabolic band. 4.3.2. Single ellipsoidal band. 4.3.3. Magnetoresistance.

1. INTRODUCTION

In this lecture I shall try to review some typical optical and transport phenomena in semiconductors starting from the basic results of the band theory of solids. Some of these topics have already been mentioned during the course of this school, particularly as regards metals. We shall show that the description of some properties of semiconductors and metals can be given by the same formalism. The main difference between metals and semiconductors seems the fact that the number of current carriers in a semiconductor is not a constant as in metals, but can be shown to be a thermodynamic quantity depending on various factors, as, e.g. temperature, impurity content, etc. It is well known that this fact is closely related to the band structure of semiconductors. Therefore the first lecture is primarily intended as a brief review of energy-band theory with special emphasis on those aspects of the band structure of semiconductors which are important for optical and transport phenomena. In the following sections we shall examine what can be said about the optical and transport phenomena when the details of the band structure are already known and, at the same time, we shall try to determine what can be inferred about the band structure from some detailed measurements of the optical and transport properties.

2. THE BAND STRUCTURE OF SEMICONDUCTORS

2.1. Free-electron model

Let us start with the free-electron model of a semiconductor, e.g. Ge or Si, to illustrate the general method. We have chosen this special case because these crystals have been carefully investigated and their

band structures are relatively very well known. Moreover, the energy bands of Ge and Si contain many of the features which are likely to be found with other semiconductors as well. The better we understand the properties of these two crystals the easier it will be to understand other semiconductors in general.



FIG.1. The diamond-type lattice.

Ge (and also Si, diamond and grey tin) possesses the diamond structure shown in Fig.1. This structure is composed of two interpenetrating face-centred cubic lattices displaced along the body diagonal by one fourth of its length. We can also say that a primitive basis of two identical atoms at (0,0,0) and a (1/4, 1/4, 1/4) is associated with each lattice point of the face-centred cubic lattice. The primitive translation vectors are given by

$$\vec{a}_1 = \frac{a}{2} \begin{pmatrix} 1\\ -1\\ 0 \end{pmatrix}, \quad \vec{a}_2 = \frac{a}{2} \begin{pmatrix} 1\\ 0\\ -1 \end{pmatrix}, \quad \vec{a}_3 = \frac{a}{2} \begin{pmatrix} 0\\ 1\\ 1 \end{pmatrix}$$
(1)

These vectors form the primitive unit cell containing two atoms. The volume of this primitive cell is

$$\Delta_{\rm p} = \frac{{\rm a}^3}{4} \tag{2}$$

The three primitive translation vectors of the reciprocal lattice are given by the relation

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \,\delta_{ij} \tag{3}$$

Using expressions (1) and (3) we get

$$\vec{\mathbf{b}}_1 = \frac{2\pi}{a} \begin{pmatrix} 1\\-1\\1 \end{pmatrix}, \quad \vec{\mathbf{b}}_2 = \frac{2\pi}{a} \begin{pmatrix} 1\\1\\-1 \end{pmatrix}, \quad \vec{\mathbf{b}}_3 = \frac{2\pi}{a} \begin{pmatrix} 1\\1\\1 \end{pmatrix}$$
(4)

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A general vector of the reciprocal lattice is given as follows:

$$\vec{K} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$$
(5)

where n_1 , n_2 , n_3 are integers.

The Brillouin zone is the same as with the face-centred cubic lattice and is shown in Fig.2. The volume of this zone is found to be

$$\Delta_{\rm BZ} = (2\pi)^3 \frac{4}{a^3} \tag{6}$$



FIG. 2. The Brillouin zone of the diamond-type lattice.

Using the well known relation between the number of electron states (including spin) corresponding to the volume $d^3\vec{k}$ of the \vec{k} space and unit volume of the semiconductor given by

$$\frac{2}{(2\pi)^3} d^3 \vec{k}$$
 (7)

we can easily find, by taking into account expressions (2) and (6), that the number of electron states in the Brillouin zone per primitive cell is

$$\frac{2}{(2\pi)^3} \frac{a^3}{4} (2\pi)^3 \frac{4}{a^3} = 2$$

As Ge has four valence electrons per atom $(4s^2 4p^2)$ we can see that at least four bands (each doubly degenerate because of the spin) in the reduced zone scheme have to be considered.

When discussing the band structure of metals it has been shown that the general aspects of the band structure and often the intricate details of the observed Fermi surface can be explained by the freeelectron model (see Ref.[1]). We shall see that even with semiconductors the empty-lattice band structure may often serve as a useful frame of reference giving the general form and degeneracy of energy bands.

When $V(\vec{r}) = 0$, the general solution of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\vec{\mathbf{r}})\right]\psi_{n\vec{\mathbf{k}}} = \epsilon_n(\vec{\mathbf{k}})\psi_{n\vec{\mathbf{k}}}$$
(8)

is clearly a plane-wave exponential whose propagation vector has to be decomposed into the sum of a reciprocal lattice vector \vec{K} (5) and a vector \vec{k} lying in the first (reduced) Brillouin zone. The corresponding Bloch function becomes

$$\psi_{\vec{k}\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}\vec{k}}(\vec{r})$$
(9)

where

$$u_{\vec{K}}(\vec{r}) = e^{i\vec{K}\cdot\vec{r}}$$
(10)

Note that \vec{K} plays here the role of the band index n. The corresponding energy eigenvalue is given by

$$\epsilon_{\vec{K}}(\vec{k}) = \frac{\hbar^2}{2m} \left(\vec{k} + \vec{K}\right)^2 \tag{11}$$

Let us now consider the behaviour and degeneracies of the energy bands in the reduced zone for an empty diamond lattice. As usual, we shall consider two special directions in the Brillouin zone only: [001] and [111] (see Fig.3).



FIG.3. Free electron energy bands for a diamond-type lattice. The heavy lines denote the position of the highest valence band and the lowest conduction band.

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The lowest energy band is given by Eq.(11) for $\vec{k} = 0$. The minimum of this band lies at $\vec{k} = 0$ (Γ_1 point, see Fig.3) and this state (and the whole first band as well) is clearly non-degenerate. Taking into account expressions (4) and (5) we see that the next energy level at $\vec{k} = 0$ is $\epsilon (2\pi/a, 2\pi/a, 2\pi/a) = (\hbar^2/2m) 12 \pi^2/a^2$ which is eight-fold degenerate (there are eight states with this energy having eight different wave vectors $(\pm 2\pi/a, \pm 2\pi/a, \pm 2\pi/a)$. Group-theoretical analysis shows that all these functions form a basis for a reducible representation of the group of the wave vector $\vec{k} = 0$. This reducible representations:

$$\Gamma_{1}(1) + \Gamma_{2}'(1) + \Gamma_{15}(3) + \Gamma_{25}'(3) \tag{12}$$

The numbers in brackets denote the degeneracy and the subscripts refer to the corresponding irreducible representations of the group of the wave vector. The degeneracy of each state is equal to the dimension of the corresponding irreducible representation and in general (for $V(\vec{r}) \neq 0$), there will be one energy value for each irreducible representation. As the lowest level at $\vec{k} = 0$ is non-degenerate (being of type Γ_1) it can accommodate two electrons only. The next free-electron state(12) is eight times degenerate, and thus it could accommodate 16 electrons; actually, we have only 6 electrons left. Even a very rough estimate indicates that of the four levels (12), Γ'_{25} will be the lowest. This level is triply degenerate and can thus accommodate the remaining six electrons. The other three Γ levels (12) will then correspond to empty (conduction) bands.

A similar argument applies to the next higher level at $\vec{k} = 0$ having an energy of $\epsilon (4\pi/a, 0, 0) = (\hbar^2/2m) 16 (\pi^2/a^2)$ which "splits" into three levels

$$\Gamma_{2}^{\prime}(1) + \Gamma_{12}^{\prime}(2) + \Gamma_{25}^{\prime}(3) \tag{13}$$

All these levels are unoccupied and thus form excited conduction levels.

Let us consider the [111] direction (Λ points, see Fig.3). The lowest two bands having wave vectors (k, k, k) and $(2\pi/a - k, 2\pi/a - k, 2\pi/a - k)$ are of the type Λ_1 . At the end point L the energy is ($\hbar^2/2m$) 3 (π^2/a^2) and the corresponding wave vectors are ($\pi/a, \pi/a, \pi/a$) and ($-\pi/a, -\pi/a, -\pi/a$) (L₁(1) and L¹₂(1)). The next energy level at L is ϵ ($\pm 3\pi/a, \mp \pi/a, \mp \pi/a$) = ($\hbar^2/2m$) 11(π^2/a^2) with six independent wave vectors. This level "splits" into four levels

$$L_{1}(1) + L_{2}'(1) + L_{3}(2) + L_{3}'(2)$$
(14)

Starting from this point one has two non-degenerate points and two doubly degenerate points Λ_3 along [111].

A similar analysis can be performed for the [001] direction. The classification of the representations of the energy bands is given in Fig.3. The numbers in parentheses indicate band degeneracy. The heavy lines denote the position of the highest occupied and the lowest unoccupied bands.

As an illustration of wave functions corresponding to the points considered we shall write the symmetrized free-electron wave functions belonging to the irreducible representations (12) estimated by the usual method of group analysis. Let us take the eight plane waves exp [i $2\pi/a$ (±x±y±z)], for example, in the order (+++), (+--), (-+-), (--+), (---), (-++), (+-+). Then in the lowest approximation the free-electron wave functions at this point may be written as follows:

Γ ₁ :φ	= +(+++)+(+))+(-+-))+(+)-il+(-)+(-++	+)+(+	+) + (+ + -	-)]	
Γ <mark>:</mark> 2:φ	= +	+	+	+	+i[+	+	+	+	1	
Γ.'.: φ1	= +	+	-	-	-i[+	+	-	-]	
φ.	= +	-	+	-	-i[+	-	+	-]	(15)
φ	= +	-	-	+	-i[+	-	+	-]	
Γ, : Φ,	= +	+	-	_	+i[+	+	-	-]	
τ <u>ο</u> φ _α		-	+	-	+i[+	-	+	-]	
φ	= +	-	-	+	+i[+	-	-	+]	

As we have seen, the free-electron model of a semiconductor enables us to obtain a qualitative insight into the band structure scheme, the classification and degeneracy of electron states with respect to the symmetry operations of the crystal and an estimation of the corresponding symmetrized wave functions at different points of the Brillouin zone.

2.2. The band structure of Ge and Si

Let us now consider $V(\vec{r}) \neq 0$ in Eq.(8). We may imagine that the potential energy varies slowly from zero to the actual value in a real crystal. The energy bands shown in Fig.3 will then slowly vary in form, the accidental degeneracies due to V = 0 (e.g. expressions (12), (13), etc.) being removed by the effect of the periodic potential. The final order of these degenerate electron states depends on the detailed form of $V(\vec{r})$ and, in general, many possible band structures can arise.

Figures 4 and 5 show the valence and low-lying conduction band structure of Ge and Si as estimated by Herman et al. using a certain modification of the OPW method [2]. Although there is a significant distortion in the band structure passing from Fig. 3 to Figs 4 and 5, some of the basic features persist. It can be seen that the fully occupied (at least at $T = 0^{\circ}K$) valence bands are separated by the energy gap from the (empty) conduction band. In comparing the band structures of Si and Ge, we see that the form of the valence bands is approximately the same in contrast to the conduction bands where some differences exist.

When discussing some transport phenomena or optical properties of semiconductors we are mostly interested in the top of the valence band and in the bottom of the conduction bands. Therefore we shall shortly investigate them in greater detail.

Figures 4 and 5 show that the top of the valence band in Si and Ge (and in other semiconductors having the diamond-like lattice structure) is defined by the triply degenerate state Γ_{25}^{l} . If we want to study the



FIG. 4. Energy band structure of Si (see Ref. [2]).



FIG. 5. Energy band structure of Ge (see Ref. [2]).

shape of an energy band around its edge in detail we usually use a special perturbation method called $\vec{k} \cdot \vec{p}$ approximation. We shall show presently that this method makes it possible to estimate the function $\epsilon_n(\vec{k})$ in the vicinity of a point in \vec{k} space using a small number of parameters which may be estimated from experiment.

When discussing the $\vec{k} \cdot \vec{p}$ approximation we usually start with the Schrödinger equation for the periodic part of the Bloch function $u_{n\vec{k}}$. Substituting $\psi_{n\vec{k}}$ into Eq.(8) we get

$$\left[\frac{1}{2m}\left(\vec{p}+\vec{n}\vec{k}\right)^{2}+V(\vec{r})\right]u_{n\vec{k}}=\epsilon_{n}\left(\vec{k}\right)u_{n\vec{k}}$$
(16)

For any given k the set of functions $u_n \vec{k}$, obtained by letting n run over all bands, forms a complete set of functions having the same periodicity as the lattice. Let us suppose that we know all solutions $u_n \vec{k}_0$ and $\epsilon_n (\vec{k}_0)$ at a chosen point of the Brillouin zone and we want to examine the function $\epsilon_n(\vec{k})$ in the vicinity of \vec{k}_0 . Denoting

$$H_{\vec{k}_0} = \frac{1}{2m} (\vec{p} + \hbar \vec{k}_0)^2 + V(\vec{r})$$
(17)

Eq.(16) can be rewritten as follows:

$$\left[H_{\vec{k}_{0}} + \frac{\hbar}{m}(\vec{k} - \vec{k}_{0})\cdot\vec{p} + \frac{\hbar^{2}}{2m}(k^{2} - k_{0}^{2})\right] u_{n\vec{k}} = \epsilon_{n}(\vec{k}) u_{n\vec{k}}$$
(18)

For small $\vec{k} - \vec{k}_0$ we can use the usual perturbation theory taking

$$H'_{\vec{k}} = \frac{\hbar}{m} (\vec{k} - \vec{k}_0) \cdot \vec{p} + \frac{\hbar^2}{2m} (k^2 - k_0^2)$$
(19)

as a small perturbation and expressing $u_{n\vec{k}}$ in terms of the complete set of the functions $u_{n\vec{k}_0}$.¹ In practice, we use either the non-degenerate or degenerate (quasi-degenerate) perturbation theory according to the degeneracy of the unperturbed level $\epsilon_n(\vec{k}_0)$. A more detailed analysis of the $\vec{k} \cdot \vec{p}$ approximation is given in Ref.[3].

We shall now return to the top of the valence band. In this case we are dealing with a triply degenerate band at $\vec{k}_0 = 0$. Let us denote the corresponding unperturbed wave functions by $|1\rangle$, $|2\rangle$ and $|3\rangle$. It can be shown (by expanding the ϕ_i given in expression (15) in series for small arguments) that these functions transform as yz, xz, xy about the centre of the line joining the two atoms in the primitive cell. Using the perturbation approach given by Van Vleck, the energy eigenvalues at $\vec{k} \neq 0$ are found to be

$$\epsilon_{v} = (k) = \epsilon_{v} (0) + \frac{\hbar^{2}}{2m} k^{2} + \lambda$$
(20)

where λ is given by the following secular equation:

$$\begin{vmatrix} L k_{x}^{2} + M(k_{y}^{2} + k_{z}^{2}) - \lambda & N k_{x} k_{y} & N k_{x} k_{z} \\ N k_{x} k_{y} & L k_{y}^{2} + M(k_{x}^{2} + k_{z}^{2}) - \lambda & N k_{y} k_{z} \\ N k_{x} k_{z} & N k_{y} k_{z} & L k_{z}^{2} + M(k_{x}^{2} + k_{y}^{2}) - \lambda \end{vmatrix} = 0 \quad (21)$$

¹ Actually, Eq.(18) is correct for any \vec{k} . In general, we can expand $u_{n\vec{k}}$ in terms of $u_{n\vec{k}}$ without using perturbation theory. Unfortunately, this approach would need far more parameters to be estimated than the present procedure.

L, M, N denote the corresponding parts of the matrix elements of H_{\perp}^{i} (19) and may be written as follows:

$$L = \frac{\hbar^2}{m^2} \sum_{\substack{m \neq v}} \frac{\langle 1 | p_x | m \rangle \langle m | p_x | 1 \rangle}{\epsilon_v - \epsilon_m}$$
(22)
$$M = \frac{\hbar^2}{m^2} \sum_{\substack{m \neq v}} \frac{\langle 1 | p_y | m \rangle \langle m | p_y | 1 \rangle}{\epsilon_v - \epsilon_m}$$
$$= \frac{\hbar^2}{m^2} \sum_{\substack{m \neq v}} \frac{\langle 1 | p_x | m \rangle \langle m | p_y | 2 \rangle + \langle 1 | p_y | m \rangle \langle m | p_x | 2 \rangle}{\epsilon_v - \epsilon_m}$$

In fact, L, M and N are determined by experiment (e.g. by cyclotron resonance measurements).

Ν

The same method can be used to calculate the constant energy surfaces in the vicinity of the bottom of the conduction band. As can be seen from a comparison of Figs 4 and 5, the conduction band edge occurs along the $\langle 100 \rangle$ axis in Si (Δ_1 point) and along the $\langle 111 \rangle$ axis in Ge (L₁ point). In both cases $\vec{k}_0 \neq 0$. The non-degenerate perturbation calculus gives the following expression:

$$\epsilon_{c}(\vec{k}) = \epsilon_{c}(\vec{k}_{0}) + \langle u_{c\vec{k}_{0}} | H_{\vec{k}}^{t} | u_{c\vec{k}_{0}} \rangle + \sum_{m \neq c} \frac{\langle u_{c\vec{k}_{0}} | H_{\vec{k}}^{t} | u_{m\vec{k}_{0}} \rangle \langle u_{m\vec{k}_{0}} | H_{\vec{k}}^{t} | u_{c\vec{k}_{0}} \rangle}{\epsilon_{c}(\vec{k}_{0}) - \epsilon_{m}(\vec{k}_{0})}$$
(23)

Inserting H' from Eq.(19), $\epsilon_{c}(\vec{k})$ can be rewritten as follows:

$$\epsilon_{c}(\vec{k}) = \epsilon_{c}(\vec{k}_{0}) + \frac{\hbar^{2}}{2} \sum_{ij} \left(\frac{1}{m}\right)_{cij} (k_{i} - k_{0i}) (k_{j} - k_{0j})$$
 (24)

Here $(1/m)_{cii}$ is the inverse effective mass tensor given by

$$\left(\frac{1}{m}\right)_{cij} = \frac{1}{\hbar^2} \left(\frac{\partial^2 \epsilon_c}{\partial k_i \partial k_j}\right)_{\vec{k} = \vec{k}_0} = \frac{1}{m} \delta_{ij} + \frac{2}{m^2} \sum_{m \neq c} \frac{p_{cm}^{(i)}(\vec{k}_0) p_{mc}^{(j)}(\vec{k}_0)}{\epsilon_c (\vec{k}_0) - \epsilon_m (\vec{k}_0)}$$
(25)

For \vec{k}_0 parallel to [001] or [111] direction symmetry considerations show that the surfaces of constant energy in the neighbourhood of each of the conduction band minima are prolate ellipsoids of revolution. There are six ellipsoids of revolution in Si (oriented along the equivalent $\langle 100 \rangle$ directions) (see Fig.6) and only four ellipsoids in Ge (oriented along the $\langle 111 \rangle$ directions), for the surfaces lying on opposite faces

FIG. 6. The many-valley model of the conduction band of Si.





FIG. 7. The many-valley model of the conduction band of Ge.

are equivalent since they are separated by a reciprocal lattice vector (see Fig.7). The energy surfaces near the minimum energy are thus described as follows:

$$\epsilon_{c}(\vec{k}) = \epsilon_{c}(\vec{k}_{0}) + \frac{\hbar^{2}}{2m_{\parallel}} (k_{x} - k_{0x})^{2} + \frac{\hbar^{2}}{2m_{\perp}} [(k_{y} - k_{0y})^{2} + (k_{z} - k_{0z})^{2}]$$
(26)

We have chosen the Cartesian co-ordinate axes with the x axis parallel to the crystal axis in Si and to the $\langle 111 \rangle$ axis in Ge. m_{\parallel} and m_{\perp} are the longitudinal and transverse masses, respectively. The actual values of m_{\parallel} and m_{\perp} in Si and Ge are given in Table I. We see that the conduction band in Ge (and in some other semiconductors as well) consists of several non-degenerate states giving rise to the so-called

TABLE I. ENERGY BAND DATA OF SI AND GE AT HELIUM TEMPERATURE (REF. [3])

Quantity	Si	Ge
۴g	1.165 eV	0.746 eV
m _{Ii}	0.97 m	1.58 m
m _⊥	0.19 m	0.082 m
Α	$-4.1\frac{\hbar^2}{2m}$	$-13.0 \frac{h^2}{2m}$
B	1.6 $\frac{\hbar^2}{2m}$	$8.9 \frac{h^2}{2m}$
c	$3.3 \frac{\hbar^2}{2m}$	10.3 $\frac{\hbar^2}{2m}$
Δ	0.044 eV	0.29 eV

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many-valley structure. In addition to these minima which define the band edge there exist additional minima with energies somewhat higher than the band edge (e.g. see Γ_2' with Ge or L_1 with Si). Thus we see that the band structure of a semiconductor may be complicated not only by a complex (multiple) band edge but also by the presence of additional extrema lying very closely to the band edge energy but quite far apart in the Brillouin zone. This problem will be discussed in greater detail later.

Up to now we have not considered the spin of the electrons except the double degeneracy of the energy levels. In fact, the spin-orbit interaction produces significant effects in many solids, especially with heavy elements (Ge, InSb, etc.) where the splitting is one of the important factors determining the gap.

Spin-orbit interaction is an essentially relativistic effect and the Hamiltonian most commonly used is obtained as an approximation from Dirac's equation. Without entering into detail let us include it by adding to the Hamiltonian in Eq. (8) an extra term

$$\frac{\hbar}{4m^2c^2}(\vec{\sigma}\times\nabla V)\cdot\vec{p}$$
(27)

where $\vec{\sigma}$ is the Pauli spin vector. The solution of the Schrödinger equation is far more complicated now, as the wave functions are also spin-dependent. Moreover, the usual group analysis has to be extended, leading to double group representations, etc. Nevertheless, our analysis using $\vec{k} \cdot \vec{p}$ approximation can be performed in a very similar way as before, giving the modified band structure corresponding to reality.

It has been shown (see Ref. [3]) with Ge that the originally six-fold degenerate valence band splits into two higher-lying bands and a lower-lying band in the neighbourhood of the band edge, all bands being doubly degenerate (opposite spins). The \vec{k} dependence of the energy surfaces of the higher two bands is given in a certain approximation ($\hbar^2 k^2/2m << \Delta$) by the following expression:

$$\epsilon(\vec{k}) = A k^2 \pm \left[B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_z^2) \right]^{\frac{1}{2}}$$
(28)

where A, B and C are constants given by the following relations:

$$A = \frac{1}{3} (L + 2M) + \frac{\hbar^2}{2m}$$
$$B = \frac{1}{3} (L - M)$$
$$C = \frac{1}{3} [N^2 - (L - M)^2]$$

In writing this expression we have placed the zero of energy at the valence band edge. The constant energy surfaces for both these bands

are warped surfaces, the surface of the highest band being to an appreciable extent anisotropic; the second highest band is nearly spherical. In spite of this fact it is sometimes desirable to neglect the warping and treat the surfaces as if they were spherical. In calculating the average curvature of the warped surfaces we get

$$\epsilon_{1,2}(k) = \left[A \pm \sqrt{B^2 + \frac{1}{6}C^2}\right]k^2$$
 (28')

It should be added that this approximation introduces a significant error in the case of the highest valence band.

The third valence band is separated from the other ones by the effect of the spin-orbit interaction; denoting by Δ this splitting at $\vec{k} = 0$, the split-off band is described by

$$\epsilon(\vec{k}) = -\Delta + A k^2 \tag{29}$$

The values of A, B, C, and Δ , as determined by experiments with Ge and Si, are given in Table I.



FIG.8. Band structure of Ge including spin-orbit effects. (After Cardona, M., Proceedings of the Int. Conference on the Physics of Semiconductors, Dunod, Paris (1964). 181).

So far we have discussed the spin-orbit splitting at the centre of the Brillouin zone and in the immediate neighbourhood of this point. We have already mentioned that since the diamond-type crystals have a centre of inversion, the spin-orbit interaction does not split the double spin degeneracy which exists at a general point of the Brillouin zone. However, the spin-orbit interaction does split certain spatial degeneracies which occur at particular symmetry points and along special symmetry axes. The general character of the spin-orbit splitting is shown in Fig.8. Note, for example, that the spin-orbit interaction splits the Λ_3 level along the $\langle 111 \rangle$ axis in the Brillouin zone, the value of the

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splitting being roughly equal to two-thirds of Δ . This comes essentially from the fact that the spin-orbit Hamiltonian (27) acts at Γ'_{25} on a triply degenerate state while Λ_3 is only doubly degenerate.

Periodi	c table	A1	Si	Р	s	SI
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cđ	In	Sn	Sb	Te	I

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FIG.9. A section of the periodic table.

FIG. 10. The zinc-blende-type lattice.

2.3. Semiconducting compounds with zinc-blende structure

So far we have studied the band structure of some diamond-type elements of the fourth column of the periodic table as e.g. Si, Ge, diamond (see Fig.9). It has been shown that a series of semiconducting compounds can be formed between the elements of the third and fifth or second and sixth columns of the periodic table with properties very similar to the fourth-column elements. These semiconducting compounds crystallize in the cubic zinc-blende (or sphalerite) structure which is the same as the diamond form except that the two different kinds of atoms form two cubic face-centred sub-lattices displaced relatively to each other by one quarter of the body diagonal of the cube (see Fig. 10). The zinc-blende structure, like diamond, has face-centred cubic translational symmetry; therefore, the reduced Brillouin zone is the same as with the diamond structure. However, the zinc-blende lattice differs from that of diamond by not having a centre of inversion. This lower symmetry (the point group of the diamond lattice is the product group of the point group of the zinc-blende lattice times the parity group E, I) affects the band structure, removing some of the degeneracies

which occur in diamond-type crystals (Fig.11). Herman [4] has developed a semi-empirical perturbation scheme for the purpose of relating the energy band structures of diamond-type and zinc-blende-type crystals.



FIG.11. Band structure of GeAs including spin-orbit effects. After Cardona, M. Proceedings of the Int. Conference on the Physics of Semiconductors, Dunod, Paris (1964) 181.

It is well known that the diamond-type crystal is invariant under inversion about the point (a/8, a/8, a/8). If we choose the origin of co-ordinates at this point we may write

$$V^{IV}(\vec{r}) = V^{IV}(-\vec{r}) \tag{30}$$

Although the potential for a zinc-blende-type crystal is not invariant under inversion $\vec{r} \rightarrow -\vec{r}$ such a potential can always be expressed as the sum of two partial potentials one of which is symmetric and the other anti-symmetric with respect to the inversion. In general, the crystal potential of any group IV, III-V, II-VI or I-VII semiconductor with diamond or zinc-blende structure can be written as

$$V = V_{S}^{IV} + V_{A}^{IV} + \lambda \left(V_{S}^{polar} + V_{A}^{polar} \right)$$
(31)

 $V_{S,A}^{polar}$ are the perturbing terms for obtaining the potential of the polar compound from the unperturbed group-IV potential. V_A^{IV} is zero both for horizontal sequences (e.g. Ge; GaAs, ZnSb, CuBr; Sn, InSb, CdTe, AgI) and non-horizontal sequences (e.g. GeSn, GaSb, ZnTe). λ represents the strength of the perturbation and for the sake of simplicity is taken equal to 1, 2 and 3 for the III-V, II-VI and I-VII compounds, respectively. The effect of V_S^{polar} seems to be very small and, in general, it is assumed

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 $V_{S}^{polar} = 0$. A more detailed analysis including even the spin-orbit splitting shows that the forbidden band width at high symmetry points is given by second-order perturbation theory:

$$\Delta \epsilon_{\rm p} = \Delta \epsilon + D\lambda^2 \qquad D > 0 \tag{32}$$

where $\Delta \epsilon_p$ and $\Delta \epsilon$ are the energy gaps of the polar and non-polar material, respectively. This can easily be shown, for example, for the energy gap between Γ_{15} and Γ_{25}^1 , using the symmetry of the relevant wave functions. In the case where $D\lambda^2 \approx \Delta \epsilon$, the use of the simple perturbation theory is not justified and a more rigorous analysis gives

$$\Delta \epsilon_{p} = \Delta \epsilon \left(1 + \frac{2D\lambda^{2}}{\Delta \epsilon}\right)^{\frac{1}{2}}$$
(33)

Later on, we shall compare these results with experiment. This analysis has been shown to hold also for non-horizontal sequences provided one takes for the gap of the hypothetical material (e.g. GeSn) the averages of the corresponding two group-IV materials.

We have seen that the spin-orbit splitting plays a very important role in the band structure of some heavier semiconductors of the fourth column of the periodic table. It can be shown with the III-V (or II-VI) compounds that the spin-orbit splitting in these crystals can be estimated from the free-atom splitting values of the constituent atoms of the compound, by taking into account some corrections to be used when the atoms are incorporated into a solid. Spin-orbit splitting of the outermost p orbitals estimated in this way for elements given in Fig.9 are presented in Table II. Moreover, the splitting in III-V or II-VI compounds can be predicted by averaging between the splitting of the

TABLE II. ATOMIC SPIN-ORBIT SPLITTINGS IN eV OFCOLUMN II, III, IV, V AND VI ELEMENTS(AFTER F. HERMAN et al., PHYS. REV. LETTERS 11 (1963) 541)

Mg	A1	Si	p	S
0.007	0.022	0.044	0.075	0.116
Zn	Ga	Ge	As	Se
0.074	0.171	0.290	0.426	0.582
Cd	In	Sn	Sb	Te
0.227	0.458	0.709	0.973 .	1.260

two elements which make up the compound. Supposing that the corresponding contribution varies linearly across the periodic table, we write

$$\Delta^{\text{III-V}} = \frac{1}{3} \Delta^{\text{III}} + \frac{2}{3} \Delta^{\text{V}}$$

$$\Delta^{\text{II-VI}} = \frac{1}{6} \Delta^{\text{II}} + \frac{5}{6} \Delta^{\text{VI}}$$
(34)

The experimental evidence of expression (34) will be discussed later.

In addition to the semiconducting compounds mentioned above, there exists another very important group of semiconductors, namely semiconducting alloys, e.g. Ge_xSi_{1-x} , $In(As_{1-x}P_x)$, etc. Their physical parameters change continuously with composition and this fact makes it possible to obtain semiconducting materials with very interesting properties.

2.4. Energy levels in a magnetic field

The strong influence of an external magnetic field on the band structure of solids has already been discussed in detail during this course especially with regard to metals. Therefore I shall treat this problem with semiconductors very briefly.

If there is a magnetic field the Schrödinger equation can be written as follows:

$$\left[\frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A}\right)^2 + V(\vec{r})\right] \psi = \epsilon^{H} \psi$$
(35)

here \vec{A} is the vector potential of the external magnetic field which is supposed to be parallel to the z direction. Then \vec{A} may be chosen in the following way:

$$A_x = A_z = 0, \qquad A_y = +Hx \tag{36}$$

When considering the motion of electrons and holes in a semiconductor we usually use the effective-mass approximation (see Ref.[5]). For simplicity, let us suppose that the simplest parabolic band structure is given by

$$\epsilon_{\rm c}(\vec{k}) = \epsilon_{\rm g} + \frac{\hbar^2}{2m_{\rm c}}k^2; \quad \epsilon_{\rm v}(\vec{k}) = -\frac{\hbar^2}{2m_{\rm v}}k^2 \tag{37}$$

Then the Schrödinger equation (35) for electrons reduces to

$$\frac{1}{2m_{c}} \left(\vec{p} + \frac{e\vec{A}}{c} \right)^{2} F(\vec{r}) = (\epsilon_{c}^{H} - \epsilon_{g}) F(\vec{r})$$
(38)

and the corresponding solutions are found to be

$$F_{k_y k_z \ell} \propto \exp \left[i k_y y + i k_z z \right] \varphi_{\ell} (x - x_0)$$
(39)

 φ_{ℓ} being the oscillator wave function for the Landau level with index ℓ taking on the values 0, 1, 2... $x_0^{=} - k_y \hbar c/e H$ denotes the x-component of the centre of the magnetic orbit. In the lowest approximation the solutions of the Schrödinger equation (35) are given as

$$\psi_{c\,\mathbf{k}_{\mathbf{y}}\mathbf{k}_{\mathbf{z}}\ell} = u_{c}(\vec{r}) F_{\mathbf{k}_{\mathbf{y}}\mathbf{k}_{\mathbf{z}}\ell} (\vec{r})$$
(40)

The energy eigenvalues are

$$\epsilon_{c\,k_{z}\ell}^{H} = \epsilon_{g} + \frac{\hbar^{2}}{2m_{c}} k_{z}^{2} + \hbar \omega_{c} \left(\ell + \frac{1}{2}\right)$$
(41)

where

$$\omega_{\rm c} = \frac{\rm e \, \rm H}{\rm m_{\rm c} \, \rm c} \tag{42}$$

Similar equations can be written for the valence band (37) as well

$$\epsilon_{\mathbf{v}\,\mathbf{k}_{\mathbf{z}}\ell}^{\mathrm{H}} = -\frac{\hbar^{2}}{2m_{v}} \,\mathbf{k}_{\mathbf{z}}^{2} - \hbar\,\omega_{v}\left(\ell + \frac{1}{2}\right) \tag{43}$$

The general character of the energy levels in a magnetic field is shown in Fig. 12.



FIG. 12. Landau levels for simple parabolic bands.
The degeneracy of the Landau levels (41) with respect to k_y values gives rise to a very interesting behaviour of the density of states. If the external magnetic field is absent, the usual density of states per unit energy interval and unit volume (including spin) is given by

$$g_{c}(\epsilon) = 2 \sum_{\vec{k}} \delta[\epsilon_{c}(\vec{k}) - \epsilon]$$
(44)

Using the well-known formula

$$\int d^{3}\vec{k} \,\delta[f(\vec{k})] = \int \frac{dS}{|\nabla_{\vec{k}}f(\vec{k})|}$$

$$f(\vec{k}) = 0$$
(45)

where the integration is performed over a surface given by $f(\vec{k}) = 0$, we easily get

$$g_{c}(\epsilon) = \frac{1}{2\pi^{2}} \left(\frac{2m_{c}}{\hbar^{2}}\right)^{\frac{3}{2}} \sqrt{\epsilon - \epsilon_{g}}$$
(46)

Similarly, in the presence of a magnetic field Eq.(44) becomes

$$g_{c}^{H}(\epsilon) = 2 \sum_{\ell} \sum_{k_{y}, k_{z}} \delta(\epsilon_{c k_{z} \ell}^{H} - \epsilon)$$
(47)

giving

$$g_{c}^{H}(\epsilon) = \frac{1}{4\pi^{2}} \left(\frac{2m_{c}}{\hbar^{2}}\right)^{\frac{3}{2}} \hbar \omega_{c} \sum_{\ell}' \left[\epsilon - \epsilon_{g} - \hbar \omega_{c} \left(\ell + \frac{1}{2}\right)\right]^{-\frac{1}{2}}$$
(48)

where the sum is understood to extend over all integers ℓ for which the summand is real. Note that the singular character of the density of states is characteristic for a one-dimensional band.

A similar expression holds for holes in the valence band as well. Figure 13 shows the density of states both for the valence and conduction bands, for H = 0 and $H \neq 0$.

So far, we have considered the simple parabolic band structure of the valence and conduction bands having their extrema at $\vec{k} = 0$. Unfortunately, in general this procedure cannot be used with complex or degenerate bands; this problem is far more complicated and cannot be discussed here in detail (see Fig.14). The reader is referred to the original articles [5].

The influence of the external magnetic field on some optical and transport phenomena in semiconductors will be discussed later.



FIG.13. Density of states in the presence of a magnetic field for simple parabolic bands. The zero field case is also shown.



FIG.14. Landau levels $(\vec{k} = 0)$ in Ge (see Ref. [5]).

2.5. Effect of homogeneous deformation on energy levels

We shall show presently that the application of the external stress on a semiconductor has a profound effect on its band structure. Therefore we can expect that those properties of semiconductors which are sensitive to details of the energy bands will change significantly with elastic deformation. In fact, there are two types of experiments used in this field. The first type of experiments uses isotropic or hydrostatic stress, the second an anisotropic stress. While the experiments of the first type give rise to the shift of the energy levels, the use of uniaxial compression or tension in general lowers the symmetry present in the free single crystal and causes the splitting of degenerate levels. We can hardly expect that the pressure dependence of the energy levels will be the same for all levels; on the contrary, the shifting of different levels is very different according to the symmetry of the wave functions of the states considered. In what follows we shall concentrate on the band edges which play a dominant role in both the optical and transport phenomena in semiconductors.

When calculating the constant energy surfaces in the vicinity of the band edges we have used the perturbation theory, namely the $\vec{k} \cdot \vec{p}$ approximation. It will be shown presently that a similar approach can be used even with semiconductors under external stress. However, one point should be emphasized in this connection. Since the deformed single crystal has a different periodicity compared to the free crystal, the perturbing term cannot simply be defined as the difference between the Hamiltonians for the deformed and undeformed crystal, and the usual perturbation approach cannot be directly applied in this case. To overcome this difficulty we have to introduce a transformation which ensures that the deformed crystal has the same periodicity as the undeformed one.

We shall start with the Hamiltonian of the undeformed crystal; let us denote it $H_0(\vec{r}, \vec{p})$. Then we have

$$H_{0}(\vec{r}+\vec{a}_{j},\vec{p}) = H_{0}(\vec{r},\vec{p})$$
(49)

where \vec{a}_i are the primitive translation vectors as defined by Eq.(1). Similarly the Hamiltonian H (\vec{r}, \vec{p}) of the deformed crystal is invariant under translations \vec{a}_i^t given by

$$\vec{a}_{i}' = (1 + \vec{\epsilon}); \vec{a}_{i}$$
(50)

i.e.

$$H(\vec{r}, \vec{p}) = H(\vec{r} + \vec{a}'_{i}, \vec{p})$$
 (51)

 $\vec{\epsilon}$ in Eq.(50) is the strain tensor.

Let us introduce a transformation to a new co-ordinate system in which the position vector \vec{r}' is given as

$$\vec{\mathbf{r}} = (1 + \vec{\epsilon}) : \vec{\mathbf{r}}' \tag{52}$$

Similarly, the momentum operator $\vec{p}' = \frac{\hbar}{i} \nabla'$ is related to \vec{p} by

$$\vec{p} = (1 + \vec{\epsilon})^{-1} : \vec{p}'$$
 (53)

The Hamiltonian (51) given in the $\vec{r'}$ is found to be

$$H(\vec{r}, \vec{p}) = H((1 + \vec{\epsilon}) : \vec{r'}, (1 + \vec{\epsilon})^{-1} : \vec{p'})$$

= H'(\vec{r'}, \vec{p'}, \vec{\epsilon}) (54)

The strain tensor $\vec{\epsilon}$ is contained in H' as a small tensor parameter. We shall show now that H' as a function of $\vec{r'}$ has the same periodicity as H₀:

$$H'(\vec{r'} + \vec{a}_i, \vec{p'} \cdot \vec{\epsilon}) = H((1 + \vec{\epsilon}) : (\vec{r'} + \vec{a}_i), \vec{p})$$

$$= H(\vec{r} + \vec{a}'_i, \vec{p})$$

$$= H(\vec{r}, \vec{p})$$

$$= H'(\vec{r'}, \vec{p'}, \vec{\epsilon})$$

(55)

Using this fact we can expand $H'(\vec{r}, \vec{p'}, \vec{\epsilon})$ in terms of $\vec{\epsilon}$

$$H'(\vec{r'}, \vec{p'}, \vec{\epsilon}) = H_0(\vec{r'}, \vec{p'}) + \sum_{ij} D_{ij}(\vec{r'}, \vec{p'})\epsilon_{ij} + \dots$$
(56)

In substituting $\vec{r'}$, $\vec{p'}$ by \vec{r} , \vec{p} the first term on the right-hand side in expression (56) is identical with the Hamiltonian of the undeformed crystal given by expression (49). The second term may be regarded as a small perturbation.

Let us apply this procedure to the $\vec{k} \cdot \vec{p}$ approximation discussed in section 2.3. The unperturbed Hamiltonian is identical with H_{k_0} and the perturbation term is given as follows:

$$H' = H'_{k} - \frac{1}{m} \sum_{ij} \epsilon_{ij} (p_{i} + \hbar k_{0i}) p_{j}$$

$$- \frac{\hbar}{m} \sum_{ij} \epsilon_{ij} (k_{i} - k_{0i}) p_{j} + \sum_{ij} V_{ij} \epsilon_{ij}$$
(57)

where

$$V_{ij} = \left[\frac{\partial V\left((1+\epsilon):\vec{r}^{\dagger}\right)}{\partial \epsilon_{ij}}\right]_{\vec{\epsilon}=0}$$
(58)

Before proceeding further it should be noted that in calculating the matrix elements we shall neglect higher-order terms than ϵ_{ij} , $(k_i - k_{0i})^2$ and ϵ_{ij} ($k_i - k_{0i}$) because their contribution is relatively small compared to the remaining terms. At the same time we shall also neglect the displacement of the band edge in the \vec{k} space due to the third term in Eq.(57). First we shall discuss the non-degenerate case as, for example, the conduction band of Ge or Si. Then the energy $\epsilon_c(\vec{k})$ can be written as follows:

$$\epsilon_{c}(\vec{k}) = \epsilon_{c}(\vec{k}_{0}) + \frac{\hbar^{2}}{2} \sum_{ij} \left(\frac{1}{m} \right)_{cij} (k_{i} - k_{0i}) (k_{j} - k_{0j}) + \sum_{ij} \langle u_{c\vec{k}_{0}} | D_{ij} | u_{c\vec{k}_{0}} \rangle \epsilon_{ij}$$

$$(59)$$

The matrix element $\langle u_{c\vec{k}_0} | D_{ij} | u_{c\vec{k}_0} \rangle$ is called the deformation potential Ξ_{ij} and is given by

$$\Xi_{ij} = -\frac{\hbar^2}{m} \langle u_{c\vec{k}_0} | \frac{\partial^2}{\partial x_i \partial x_j} | u_{c\vec{k}_0} \rangle + \langle u_{c\vec{k}_0} | V_{ij} | u_{c\vec{k}_0} \rangle$$

$$+ \frac{\hbar^2}{m} k_{0i} k_{0j}$$
(60)

This can be written, in general, as follows:

$$\Xi_{ij} = \Xi_{d} \delta_{ij} + \frac{\kappa_{0i} \kappa_{0j}}{\kappa_{0}^{2}} \Xi_{u}$$
(61)

The shift in energy of the conduction band edge of the r-th valley is thus given by

$$\delta \epsilon_{c k_{r}} = \sum_{ij} \left(\Xi_{d} \delta_{ij} + \frac{k_{ri} k_{rj}}{k_{r}^{2}} \Xi_{u} \right) \epsilon_{ij}$$
(62)

Note that $\Xi_d + \frac{1}{3} \Xi_u$ is the deformation potential for pure dilatation, Ξ_u is the deformation potential for pure shear. Typical values for Ge are as follows: $\Xi_d \approx -7 \text{ eV}$, $\Xi_u \approx 18 \text{ eV}$.

As an example, let us consider the conduction band of Si. In this case the vectors \vec{k}_r lie along the crystallographic axis. Supposing that a stress is applied in the (100) direction, $\epsilon_{22} = \epsilon_{33} \neq \epsilon_{11}$, $\epsilon_{12} = \epsilon_{13} = \epsilon_{23} = 0$. Then the shift in energy of the conduction band minima is given as follows:

$$\vec{k}_{r} = (\pm k_{r}, 0, 0)$$

$$\delta \epsilon_{c} = \Xi_{d} (\epsilon_{11} + \epsilon_{22} + \epsilon_{33}) + \Xi_{u} \epsilon_{11}$$

$$\vec{k}_{r} = (0, \pm k_{r}, 0), \qquad (0, 0, \pm k_{r})$$

$$\delta \epsilon_{c} = \Xi_{d} (\epsilon_{11} + \epsilon_{22} + \epsilon_{33}) + \Xi_{u} \epsilon_{22}$$
(64)

Without entering into detail we see that in general different valleys are shifted in different ways according to their positions with regard to the external stress. Of course, similar considerations are valid for the conduction band of Ge and for other semiconductors as well.

The influence of the external stress on a degenerate band, for example the valence band of Ge, is far more complicated and we shall not discuss it in detail here [6]. Nevertheless, the calculation proceeds in a very similar way as with the $\vec{k} \cdot \vec{p}$ approximation. If spin is

neglected, the relevant secular equation has the same form as Eq.(21), only the matrix elements include additional terms corresponding to the perturbation Hamiltonian (57). For example, the matrix element $\langle 1|\mathbf{H}_{1}^{\prime}|1 \rangle$ corresponding to the matrix element $\langle 1|\mathbf{H}_{1}^{\prime}|1 \rangle$ is now given by

$$L k_{x}^{2} + M (k_{y}^{2} + k_{z}^{2}) + \ell \epsilon_{xx} + m (\epsilon_{yy} + \epsilon_{zz})$$
(65)

where l and m are defined by

$$\ell = \langle 1 | D_{xx} | 1 \rangle; \quad m = \langle 1 | D_{yy} | 1 \rangle$$
(66)

A similar method of calculation can be used even if we take the spin into account. In this case, instead of expression (28), we get the following expression:

$$\epsilon(\vec{k}) = A k^2 + \frac{1}{3} (\ell + 2m) (\epsilon_{11} + \epsilon_{22} + \epsilon_{33}) \pm \sqrt{E_{\vec{k}}^2 + E_{\vec{k}}^2 + E_{\vec{k}}^2}$$
(67)

Here $E_{\vec{k}}$ is the same expression as in Eq.(28). E_{ϵ} includes terms depending on ϵ_{ij} , $E_{\epsilon\vec{k}}$ depends both on ϵ_{ij} and k_i . In the absence of strain Eq.(67) reduces to Eq.(28). Otherwise uniaxial stress destroys the cubic symmetry of the crystal and removes the degeneracy of the bands, at $\vec{k} = 0$ by an amount of $2E_{\epsilon}$. It should be noted that hydrostatic pressure gives rise to the shift of the bands only.

3. THE OPTICAL PROPERTIES OF SEMICONDUCTORS

It is well known that optics played a dominant role in the study of the electronic structure of atoms and molecules. Similarly the study of the optical properties of semiconductors is one of the most powerful methods providing a great deal of information about their band structure. Therefore this section will be mainly devoted to a discussion of the optical properties of semiconductors, especially of those with diamond and zinc-blende structures, and their relationship to the band structure of these materials as reviewed in section 2.

3.1. Optical constants

When discussing the optical properties of semiconductors we usually start the macroscopic description of these phenomena based on Maxwell's equations for an uncharged medium

$$\nabla \times \vec{H} = \frac{1}{c} \frac{\partial \vec{D}}{\partial t} \qquad \nabla \cdot \vec{D} = 0$$

$$\nabla \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t} \qquad \nabla \cdot \vec{B} = 0$$
(68)

Denoting \vec{P} the polarization of the medium we can write

$$\vec{\mathbf{D}} = \vec{\mathbf{E}} + 4\pi \vec{\mathbf{P}} \tag{69}$$

The properties of matter are introduced into Eq.(68) phenomenologically as represented by a dielectric constant ϵ and a permeability μ , without taking into account the mechanism of the interaction of matter and external fields. The microscopic quantum-mechanical description of these phenomena will be given later. Now we shall try to obtain some general information which can be drawn from macroscopic considerations and which are independent of special microscopic models.

As we are interested in non-magnetic materials (μ = 1), only the dielectric constant ϵ needs to be considered. We shall limit ourselves below to the linear relations between \vec{D} and \vec{E} so that we have in general

$$D_{i}(\vec{r},t) = \sum_{j} \int_{\infty}^{t} dt' \int d^{3}\vec{r}' \epsilon_{ij} (\vec{r},\vec{r}',t,t') E_{j}(\vec{r}',t')$$

Note that, following the principle of causality, the electric displacement \vec{D} at a time t is determined by all electric fields at all times previous to t. It can easily be seen that ϵ_{ij} can be interpreted as the electric displacement response in \vec{r} at time t to a unit delta-function electric field pulse $\vec{e}\delta(t')\delta(\vec{r'}), |\vec{e}| = 1$.

Supposing that the properties of the material do not change with time (time uniformity), we can write

$$\epsilon_{ii}(\vec{\mathbf{r}},\vec{\mathbf{r}}',t,t') = \epsilon_{ij}(\vec{\mathbf{r}},\vec{\mathbf{r}}',t-t')$$
(70)

It is well known that crystals are not spatially homogeneous and in fact it holds that

$$\epsilon_{ij}(\vec{\mathbf{r}},\vec{\mathbf{r}}',t-t') = \epsilon_{ij}(\vec{\mathbf{r}}+\vec{a},\vec{\mathbf{r}}'+\vec{a},t-t')$$
(71)

where a is any translation of the translation group. Fortunately, it can be shown that with most homopolar semiconductors, the spatial inhomogeneity does not play any serious role so that we can write to a good approximation

$$\epsilon_{ij}(\vec{\mathbf{r}},\vec{\mathbf{r}}',t,t') = \epsilon_{ij}(\vec{\mathbf{r}}-\vec{\mathbf{r}}',t-t')$$
(72)

Using the Fourier expansion for \vec{E} , \vec{D} and ϵ

$$E_{j}(\vec{r},t) = \int \int E_{j}(\vec{k},\omega) \exp[i(\vec{k}\cdot\vec{r}-\omega t)] d^{3}\vec{k} d\omega$$
(73)

$$D_{i}(\vec{k},\omega) = \sum_{j} \epsilon_{ij} (\vec{k},\omega) E_{j}(\vec{k},\omega)$$
(74)

where

$$\epsilon_{ij}(\vec{k},\omega) = \int_{0}^{\infty} d\tau \int d^{3}\vec{R} \exp\left[-i(\vec{k}\cdot\vec{R}-\omega\tau)\right]\epsilon_{ij}(\vec{R}\tau)$$
(75)

is the tensor of the complex dielectric constant. In these formulas \vec{k} and ω are taken to be real quantities. Separating the real and complex part of the dielectric constant we can write

$$\epsilon_{ij}(\vec{k},\omega) = \epsilon_{1ij}(\vec{k},\omega) + i\epsilon_{2ij}(\vec{k},\omega)$$
(76)

Because of the fact that a real \vec{D} has to correspond to a real \vec{E} , it holds that

$$\epsilon_{ij}(\vec{k},\omega) = \epsilon_{ij}^*(-\vec{k},-\omega)$$
(77)

Moreover, it can be shown that with crystals (or other substances) having a symmetry centre

$$\epsilon_{ii}(\vec{k},\omega) = \epsilon_{ii}(\vec{k},\omega) \tag{78}$$

The two parts of the complex dielectric tensor $\epsilon_{1ij}(\vec{k},\omega)$ and $\epsilon_{2ij}(\vec{k},\omega)$ are related to one another by the Kramers-Kronig relations

$$\epsilon_{1ij}(\vec{k},\omega) - \delta_{ij} = \frac{1}{\pi} \mathscr{P} \int_{-\infty}^{\infty} \frac{\epsilon_{2ij}(\vec{k},\omega')}{\omega' - \omega} d\omega'$$

$$\epsilon_{2ij}(\vec{k},\omega) = -\frac{1}{\pi} \mathscr{P} \int_{-\infty}^{\infty} \frac{\epsilon_{1ij}(\vec{k},\omega') - \delta_{ij}}{\omega' - \omega} d\omega'$$
(79)

Here \mathscr{P} stands for the principal values. The derivation of the dispersion relations contains only three major assumptions: causality, linearity and bondedness of the left-hand side quantities. I do not intend to discuss them in detail because this has been done by des Cloizeaux in this book[7].

We have shown that in general the dielectric constant is a tensorial quantity having different numbers of components in different crystal lattices. It reduces to a scalar quantity for crystals having cubic symmetry (or for isotropic materials).

We have also seen that in general the dielectric constant depends on the wave vector \vec{k} . However, it can be shown that this dependence can be neglected in the case when the wavelengths of photons in the medium are much longer than the atomic distances, i.e.

$$\lambda_{\rm m} >> a$$
 (80)

This condition is fulfilled up to the wavelength in the X-ray range; nevertheless there exist some optical phenomena (e.g. optical activity) in which the spatial dispersion plays a fundamental role. Supposing that condition (80) is fulfilled and denoting $\epsilon(0,\omega) = \epsilon(\omega)$, it follows from Eq.(77) that

$$\begin{aligned} \epsilon_1(\omega) &= \epsilon_1(-\omega) \\ \epsilon_2(\omega) &= -\epsilon_2(-\omega) \end{aligned} \tag{81}$$

Note that when using in (1) $(4\pi/c)_{\vec{j}}$ instead of (1/c) $\frac{\partial \vec{D}}{\partial t}$ it can be

shown that the properties of the medium can be described by a complex conductivity tensor $\sigma_{ij}(\omega) = \sigma_{1ij}(\omega) + i\sigma_{2ij}(\omega)$. By comparing the relevant expression we can easily get the following relations for our special case:

$$\sigma_1 = \frac{\omega}{4\pi} \epsilon_2 \quad ; \qquad \sigma_2 = \frac{\omega}{4\pi} \ (1 - \epsilon_1) \tag{82}$$

Let us revert to the optical properties of solids. When discussing the propagation of electromagnetic plane waves in crystals it is well known that instead of using ϵ_{1ij} and ϵ_{2ij} which are not directly determined by optical measurements, new quantities, the principal indices of refraction N_i, are introduced. With cubic crystals or isotropic materials there exists only one (complex) index of refraction N defined by the following relation:

$$N(\omega) = n(\omega) + ik(\omega) = (\epsilon_1 + i\epsilon_2)^{2}$$
(83)

here n is the ordinary (real) refractive index and k is the extinction coefficient; both quantities are real and positive. The relation between ϵ_1, ϵ_2 and n, k may be deduced at once from Eq.(83)

$$\epsilon_1 = n^2 - k^2, \quad \epsilon_2 = 2 n k$$
 (84)

Moreover, in practice one often uses the absorption coefficient α defined as follows:

$$\alpha = \frac{2 k \omega}{c} = \frac{4 \pi k}{\lambda} = \frac{4 \pi \sigma_1}{nc} = \frac{\omega \epsilon_2}{nc}$$
(85)

The physical meaning of these quantities is easily seen from the following expression describing the propagation of an electromagnetic

plane wave along the x axis in a crystal

$$\vec{E}(x,t) = \vec{E}_0 \exp\left[-i\omega\left(t-N\frac{x}{c}\right)\right] = \vec{E}_0 \exp\left(-\frac{k\omega x}{c}\right)\exp\left[-i\omega\left(t-\frac{n}{c}x\right)\right]$$
(86)

This expression represents a wave travelling with velocity c/n and suffering attenuation characterized by the extinction coefficient k , (provided that attenuation is not too great). The absorption coefficient α is defined in terms of the exponential fall-off in intensity by means of the equation

$$\left|\vec{E}\right|^2 = \left|\vec{E}_0\right|^2 \exp\left(-\alpha x\right) \tag{87}$$

The rate of loss of energy per unit volume due to Joule heating is given by the expression

$$\frac{1}{2}\sigma_1(\omega)\vec{E}\cdot\vec{E}^* = \frac{\omega}{8\pi}\epsilon_2\vec{E}\cdot\vec{E}^*$$
(88)

The functions $n(\omega)$ and $k(\omega)$ are, of course, again related to each other by Kramers-Kronig relations. This means that if we measure n and k at one frequency we can find arbitrary values for them. However, if we consider $n(\omega)$ and $k(\omega)$ as functions of ω in the interval $(0,\infty)$, we need to know only one of these functions because the second quantity is determined using the Kramers-Kronig relations.

Note that, following Eq.(84), if k = 0, $n = \sqrt{\epsilon_1}$; i.e. the propagation of electromagnetic waves is not damped. On the other hand, if $\epsilon_1 < 0$, n = 0, $k = \sqrt{-\epsilon_1}$ this means that the wave is damped but this damping is not accompanied by absorption. These conditions correspond to the total reflection(see Eq.(91) below).

We shall be interested below in the optical properties of semiconductors in the visible and ultraviolet region. However, in this region the direct estimation of n and k is not possible and we have to use reflectivity measurements. It is well known that at normal incidence the complex constant of reflection r is given as

$$r = \frac{N-1}{N+1} \tag{89}$$

r can be written in the form

$$\mathbf{r} = \sqrt{\mathbf{R}} \exp\left(\mathbf{i}\,\boldsymbol{\varphi}\right) \tag{90}$$

where R is the reflection constant

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$
(91)

and ϕ is the phase angle. Provided that we know the reflection constant R in the whole frequency range we can find the phase angle using the

Kramers-Kronig relations

$$\varphi(\omega) = -\frac{\omega}{\pi} \int \frac{1}{\xi^2 - \omega^2} \, \lg \, \mathrm{R}(\xi) \, \mathrm{d}\xi \tag{92}$$

This is the way in which the optical constants n and k are usually determined in practice. In fact, we always know an optical constant only in a limited range of frequencies. Fortunately, the form of the dispersion relation is such that e.g. the values of $R(\xi)$ in Eq.(92) for ξ very distant from ω are of little importance and can thus be approximately estimated using an extrapolation procedure.

3.2. Optical transitions

In this section we shall deal with the quantum mechanical calculation of the spectral dependence of the dielectric constant. In doing this we can use different methods corresponding to different points of view. A very general and elegant approach was used by des Cloizeaux in his lecture in this book. It might be useful to summarize briefly the main points of this general formulation.

In this case we are studying the dielectric response of a solid to a small external perturbation represented by a monochromatic light wave; let us denote the perturbing Hamiltonian H[']. Then the total Hamiltonian is given by

$$H = H_0 + H' \tag{93}$$

and the corresponding density matrix ρ obeys the following equation:

$$i\hbar\dot{\rho} = [H,\rho]$$
 (94)

Now the electric current induced by the light wave is given as

$$\vec{j} = Tr \langle \rho \, \vec{j}_{op} \rangle$$
 (95)

where j_{op} is the current operator. In calculating the density matrix $\rho = \rho_0 + \rho_1$, a linearization procedure is used to simplify Eq.(94)

$$i\hbar\dot{\rho}_{1} = [H_{0}, \rho_{1}] + [H', \rho_{0}]$$
 (96)

Substituting the solution of Eq. (96) into (95) we find after some further algebraic rearrangement that the expression for the current density has the same form as the corresponding macroscopic equation. By comparing the relevant parts we get an explicit expression for the complex dielectric constant.

Naturally, there is no sense in going into detail here and thus repeating the lecture by des Cloizeaux. On the contrary, it seems to me of interest and useful to treat the same problems from a somewhat different point of view by using a simpler formulation.

3.2.1. Direct (vertical) interband transitions

In fact we have to calculate only either the real part $\epsilon_1(\omega)$ or the imaginary part $\epsilon_2(\omega)$, because the other quantity – as we have shown in the previous section – can be determined by using the Kramers-Kronig relations. As usual, we shall choose ϵ_2 describing absorption (one-photon) processes in solids while ϵ_1 describing dispersion (two-photon processes) is more complicated. Moreover, we shall see that the spectral dependence of ϵ_2 is very closely related to the band structure, providing much valuable information about the form of the energy bands.

In general, the total Hamiltonian describing the solid and the radiation as a whole can be written as follows:

$$H = H_{el} + H_{rad} + H_{el, rad} + H_{phon} + H_{el, phon} + H_{phon, rad}$$
(97)

As we are not directly interested in lattice vibration effects for the time being, we shall not consider the last three terms in expression (97). Moreover, for small perturbations represented by the light wave, we even do not have to consider the term H_{rad} describing the properties of the radiation field in the semiconductor and thus we can limit ourselves to the semi-classical formulation treating H_{el} as the unperturbed Hamiltonian and $H_{el, rad}$ as a small perturbation. Usually, the one-electron approximation is used

$$H_{e1} = \sum_{i} \left[\frac{1}{2m} \vec{p}_{i}^{2} + V(\vec{r}_{i}) \right]$$
(98)

$$H_{el. rad} = \sum_{i} \left[\frac{e}{mc} \vec{A}(\vec{r}_{i}) \cdot \vec{p}_{i} + \frac{e^{2}}{2mc^{2}} \vec{A}^{2}(\vec{r}_{i}) \right]$$
(99)

 \vec{p}_i being the momentum operator of the i-th electron, $V(\vec{r}_i)$ the crystal potential, \vec{A} the vector potential of the radiation field, e the electronic charge, m the free electron mass, and c the velocity of light. Note that we are working in the transverse gauge

$$\nabla \cdot \mathbf{A} = \mathbf{0}$$

and taking the scalar potential of the electromagnetic field as zero. The vector potential is given by

$$\vec{A}(\vec{r}) = A_0 \vec{e} \exp\left[i\left(\vec{q}\cdot\vec{r}-\omega t\right)\right] + c.c.$$
(100)

where \vec{q} is the wave vector of the photon and \vec{e} is the polarization vector in the direction of the electric field. It can also be shown that the second term in $H_{el, rad}$ (99) is a small quantity of higher order and can thus be neglected.

The probability of the optical transitions, i.e. the absorption or induced emission of photons, can be calculated in the usual way by

using the ordinary time-dependent perturbation theory. The wave function of the initial ground state $\overline{\psi}_i$ is represented by a Slater determinant of one-electron Bloch wave functions of the valence electrons. The wave function of the final excited state $\overline{\psi}_f$ contains a definite number of wave functions of the conduction band states. The transition rate from an initial state to a final state is given by the well known formula (golden rule)

$$P_{fi} = \frac{2\pi}{\hbar} \left| \langle f | H_{el, rad} | i \rangle \right|^2 \delta(E_f - E_i)$$
(101)

where E_f and E_i denote the total energy of the system of electrons in the final and initial states, respectively.

Since $H_{el, rad}$ is given as the sum of one-electron operators, only one-electron transitions are induced. When considering only the absorption process the corresponding matrix elements are given as follows:

$$\langle \mathbf{n'} \, \vec{k'} \Big| \frac{\mathrm{e}}{\mathrm{m}\,\mathrm{c}} \, A_0 \exp(\mathrm{i}\,\vec{q}\cdot\vec{r}) \,\vec{e}\cdot\vec{p} \Big| \,\mathbf{n}\,\vec{k} \rangle$$
 (102)

and

$$E_{f} - E_{i} = \epsilon_{n'} (k') - \epsilon_{n}(k) - \hbar \omega$$
(103)

Bearing in mind that $|nk\rangle$ is a one-electron Bloch function

$$\psi_{\vec{n}\vec{k}} = \exp(i\vec{k}\cdot\vec{r}) u_{\vec{n}\vec{k}}(\vec{r})$$

where

$$u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}+\vec{a})$$

the matrix element can easily be shown to be different from zero only if

$$\vec{k}' = \vec{k} + \vec{q} + \vec{K}$$
(104)

where K is a reciprocal lattice vector appearing in Eq.(104) to guarantee that \vec{k}' , \vec{k} and \vec{q} all lie in the reduced Brillouin zone. Since the wavelength of a visible or ultraviolet photon is very large compared with the lattice constant, the photon momentum \vec{q} is a negligible quantity, thus $\vec{K} = 0$, and we can rewrite Eq.(104) as follows:

$$\vec{k}' = \vec{k} \tag{104'}$$

On multiplying Eq. (104') by \hbar , this equation may be considered as the quasi-momentum conservation rule analogous to the selection rules governing optical transitions with atoms. The second selection rule,

namely the energy conservation condition, is assured by the δ -function factor in Eq.(101) giving (see Eqs (103) and (104')):

$$\epsilon_{n} (\vec{k}) = \epsilon_{n} (\vec{k}) + \hbar \omega \qquad (105)$$

Moreover, it holds that $n' \neq n$, i.e. no intraband transitions are allowed. This can be shown as follows:

 $\Delta \epsilon = \hbar \omega$ $\hbar \left| \Delta \vec{k} \right| = \hbar \left| \vec{g} \right| = \frac{\hbar \omega n}{c}$ (106)

Using both these equations we get that the mean value of the velocity of an electron should be equal to

$$\frac{1}{\hbar} \quad \frac{\Delta \epsilon}{\Delta k} = \frac{c}{n}$$

As the velocity of electrons is, in fact, far lower than the velocity of light in the medium, conditions (106) cannot be fulfilled simultaneously and therefore intraband optical transitions are not allowed (at least, in the first-order approximation of perturbation theory).

To sum up, we have seen that optical transitions involving the absorption (or emission) of photons are vertical (the line connecting the initial and the final states on an energy band diagram is a vertical line) interband transitions (see Fig.15).



FIG. 15. Direct (vertical) transitions.

Let us revert to the calculation of the transition rate. When considering, for simplicity, optical transitions between each pair of bands separately, one band fully occupied and the other empty, Eq.(101) can be rewritten in the following way:

$$P(\vec{nk}; n'\vec{k}; \omega) = \frac{2\pi}{\hbar} \left(\frac{e}{mc}\right)^2 A_0^2 \left| \langle n'\vec{k} | \vec{e} \cdot \vec{p} | n\vec{k} \rangle \right|^2 \delta[\epsilon_{n'}(\vec{k}) - \epsilon_{n}(\vec{k}) - \hbar\omega]$$
(107)

Provided that all valence bands are full and all conduction bands are empty, the total number of transitions per unit volume (this is

accomplished by normalizing the Bloch wave functions for unit volume) and time is therefore given by

$$\sum_{n',n} \int_{\cdot}^{\cdot} \frac{\mathrm{d}^3 \vec{k}}{4\pi^3} P(n\vec{k}; n'\vec{k}; \omega)$$
(108)

integration being over the first Brillouin zone taking into account the two spin states of the electron. It can immediately be shown that the optical constants due to direct interband transitions can be obtained from this formula. If we consider the radiation in the form of a beam normal to the surface of the semiconductor, then the absorption coefficient α is defined as the ratio of the energy absorbed from the incident beam per unit time and unit volume to the incident flux

$$\alpha = \frac{\hbar\omega \times \text{number of transitions per unit time and volume}}{\text{incident flux}}$$
(109)

The incident flux is given as the product of the energy density and the propagation velocity of the beam in the medium c/n. The energy density in the medium averaged over a cycle is given by

$$\frac{n^2 \omega^2 A_0^2}{2\pi c^2}$$
(110)

The absorption coefficient α is therefore given by

$$\alpha = 4\pi^2 \left(\frac{e}{m}\right)^2 \frac{1}{n\omega c} \sum_{nn'} \int \frac{d^3k}{4\pi^3} P(n\vec{k}; n'\vec{k}; \omega)$$
(111)

Note that the imaginary part of the dielectric constant ϵ_2 is related to the absorption coefficient α by

$$\epsilon_2(\omega) = \frac{n c \alpha(\omega)}{\omega} \tag{112}$$

Before proceeding further let us rewrite the integration in Eq.(111) using the well-known property of the δ -function

$$\int g(\vec{k}) \delta[f(\vec{k})] d^{3}\vec{k} = \int g(\vec{k}) \frac{dS}{|\nabla_{\vec{k}}f|}$$
(113)

 ϵ_{o} can be thus written as

$$\epsilon_{2}(\omega) \approx \sum_{\mathbf{n},\mathbf{n}'} \int \left| \langle \mathbf{n}'\vec{\mathbf{k}} \, \middle| \, \vec{\mathbf{e}} \cdot \vec{\mathbf{p}} \, \middle| \, \mathbf{n}\vec{\mathbf{k}} \rangle \right|^{2} \frac{\mathrm{dS}}{\left| \nabla_{\vec{\mathbf{k}}} [\epsilon_{\mathbf{n}'}(\vec{\mathbf{k}}) - \epsilon_{\mathbf{n}}(\vec{\mathbf{k}})] \right|}$$
(114)

where dS represents a surface element in \vec{k} space on the surfaces defined by

$$\epsilon_{n} \cdot (\vec{k}) - \epsilon_{n} (\vec{k}) = \hbar \omega \tag{115}$$

 $\epsilon_2(\omega)$ thus depends on two factors: the first is the square of the matrix elements, the second is closely related to the energy bands. Direct calculations of the matrix elements throughout the Brillouin zone have shown that they are not very \vec{k} dependent for a given set of bands. In a good approximation one may consider them constant so that Eq.(114) may be rewritten as follows:

$$\epsilon_{2}(\omega) \approx \sum_{\mathbf{n},\mathbf{n}'} \left| \langle \mathbf{n}' | \vec{\mathbf{e}} \cdot \vec{\mathbf{p}} | \mathbf{n} \rangle \right|^{2} \int \frac{\mathrm{dS}}{\left| \nabla_{\rho} [\epsilon_{\mathbf{n}'} (\rho) - \epsilon_{\mathbf{n}}(\rho)] \right|}$$
(116)

The integral on the right-hand side of Eq.(116) multiplied by $1/8\pi^3$ is called the joint density of states for interband transitions and the spectral dependence of $\epsilon_2(\omega)$ is primarily determined by this function showing strong variations near special points in the Brillouin zone. From Eq.(116) we see that these so-called critical points are those points in the Brillouin zone at which the analytic character of the joint density of states is singular

$$\nabla_{\vec{k}} \left[\epsilon_{n'} (\vec{k}) - \epsilon_{n} (\vec{k}) \right] = 0$$

$$\epsilon_{n'} (\vec{k}) - \epsilon_{n} (\vec{k}) = h \omega$$
(117)

Usually we distinguish between symmetry interband points for which

 $\nabla_{\vec{k}} \epsilon_{n'}(\vec{k}) = \nabla_{\vec{k}} \epsilon_{n}(\vec{k}) = 0$

and general interband points for which

$$\nabla_{\vec{k}} \epsilon_{n'}(\vec{k}) = \nabla_{\vec{k}} \epsilon_{n}(\vec{k}) \neq 0$$

While the former occur only at highly symmetrical points of the Brillouin zone, the latter may occur on symmetry planes, lines or even at general points.

Before proceeding further let us consider an instructive example using a simple two-band (n = v, n' = c) parabolic model of a semiconductor having extrema at $\vec{k} = 0$

$$\epsilon_{v}(\vec{k}) = -\frac{\hbar^{2}}{2m_{v}}k^{2}; \qquad \epsilon_{c}(\vec{k}) = \epsilon_{g} + \frac{\hbar^{2}}{2m_{c}}k^{2}$$
(118)

 m_v and m_c are effective masses of the valence band and conduction band, respectively, ϵ_g is the corresponding energy gap between the two bands. When evaluating the matrix element $\langle c \vec{k} | \vec{e} \cdot \vec{p} | v \vec{k} \rangle$ we can

proceed in the following manner. Since we are interested in small wave vectors \vec{k} in the vicinity of the band extrema, let us expand the matrix element in the following way:

$$\langle c\vec{k} | \vec{e} \cdot \vec{p} | v\vec{k} \rangle = \langle c\vec{k} | \vec{e} \cdot \vec{p} | v\vec{k}_{\vec{k}=0} \rangle + \vec{k} \left[\frac{\partial}{\partial \vec{k}} \langle c\vec{k} | \vec{e} \cdot \vec{p} | v\vec{k} \rangle_{\vec{k}=0} \right] + \dots$$
(119)

retaining only the first non-zero term. Two separate cases must be considered:

(a) Allowed transitions: $\langle c0|\vec{e}\cdot\vec{p}|v0\rangle \neq 0$. In this case the second term can be usually taken as vanishingly small and can be neglected. In the vicinity of the absorption edge we have

$$\epsilon_{c}(\vec{k}) - \epsilon_{v}(\vec{k}) = \hbar\omega_{cv\vec{k}} = \epsilon_{g} + \frac{\hbar^{2}}{2m_{i}}k^{2}$$
(120)

where $m_{j}^{\text{-}1}$ = $m_{c}^{\text{-}1}$ + $m_{v}^{\text{-}1}$. Using formulas (114) and (116), respectively, we get

€₂∝k

which gives, following Eq.(120)

$$\epsilon_2 \approx (\hbar \omega - \epsilon_g)^{\frac{1}{2}}$$
(121)

Note that there exists a threshold with ϵ_2 given by $\hbar \omega = \epsilon_g$.

(b) Forbidden transitions:
$$\langle c0 | \vec{e} \cdot \vec{p} | v0 \rangle = 0$$
, $\left[\frac{\partial}{\partial \vec{k}} \langle \dots \rangle_{\vec{k}=0} \right] \neq 0$

It can be immediately seen that in this case the relevant matrix element is proportional to ${\bf k}^2$ and therefore

giving

$$\epsilon_2 \approx (\hbar \omega - \epsilon_g)^{3/2}$$
 (122)

Of course, the general level of ϵ_2 is lower than in the case of allowed transitions. It is quite clear that the shape of $\epsilon_2(\omega)$ or of the absorption coefficient $\alpha(\omega)$ is different according to whether the transitions are allowed or forbidden. However, in most cases the wave functions are not explicitly known and the relevant matrix elements cannot be determined directly. Fortunately, we usually know the symmetry properties of these functions and this enables us to calculate the selection rules using group theoretical analysis, i.e. to determine whether the matrix element $\langle n'\vec{k} | \vec{e} \cdot \vec{p} | n\vec{k} \rangle$ has zero or finite values. Note that a detailed discussion of the matrix element $\langle i\vec{k} | \vec{e} \cdot \vec{p} | v\vec{k} \rangle$ shows that the use of plane waves instead of Bloch functions may not be a good approximation for this calculation.

We have seen that by carrying out the measurement of the spectral dependence of ϵ_2 and α , respectively, near the absorption edge we could obtain information about the (direct) energy gap ϵ_g and the joint density of states, and distinguish between allowed and forbidden transitions at the critical point $\vec{k} = 0$. Similarly, we can expect that analogous correlations between the band structure and appropriate measurements exist for other critical points as well.

To get some idea of the other critical points let us consider the analytic behaviour of $\epsilon_{n'}(\vec{k}) - \epsilon_{n}(\vec{k})$ in the vicinity of a critical point. Supposing that the matrix element is a constant different from zero we can expand $[\epsilon_{n'}(\vec{k}) - \epsilon_{n}(\vec{k})]$ in relation (116) in a Taylor series about the critical point (\vec{k}_{0})

$$\epsilon_{n'}(\vec{k}) - \epsilon_{n}(\vec{k}) = \epsilon_{0nn'} + \sum_{i=1}^{3} a_{i}(k_{i} - k_{0i})^{2}$$

If the three coefficients are positive (i.e. we are dealing with a minimum) the behaviour of the joint density of states (and therefore of ϵ_2 and α , respectively, as well) is proportional to $(\hbar\omega - \epsilon_0)^{\frac{1}{2}}$. A similar result holds for a maximum having all a_i negative; the joint density of states is proportional to $(\epsilon_0 - \hbar\omega)^{\frac{1}{2}}$ for $\hbar\omega < \epsilon_0$. Such points are denoted by M_0 and M_3 , respectively.



FIG.16. Schematic representation of the joint density of states (After Bassani, F., in The Optical Properties of Solids (TAUC, J., Ed.), Academic Press, New York, (1966)33).

If one coefficient is negative and two positive or if two coefficients are negative and one positive we have to deal with saddle points M_1 and M_2 , respectively. The schematic behaviour of the corresponding joint density of states is given in Fig.16.

In fact, we can hardly expect that the experimental curves of ϵ_2 will always show such a sharp structure; especially at higher energies the main contributions to those peaks will probably occur at clusters of critical points rather than at one special point. Moreover, we have to add all other transitions occurring simultaneously at many regions of the Brillouin zone and giving rise to the smoothly changing absorption "background".

We shall now compare the experimental and theoretical spectral dependence of $\epsilon_2(\omega)$ with Ge given in Fig.17 [2]. The lowest direct edge $(\Gamma_{25}^{\prime} \rightarrow \Gamma_{15})$ is seen to be nearly parabolic. Unfortunately, the present band structure calculations neglect the spin-orbit splitting which is of great importance in Ge as has been shown previously. Therefore I shall pay no attention to spin-orbit splitting for the time being and we shall discuss this effect later.



FIG.17. Calculated and experimental values of the imaginary part of the dielectric constant (ε_2) of Ge (see Ref. [8]).

We can see that the beginning of the steep rise of the ϵ_2 curve is due to $(L_3^! \rightarrow L_1)$ transitions which correspond to the M_0 critical point. The following peak, which corresponds to an M1 critical point, is mainly due to $(\Lambda_3 \rightarrow \Lambda_1)$ transitions. The small shoulder between 3.1 and 3.8 eV, which reproduces the experimental line shape quite accurately, starts with an M_0 critical point $(\Gamma_{25}^{\prime} \rightarrow \Gamma_{15})$ and includes also an M_1 critical point in the [100] directions close to $\vec{k} = 0$. The second peak, while reproducing well the experimental line shape, is shifted towards higher energies. This is mainly due to the choice of some empirical parameters used in calculating the band structure at the X point. It is seen that this peak corresponds to clusters of critical points near X and $\Sigma(\Sigma_2 \rightarrow \Sigma_3)$. It is probable that a slight lowering of the $X_4 \rightarrow X_1$ gap in these calculations would give a better fit to the experimental data. Summing up we can say that the agreement between the theoretical and experimental values of the imaginary part of the dielectric constant of germanium is reasonably good. A similar analysis has also been given for Si. It should be noted that the real and imaginary parts of the dielectric constant were determined using reflectivity measurements as mentioned in the previous section. Figure 18 shows the experimental values of $R_1\epsilon_1$ and ϵ_2 with Ge as functions of photon energy.

Let us return to the spin-orbit splitting problem. When discussing the band structure of Ge we mentioned that the split-off valence band should be separated from the two higher valence bands by the spin-orbit splitting $\Delta . \Delta$ has been determined experimentally as 0.29 eV in Ge and 0.044 eV in Si. Taking into account the complex structure of the



FIG.18. Reflection spectrum and ϵ_1 , ϵ_2 of Ge (after Phillip, H.R., Ehrenreich, H., Phys. Rev. <u>129</u> (1963) 1550).



FIG. 19. Absorption constant of Ge (after Antončík, E., Klima, J., Czech. J. Phys. B15 (1965) 937).

valence bands in the vicinity of the centre of the Brillouin zone, the absorption edge can be calculated in a similar way as previously. Figure 19 shows the theoretical values of the absorption coefficient and comparison with experiment. Optical measurements of this type permit direct determination of the spin-orbit splitting Δ . Unfortunately,

the corresponding transitions at the Γ point are rather weak in comparison with the $\Lambda_3 \rightarrow \Lambda_1$ transition. Following group theoretical analysis, including spin-orbit interaction, the double degenerate Λ_3 level is split into two levels and this splitting is roughly equal to two-thirds Δ . Figure 20 shows this doublet in the reflection spectrum due to spin-orbit interaction with GaAs, InAs, GaSb, and InSb. A comparison between the spin-orbit splitting estimates, using Eq.(34), and experimental values is given in Table III. We can see that the agreement with experiment is relatively very good. A similar analysis can be given for other peaks (transitions) as well.



FIG. 20. Reflection spectra of some $A^{III} B^V$ compounds (after Tauc, J., Abrahám, A., Proceedings of the Int. Conference on Physics of Semiconductors, Prague (1960) 377).

TABLE III. SPIN-ORBIT SPLITTING (IN eV) OF SOME $A^{III}B^V$ and $A^{II}B^{VI}$ compounds.

Compound	Calculated .	Experimental
GaAs	0.34	0.35
GaSb	0.71	0.70
InAs	0.44	0.43
InSb	0.80	0.81
ZnSe	0.50	0.44
CdTe	1.09	0.86

In general, the identification of peaks in the reflection or absorption spectra of semiconductors is by no means a simple procedure especially with materials with not very well known band structure. We have seen that the observation of the spin-orbit splitting is a very useful means of identifying the type of the peak (transition). Fortunately, there exist other possibilities (methods) as well and I shall mention them briefly.

One of the most useful methods is based on an empirical rule concerning the shift of different peaks due to external hydrostatic pressure. This rule has been formulated by Paul in the following way: The pressure coefficient of the energy difference between two states of given symmetry in different materials is approximately equal. This empirical rule probably comes from a very basic similarity in the properties of wave functions of a given symmetry and the sensitivity of the corresponding levels. It can provide criteria for identifying the transition associated with a particular energy gap. It should be noted that the temperature shift of these peaks provides a similar test.



FIG. 21. Energy gaps of the non-horizontal sequence α -Sn-Ge, GaSb, Zn-Te, Cu-I (After Cardona, M., Greenaway, D.L., Phys. Rev. 131 (1963) 98).

Another method is based on the Herman's relations derived in the previous lecture (see Eqs (32) or (33)). These relations correlated the energies of corresponding transitions in isoelectronic series. Figure 21 shows the shift of the peaks in the reflection spectra corresponding to the same transitions in the following non-horizontal isoelectronic series: α -SnGe, GaSb, ZnTe, CuI.

Very interesting information can also be obtained by correlating reflection spectra of both zinc-blende and wurtzite semiconductors in the same isoelectronic series. The crystal structure of wurtzite is hexagonal but can also be regarded as a cubic lattice slightly deformed along the body diagonal. In the case of ZnS we can directly compare the reflectivity spectra of the cubic and hexagonal modifications (see Fig. 22). The three spectra are essentially the same except for a few differences. A qualitatively very similar spectrum to that of ZnS (hexagonal) has been found with CdS and CdSe. Anyway we have seen that most of the reflection structure can be interpreted qualitatively using energy band scheme and selection rules.

Finally, let us note that some conclusions can also be drawn by studying semiconducting alloys, e.g. Ge-Si or even ternary compounds, represented by formulas $In(As_{1-x}P_x)$, $(In_{1-x}Ga_x)$ Sb, etc. where x represents the mole fraction of the second group III or V element in the alloy. These mixed crystals can be thought of simply as an additional group of semiconductors in which the various energy band parameters are continuously variable with composition giving rise to continuous changes in optical properties.



FIG. 22. Reflection spectrum of cubic and hexagonal ZnS. (After Cardona, M., Harbeke, G., Proceedings of the Int. Conference on Physics of Semiconductors, Paris (1964) 217).

To sum up, we have found that the interpretation of the spectral dependence of ϵ_2 discussed so far is based on the existence of the critical points in the joint density of states. As the concept of the wave vector \vec{k} , the Brillouin zone, etc. is strongly connected with the translational symmetry of the crystal, one should expect that the sharp fine structure of ϵ_2 , due to the existence of critical points, will disappear if the long-range order is lost. This conclusion can be easily proved by measuring the optical properties of some amorphous semiconductors, e.g. Ge. It is known that amorphous Ge has the same short-range order as crystalline Ge, while there is no long-range order. Figure 23 shows the reflection spectra of Ge in the crystalline, polycrystalline and amorphous state. We can see indeed that the fine structure in the reflection spectra has disappeared.

3.2.2. Indirect interband transitions

Up to now we have discussed direct (vertical) optical transitions only. In many semiconductors and, in particular, in Ge and Si, as has been shown in the first lecture, the bottom of the conduction band lies in a part of the Brillouin zone different from the top of the valence band. In this case the threshold photon energy for direct transitions is larger than the minimum energy gap ϵ_g since the direct transitions with photon energy close to ϵ_g are forbidden. Nevertheless, a fairly strong absorption may begin at about $\hbar \omega = \epsilon_g$ due to a violation of the selection rule (105) in indirect transitions which may result from simultaneous interaction of electrons with photons and phonons, holes and other lattice imperfections, respectively. In fact, this additional interaction makes possible large changes of the quasi-momentum of electrons without appreciably changing their energy. In what follows we shall be interested in indirect transitions due to lattice vibrations.



FIG.23. Comparison of the reflection spectra of Ge: curve 1) single crystal, curve 2) polycrystalline layer, curve 3) amorphus layer. (After Tauc, J., et al., Proc. Int. Conference on Physics of Noncrystalline Solids, Delft (1964) 606).

The theoretical description of the indirect transitions is based on the assumption that the electron-phonon interaction, $H_{el,\,phon}$ is small, and thus can be treated together with the radiation field interaction, $H_{el,\,rad}$, as perturbations. The corresponding expression for the transition probability P_{fi} analogous to Eq.(101) is given in the same form as Eq.(101), but the matrix element $\langle f | H_{el,\,rad} | i \rangle$ has to be replaced by a second-order expression

$$\sum_{m} \frac{\langle \mathbf{f} | \mathbf{H}_{el, phon} + \mathbf{H}_{el, rad} | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{H}_{el, phon} + \mathbf{H}_{el, rad} | \mathbf{i} \rangle}{\mathbf{E}_{\mathbf{i}} - \mathbf{E}_{\mathbf{m}}}$$
(123)

where only terms involving both photon and phonon matrix elements are considered; the index m refers to the intermediate states.

We shall not attempt a completely rigorous treatment of the problem but shall try to determine the dependence of the absorption coefficient for a simple model shown in Fig.24, being analogous to the two-band parabolic models considered previously and having a minimum of the conduction band at $\vec{k}_c \neq 0$. The absorption may be accomplished by two virtual processes: 1) The electron is optically

excited from the top of the valence band to the intermediate state in the conduction band $(v, \vec{k}) \rightarrow (c, \vec{k})$ and then scattered by a phonon from (c, \vec{k}) into the final state in the conduction band minimum (c, \vec{k}') . 2) An electron is excited from (v, \vec{k}') to $(c, \vec{k'})$ followed by the transition of the electron (v, \vec{k}) to the hole at $(v, \vec{k'})$ due to the electron-phonon interaction. Either of the processes 1) and 2) may involve either the absorption or the emission of a phonon. Note that if excited states in higher and/or lower bands were taken into account as well, we could get additional transitions; unfortunately, this procedure would rather complicate our calculation and therefore we shall restrict ourselves to the simplest case.



FIG. 24. Phonon-assisted (indirect) interband transitions.

We shall now proceed in a similar way as with direct transitions. Supposing that we are dealing with allowed optical transitions, this means that the corresponding matrix elements do not vanish at the band extrema, all the matrix elements become constant if each state is taken to be either $\vec{k} = 0$ or \vec{k}_c . For example, the corresponding matrix elements in expression (123) can be written approximately as follows:

$$<0; N_{\vec{k}_{c}j}|H_{el. rad}|c0, v0; N_{\vec{k}_{c}j} > (124)$$

where $N_{\vec{k}_{c}\,j}$ is the average number of phonons with wave vector $\vec{k}_{c}\,,j$ being the index denoting different phonon branches and $|0,N_{\vec{k}_{c}\,j}\rangle$ denotes the initial unperturbed state; $N_{\vec{k}_{c}\,j}$ is given by

$$N_{\vec{k}_{c}j} = \left[\exp\left(\frac{\hbar \omega_{\vec{k}_{c}j}}{\vec{k}_{B}T}\right) - 1 \right]^{-1}$$
(125)

$$\begin{split} \hbar \omega_{\vec{k_c}j} \text{ is the energy of the phonon considered. Note that the matrix} \\ \text{element for the absorption of a phonon is proportional to } \sqrt{N_{\vec{k_c}j}}, \text{ while} \\ \text{the matrix element for phonon emission is proportional to } \sqrt{N_{\vec{k}_j}} + 1. \end{split}$$

Assuming that expression (124) can be taken as a constant except for the temperature dependence, ϵ_2 is thus expressible in the form (analogous to Eq.(116))

$$\epsilon_{2} \approx \int d^{3}\vec{k} \int d^{3}\vec{k}' \,\delta \left[\epsilon_{c}(\vec{k}'_{1}) - \epsilon_{v}(\vec{k}) - \hbar\omega \pm \hbar\omega_{\vec{k}_{c}j'}\right]$$
(126)

where the integration is over a range of initial and final states. Since the densities of states in the conduction and valence bands are proportional to $\sqrt{-\epsilon_v d\epsilon_v}$ and $\sqrt{\epsilon_c - \epsilon_g} d\epsilon_c$, respectively, the following integrals have to be evaluated

$$\int \int \sqrt{-\epsilon_{v}} \sqrt{\epsilon_{c} - \epsilon_{g}} \, \left\{ \epsilon_{c} - \epsilon_{v} - \hbar\omega \pm \hbar\omega_{\vec{k}_{c}j} \right\} d\epsilon_{v} d\epsilon_{c}$$

The integral over ϵ_v gives

$$\int \sqrt{(\epsilon_{\rm c} - \epsilon_{\rm g})} (\hbar\omega \neq \hbar\omega_{\rm k_{\rm c}\,\rm j} - \epsilon_{\rm c}) \, \mathrm{d}\epsilon_{\rm c}$$

When integrating this integral within the limits ϵ_g and $\hbar\omega \mp \hbar\omega_{\vec{k}_c j}$: we obtain

$$\frac{\pi}{8}$$
 (h $\omega \neq$ h $\omega_{\vec{k}_c j} - \epsilon_g$)²

where the $\bar{+}\hbar\omega_{\vec{k}cj}$ corresponds to the emission or absorption of the phonon. Combining this expression with the factors involving Eq.(125) we get

$$\epsilon_{2} \approx \sum_{j} \{ c_{j}^{a} N_{\vec{k}cj} [\hbar \omega - (\epsilon_{g} - \hbar \omega_{\vec{k}cj})]^{2} + c_{j}^{\ell} (N_{\vec{k}cj} + 1) [\hbar \omega - (\epsilon_{g} + \hbar \omega_{\vec{k}cj})]^{2} \}$$
(127)

in which c_j^f , c_j^a are constants containing the remaining factors. When considering only one branch of the phonon spectrum and plotting $\sqrt{\epsilon_2}$ against h ω , the curve lies close to the straight line for $\epsilon_g -\hbar \omega_{\vec{q}_c j} < \hbar \omega < \epsilon_g + \hbar \omega_{\vec{q}_c j}$ and close to a steeper line for $\hbar \omega > \epsilon_g + \hbar \omega_{\vec{q}_c j}$ giving rise to two thresholds. However, it is necessary to bear in mind that the threshold corresponding to the phonon absorption process becomes negligibly small as $N_{\vec{k},i}$ approaches zero for $T \rightarrow 0$.

If the transitions are forbidden at the band extrema we can proceed in a similar way as with the direct transitions in the previous section. Supposing that the corresponding matrix elements are proportional to \vec{k} and $\vec{k} - \vec{k}_c$, respectively, we can derive expressions similar to expression (127) which differ in the exponent only.

In practice we are dealing with several branches of the phonon spectrum and the corresponding analysis is therefore far more complicated. Figure 25 shows the absorption edge in Ge.

It should be noted that from such an analysis of the experimental curves we are able to estimate not only the temperature dependence of the energy gap ϵ_g but even the value of the wave vector $\vec{k_c}$. Figure 26 shows the temperature dependence of the gap ϵ_g in Ge. This dependence is quadratic at very low temperatures while at higher temperatures it is linear. From the theoretical point of view the temperature dependence of the gap or, better, of the corresponding levels may be calculated using the second-order perturbation theory taking into account the emission and re-absorption of virtual phonons. In considering the simple two-band model of a semiconductor it can easily be shown that the shift of the energy level is given by

$$\delta \epsilon(\vec{k}) = \sum_{\vec{q}} \left\{ \frac{\left| \langle \vec{k}, N_{\vec{q}} \right| H_{el, phon} \left| \vec{k} + \vec{q}, N_{\vec{q}} + 1 \right\rangle \right|^2}{\epsilon(\vec{k}) - \epsilon(\vec{k} + \vec{q}) + \hbar \omega_{\vec{q}}} + \frac{\left| \langle \vec{k}, N_{\vec{q}} \right| H_{el, phon} \left| \vec{k} - \vec{q}, N_{\vec{q}} - 1 \right\rangle \right|^2}{\epsilon(\vec{k}) - \epsilon(\vec{k} - \vec{q}) - \hbar \omega_{\vec{q}}}$$
(128)



FIG. 25. Absorption curves for Ge. (After G. Macfarlane et al., Phys. Rev. 108 (1957) 1377).

Although the temperature dependence of the gap and even of some higher absorption peaks based on formula (128) is in semi-quantitative agreement with experiment, the general formulation of this rather complex problem is not yet satisfactory and will not be discussed here.

We have seen that the simultaneous interaction of electrons with photons and phonons, giving rise to indirect transition, makes it possible to produce absorption at energies lower than the direct energy gap. A similar effect can take place if we consider, instead of the electronphonon interaction, another interaction, namely the electron-hole interaction. It can be shown that the mutual Coulomb attraction of the electronhole pair allows bound states - excitonic states - with energies less than those of the free pair of particles. Absorption can take place into these excitonic states at energies lower than the gap and, moreover,



FIG. 26. Variation of energy gap ϵ_g with temperature for Ge. (After G. Macfarlane et al., Phys. Rev. 108 (1957) 1377).

the continuous absorption beginning at the gap is modified in shape from that given by Eqs (54) and (55). Unfortunately, there is no time left for this rather complex problem, being beyond the one-electron approximation, and we shall not discuss it in detail here.

3.2.3. Direct intraband transitions

Transitions of this type take place in a complex band consisting of several overlapping bands as for example the valence band in Si, Ge, $A^{\rm III} B^{\rm V}$ compounds, etc. (Fig.27). In fact, electrons in a fully occupied valence band do not contribute to intraband transitions because of the Pauli exclusion principle. Thus, these transitions occur because there are holes in the valence band, and we may expect that the whole effect will be strongly dependent on temperature.



FIG. 27. Direct intraband transitions near the top of a complex valence band.

In calculating the absorption coefficient or $\epsilon_2(\omega)$ we have to generalize formula (107) for this case. Denoting the electron distribution function $f(\epsilon_n(\vec{k}))$, the right-hand side of Eq.(107) has to be multiplied by the following factor:

$$\{f(\boldsymbol{\epsilon}_{n}(\vec{k}))[1-f(\boldsymbol{\epsilon}_{n^{*}}(\vec{k}))] - f(\boldsymbol{\epsilon}_{n^{*}}(\vec{k}))[1-f(\boldsymbol{\epsilon}_{n}(\vec{k}))]\}$$

$$=\{f(\boldsymbol{\epsilon}_{n}(\vec{k})) - f(\boldsymbol{\epsilon}_{n^{*}}(\vec{k}))\}$$
(129)

The first term in (129) corresponds to the absorption process $(n, \vec{k}) \rightarrow (n', \vec{k})$, while the second term corresponds to the induced emission for the $(n', \vec{k}) \rightarrow (n, \vec{k})$ transition. When dealing with interband transitions we usually consider completely filled or completely empty bands. Therefore expression (129) may be replaced by unity as has been done previously.

Let us assume that the \vec{k} dependence of the three energy bands of the valence band considered can be written as (see Fig. 27: $m_1 > m_3 > m_9$)

$$\vec{\epsilon}_{i}(\vec{k}) = \Delta_{i} - \frac{\hbar^{2}}{2m_{i}}k^{2}$$
 $i = 1, 2, 3$ (130)

Here $\Delta_1 = \Delta_2 = 0$, $\Delta_3 = -\Delta$. An equation analogous to Eq. (120) gives

$$\hbar\omega_{ij} = \Delta_i - \Delta_j + \frac{\hbar^2}{2m_{ij}}k^2$$
(131)

where $m_{ij}^{-1} = m_j^{-1} - m_i^{-1}$.

It can be shown that, owing to the symmetry of the wave functions, optical transitions between these bands are forbidden at $\vec{k} = 0$. As in the case of forbidden transitions (see Eq.(119)), this selection rule breaks down away from $\vec{k} = 0$, and dipole transitions can occur.

We shall now consider the distribution functions for different bands. It is well known that the distribution function for electrons in the conduction band is given by

$$f(\epsilon) = \left[\exp\left(\frac{\epsilon - \epsilon_{\rm F}}{k_{\rm B}T}\right) + 1 \right]^{-1} \quad \epsilon \ge \epsilon_{\rm g}$$
(132)

If it is assumed that $\epsilon - \epsilon_F >> k_B T_i$ the term with 1 can be neglected and we get the classical expression

$$f(\epsilon) = \exp\left(-\frac{\epsilon - \epsilon_{\rm F}}{k_{\rm B}T}\right) \tag{133}$$

Accordingly, the classical distribution functions for holes in the valence band are given by

$$1 - f_{i}(\epsilon_{i}) = \exp\left(-\frac{\epsilon_{F} - \epsilon_{i}}{k_{B}T}\right) \quad \epsilon_{i} \leq 0$$
(134)

except for band 3 where, owing to the fact that $\Delta >> k_{\rm B}T$, holes can be neglected. As in general the concentration of holes given by Eq.(134) is small, the distribution functions for electrons in the valence bands are assumed to be equal to unity.

The Fermi level $\epsilon_{\rm F}$ in Eqs (133) and (134) is estimated using the fact that the number of electrons N_e in the conduction band must be equal to the number of holes N_h in the valence bands. Taking into account the corresponding densities of states we can easily obtain

$$1 - f_1(\epsilon_1) = \frac{N_h m_1^{3/2}}{(m_1^{3/2} + m_2^{3/2})} - \frac{h^3}{2(2\pi m_1 k_B T)^{3/2}} \exp\left[\frac{\epsilon_1(\vec{k}) - \Delta_1}{k_B T}\right]$$
(135)

A similar expression holds for band 2 as well.

Let us consider $2 \rightarrow 1$ interband transition. In this case expression(129) can be simplified as follows:

$$\{ \} = [1 - f_1(\epsilon_1(\vec{k}))] - [1 - f_2(\epsilon_2(\vec{k}))]$$
(136)

Using relation (131) we get

$$k^2 = \frac{2m_{12}}{\hbar^2} \hbar \omega \tag{137}$$

Substituting this expression in Eq.(136) we get

1 10

$$\{ \} \approx \exp\left[\frac{m_2}{m_2 - m_1} \frac{\hbar\omega}{k_B T}\right] - \exp\left[\frac{m_1}{m_2 - m_1} \frac{\hbar\omega}{k_B T}\right]$$
(138)

Taking into account all the necessary quantities, the absorption coefficient for $(2 \rightarrow 1)$ transition is proportional to

$$\alpha_{21} \approx \frac{N_{h}(\hbar\omega)^{1/2}}{(k_{B}T)^{3/2}} \left\{ \exp\left[\frac{m_{2}}{m_{2}-m_{1}} \frac{\hbar\omega}{k_{B}T}\right] - \exp\left(\frac{m_{1}}{m_{2}-m_{1}} \frac{\hbar\omega}{k_{B}T}\right) \right\}$$
(139)

Similar expressions can be given for the transitions $(3 \rightarrow 1)$ and $(3 \rightarrow 2)$, respectively

$$\begin{aligned} \alpha_{31} &\approx \frac{N_{h} \left(\hbar \omega - \Delta\right)^{3/2}}{\hbar \omega \left(k_{B}T\right)^{3/2}} &\exp\left[\frac{m_{3}}{m_{3} - m_{1}} \frac{\hbar \omega - \Delta}{k_{B}T}\right]; \quad \hbar \omega > \Delta \end{aligned} \tag{140} \\ \alpha_{32} &\approx \frac{N_{h} \left(\Delta - \hbar \omega\right)^{3/2}}{\hbar \omega \left(k_{B}T\right)^{3/2}} &\exp\left[\frac{m_{3}}{m_{2} - m_{3}} - \frac{\Delta - \hbar \omega}{k_{B}T}\right]; \quad \hbar \omega < \Delta \end{aligned}$$

Note that owing to the inequality $\Delta >> k_B T$ no induced emission occurs into band 3.

Taking into account the corresponding matrix elements, effective masses etc., we can compare the calculated absorption coefficients with experimental data. This has been done both for the simple parabolic bands given by Eq.(130) and also for more realistic energy bands as calculated by Kahn [9] who used the $\vec{k} \cdot \vec{p}$ method. Figure 28 shows the calculated and measured absorption coefficients for $N_h = 6 \times 10^{15}$ holes at 300°K. Without going into details we can say that the agreement between theory and experiment is reasonably good.



FIG. 28. Absorption spectra of p-type Ge. (After Kane, E.O., J. Phys. Chem. Solids 1 (1956)82).

It should be noted that the α_{12} peak is overlapped on the low-energy side by another absorption process due to the absorption of free electrons in the conduction band. Absorption of this type is identical with that occurring with metals. In this case, we are dealing with indirect intraband transitions; absorption arises through the interaction of electrons with phonons (or impurities) just as the indirect intraband transitions discussed previously. We shall not discuss this problem in detail here.

3.2.4. Interband transitions in a magnetic field

We have shown previously that the external magnetic field gives rise to significant changes in the band structure of semiconductors. For example, this fact reflects very radically on the density of states as can be seen from Fig.13. On the other hand, we have seen that the density of states - or more accurately, the joint density of states determines to a great extent the spectral dependence of the absorption constant. Thus, we can expect a considerable effect of a magnetic field on the optical absorption in semiconductors as developed previously.

If we take into account both the external magnetic field and the radiation field the complete one-electron Hamiltonian (remember that we have to deal with one-electron transitions) is

$$\frac{1}{2m}\left(\vec{p} + \frac{e}{c}\vec{A}_{ext} + \frac{e}{c}\vec{A}\right)^2 + V(\vec{r})$$
(141)

where \vec{A}_{ext} is the vector potential of the external magnetic field, and \vec{A} is given by Eq.(100). As the radiation field is small we can proceed in the same way as in previous sections and use the perturbation theory. The perturbing Hamiltonian is now

$$H' = \frac{e}{mc} \vec{A} \left(\vec{p} + \frac{e}{c} \vec{A}_{ext} \right)$$
(142)

and the zero-order Hamiltonian is the same as in Eq.(98).

Hence the matrix element which appears in the calculation of the transition probability (see Eq.(102)) is given by

$$\langle u_{n}, F_{k_{y}^{\prime}k_{z}^{\prime}\ell}, \left| \frac{e}{mc} A_{0} \vec{e} \cdot \left(\vec{p} + \frac{e}{c} \vec{A}_{ext} \right) \right| u_{n} F_{k_{y}^{\prime}k_{z}^{\prime}\ell} \rangle$$
(143)

where the space variation of \vec{A} has been neglected ($\vec{q} = 0$).

Since the F and \vec{A}_{ext} are slowly varying functions compared to the periodic functions $u_{n'}$, u_{n} , and can thus be treated as constants over the unit cell, the matrix element (76) can be split into two integrals

$$\langle \mathbf{F}_{\mathbf{k}_{\mathbf{y}}^{\prime}\mathbf{k}_{\mathbf{z}}^{\prime}\ell^{\prime}} \left| \frac{\mathbf{e}}{\mathbf{mc}} \mathbf{A}_{0} \vec{\mathbf{e}} \cdot \left(\vec{\mathbf{p}} + \frac{\mathbf{e}}{\mathbf{c}} \vec{\mathbf{A}}_{ext} \right) \left| \mathbf{F}_{\mathbf{k}_{\mathbf{y}}\mathbf{k}_{\mathbf{z}}\ell} \right\rangle \langle \mathbf{u}_{n}, \mathbf{u}_{n} \rangle$$

$$+ \langle \mathbf{F}_{\mathbf{k}_{\mathbf{y}}^{\prime}\mathbf{k}_{\mathbf{z}}^{\prime}\ell^{\prime}} \left| \mathbf{F}_{\mathbf{k}_{\mathbf{y}}\mathbf{k}_{\mathbf{z}}\ell} \right\rangle \langle \mathbf{u}_{n^{\prime}} \left| \frac{\mathbf{e}}{\mathbf{mc}} \mathbf{A}_{0} \vec{\mathbf{e}} \cdot \vec{\mathbf{p}} \right| \mathbf{u}_{n} \rangle$$

$$(144)$$

while the matrix elements involving u_n , u_n are integrals over a unit cell only, matrix elements involving F are evaluated over the whole crystal.

When considering the usual interband transitions the u for two different bands are assumed to be orthogonal to one another. In this case the first term in expression (143) vanishes. Supposing that we are dealing with allowed transitions, the selection rules are determined by the matrix element $\langle F_{k_z} k_{v_\ell} \ell' | F_{k_z k_v \ell} \rangle$ which must be non-zero:

$$\Delta k_{z} - \Delta k_{y} = 0; \quad \Delta \ell = 0 \tag{145}$$

Transitions of this type are shown in Fig. 29.

Let us return to the spectral dependence of the absorption coefficient or of ϵ_2 for the two-hand parabolic model (see Eq.(37)). In the presence of the magnetic field we have an absorption edge corresponding to each







FIG. 30. Absorption coefficient corresponding to the transitions between Landau levels. (After Roth, L. M. et al., Phys. Rev. <u>114</u> (1959) 90).



FIG.31. Photon energy of transmission minima versus magnetic field for Ge. (T = 298° K). (After Zwedling, S. et al., Phys. Rev. <u>108</u> (1957) 1402).

pair of Landau levels. On the same assumption as in relation (116) - that the matrix element is a constant - we can write

$$\epsilon_{2} \approx 2 \sum_{\ell} \delta \left(\hbar \omega - \epsilon_{c \, k_{Z} \ell}^{H} + \epsilon_{v \, k_{Z} \ell}^{H} \right)$$

$$= 2 \sum_{\ell} \int_{\frac{\ell}{2\hbar c}}^{\frac{eH}{2\hbar c}} \frac{dk_{y}}{2\pi} \int_{\frac{eH}{2\pi}}^{\frac{dk_{z}}{2\pi}} \delta (\hbar \omega - \epsilon_{c \, k_{Z} \ell}^{H} + \epsilon_{v \, k_{Z} \ell}^{H})$$

$$(146)$$

Here the limits of the integral over k_y are given by the fact that the x component of the centre of the magnetic orbit has to lie inside the crystal (see Eq.(39)). Calculation of the integrations lead to the result

$$\epsilon_{2} \approx \frac{1}{4\pi^{2}} \frac{\text{eH}}{\text{hc}} \sum_{\ell} \left| \frac{d}{dk_{z}} \left(\epsilon_{\mathbf{k}_{z}\ell}^{H} - \epsilon_{\mathbf{v}k_{z}\ell}^{H} \right) \right|_{\epsilon_{\mathbf{k}_{z}\ell}^{H} - \epsilon_{\mathbf{v}k_{z}\ell}^{-1} = \hbar\omega}$$

$$\approx \frac{\text{eH}}{\text{hc}} \sum_{\ell} \left(\hbar\omega - \hbar\omega_{\ell} \right)^{-\frac{1}{2}}$$
(147)

where $\hbar \omega_{\ell} = \epsilon_g + (\ell + 1/2)\hbar (\omega_c + \omega_v)$. Equation (147) shows that $\epsilon_2(\omega)$ will always be singular when $\omega = \omega_{\ell}$ for each Landau level. The spectral dependence of ϵ_2 has an oscillatory character showing peaks changing linearly with magnetic field. In fact, these peaks are broadened by collisions and this is shown in Fig. 30. The experimental dependence of different peaks on the magnetic field in Ge is shown in Fig. 31. Note that this dependence gives not only the experimental value of the energy gap ϵ_g but the slopes of the lines enable us to evaluate the reduced effective mass given by $(m_c^{-1} + m_v^{-1})^{-1}$.



FIG. 32. Direct transitions between Landau levels in Ge ($k_z = 0$) allowed for E H. (After Roth. L. M. et al., Phys. Rev. 114 (1959)90).

So far we have discussed the simple two-band model. Unfortunately, because of the complexity of valence bands in most semiconductors, the real situation is far more complex, as can be seen e.g. from Fig.32. We shall not discuss this problem in detail here. Similarly, no attempt will be made to deal here with the influence of a magnetic field on absorption due to indirect interband or intraband transitions (the latter transitions are due to the first term in expression (144) giving the following selection rule:

$$\Delta k_v = \Delta k_z = 0$$
, $\Delta \ell = \pm 1$

and are observed in cyclotron resonance experiments). The reader is referred to the review article by Lax [10].

4. ELECTRICAL CONDUCTIVITY IN SEMICONDUCTORS

In this section no attempt will be made to review the present stage of transport phenomena in semiconductors because this would require far more space. As this course is devoted to simple homogeneous materials containing no defects I shall not deal with effects due to impurities, thermal gradients, etc. In what follows I shall limit myself to some conduction and galvanomagnetic phenomena and related problems observable at low electric and magnetic fields. At the same time I shall try to emphasize such aspects of these phenomena which are closely related to the complex band structure of semiconductors.

When one begins to investigate a semiconductor without any precise information about the band structure the only reasonable procedure seems to be to assume the form of the energy bands, to calculate the parameters needed and to compare them with experimental values. Agreement or disagreement between theory and experiment indicate whether our suppositions concerning the band structure are at least approximately correct.

It is shown in lectures given by Garcia-Moliner in this book [11] how these calculations proceed in practice provided that we are dealing with a simple form of the energy bands. Before proceeding further let us briefly summarize some results we shall use in our lecture.

4.1. Electrical conductivity

In order to find the electrical conductivity we usually start with the solution of the Boltzmann equation which can be written for a homogeneous n-type semiconductor at constant temperature as follows:

$$-\frac{e}{\hbar}\vec{E}\cdot\nabla_{\vec{k}}f(\vec{k}) = \left(\frac{\partial f(\vec{k})}{\partial t}\right)_{\text{coll.}}$$
(148)

Here $f(\vec{k})$ is the non-equilibrium distribution function which specifies the probability that a state with wave vector \vec{k} is occupied.

The collision term in Eq.(148) is generally a complicated integral. Fortunately, in many cases of physical interest it may be expressed in the following way:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} = -\frac{f - f_0}{\tau (\mathbf{k})} \tag{149}$$

Here f_0 is the thermal equilibrium distribution function and $\tau(k)$ is referred to as the relaxation time. This approximation is thoroughly discussed by Garcia-Moliner in this book. It is well known that in general a relaxation time does not exist for some types of scattering; in this case an assumption of type (149) cannot be used and one has to perform the analysis using the Boltzmann integral equation. Nevertheless, we shall use the relaxation-time approximation to get a greater insight into the nature of transport processes without being very interested in precise numerical results which are not necessary for a general discussion.

4.1.1. Simple parabolic band

Substituting expression (149) in (148) we get

$$f(\vec{k}) = f_0(\vec{k}) + \frac{e}{h} \tau(\vec{k}) \vec{E} \cdot \nabla_{\vec{k}} f(\vec{k})$$
(150)

Assuming that the non-equilibrium distribution is near the equilibrium distribution f_0 for the field \vec{E} normally of interest, we may replace $f(\vec{k})$ on the right-hand side of Eq.(150) by $f_0(\vec{k})$. In general the thermal equilibrium distribution is given by the Fermi-Dirac distribution function. However, in contrast to metals, the Fermi level in a non-degenerate semiconductor lies in the energy gap. Supposing that we are dealing with a non-degenerate semiconductor, f_0 can be equated to the classical Maxwell distribution function (see Eq.(65)). For simplicity, let us assume that

$$\epsilon_{\rm c}(\vec{\rm k}) = \frac{\hbar^2}{2m_{\rm c}} {\rm k}^2 \tag{151}$$

then $f_0(\epsilon_c(\vec{k}))$ is given by

$$f_{0}(\epsilon(\vec{k})) = \exp\left[\frac{\epsilon_{F} - \epsilon_{c}(\vec{k})}{k_{B}T}\right]$$

$$= \frac{N}{2} \left(\frac{h^{2}}{2\pi m_{c}k_{B}T}\right)^{3/2} \exp\left(-\frac{\epsilon_{c}(\vec{k})}{k_{B}T}\right)$$
(152)

A similar expression holds for holes in the valence band as well (see Eq.(67)).
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The current density due to conduction electrons is given by

$$\vec{j} = -\frac{e}{4\pi^3} \int \vec{v} f d^3 \vec{k}$$
(153)

where

 $\vec{v} = \frac{1}{\hbar} \nabla_{\vec{k}} \epsilon_{c}(\vec{k})$ (154)

writing

.

$$j_{i} = \sum_{j} \sigma_{ij} E_{j} \qquad i, j = x, y, z \qquad (155)$$

the (ij) component of the electrical conductivity tensor is given by

$$\sigma_{ij} = -\frac{e^2}{4\pi^3} \int \frac{\partial f_0}{\partial \epsilon} \tau(\vec{k}) v_i v_j d^3 \vec{k}$$
(156)

We shall now make a further approximation

$$\tau(\vec{k}) = \tau(\epsilon) \tag{157}$$

Then Eq.(156) can be written as

$$\sigma_{ij} = \frac{Ne^2}{m_e} \langle \tau \rangle \delta_{ij}$$
(158)

where the following notation has been introduced:

$$\langle \tau^{n} \rangle = \frac{\int_{0}^{\infty} \tau^{n} \epsilon^{3/2} \exp\left(-\frac{\epsilon}{k_{B}T}\right) d\epsilon}{\int_{0}^{\infty} \epsilon^{3/2} \exp\left(-\frac{\epsilon}{k_{B}T}\right) d\epsilon}$$
(159)

We see that σ_{ij} is in fact a scalar quantity σ_e . It is convenient to introduce a quantity μ_e called the electron mobility defined by means of the equation

$$\mu_{\mathbf{e}} = \frac{\mathbf{e} \langle \mathbf{\tau} \rangle}{\mathbf{m}_{\mathbf{e}}} \tag{160}$$

so that

$$\sigma_{\rm e} = {\rm Ne}\,\mu_{\rm e} \tag{161}$$

Similar expressions hold for holes as well.

4.1.2. Simple ellipsoidal band

Let us consider a more general case of a single ellipsoidal band in its principal-axis co-ordinate system²

$$\epsilon_{c}(\vec{k}) = \frac{\hbar^{2}}{2} \left(\frac{k_{x}^{2}}{m_{1}} + \frac{k_{y}^{2}}{m_{2}} + \frac{k_{z}^{2}}{m_{3}} \right)$$
(162)

On the assumption that the relaxation time is a function of energy only we can proceed in a similar way as in A by introducing the following transformation of co-ordinates:

$$\kappa_{i} = \sqrt{\frac{m_{e}}{m_{i}}} k_{i}$$
(163)

Then we can still use expression (156) bearing in mind that

$$v_{i} = \frac{\hbar k_{i}}{m_{i}} = \frac{\hbar \kappa_{i}}{m_{e}} \sqrt{\frac{m_{e}}{m_{e}}}$$
(164)

Expression (158) can be rewritten as follows:

$$\sigma_{ij} = \frac{Ne^2}{m_i} \langle \tau \rangle \delta_{ij}$$
(165)

Similarly the mobility tensor is defined by

$$\mu_{ij} = \frac{e}{m_i} \langle \tau \rangle \,\delta_{ij} \tag{166}$$

The foregoing expressions have been obtained on the assumption that the relaxation time τ is isotropic. However, this assumption may be generalized by using a tensor form for τ which takes into account the variation of τ with direction. Herring and Vogt [12] have shown that for transport processes in steady fields the effect of the anisotropy in τ is to weight each component of the reciprocal mass tensor with the corresponding component of the relaxation time tensor, namely,

$$\frac{\langle \tau \rangle}{m_i} \to \frac{\langle \tau_i \rangle}{m_i} \tag{167}$$

For simplicity, we shall not use this approximation in our calculations. Nevertheless, all formulas based on the isotropic relaxation time approximation (e.g. Eqs (165) and (166)) can easily be generalized by the simple prescription given above.

² It should be remembered, however, that because of the symmetry of cubic crystals constant energy surfaces of this type cannot exist in the centre of the Brillouin zone.

4.1.3. Many-valley band

We have shown in the first lecture that the conduction band of Ge and Si consists of several ellipsoidal constant energy surfaces with their major axes colinear with one of the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions, respectively (see Figs 6 and 7). Of course, this fact rather complicates the evaluation of the conductivity tensor (in effect it is a scalar quantity because of the symmetry of the cubic lattice). Up to now, when considering the relaxation time, we had to take into account the intravalley scattering only. Now another type of scattering takes place simultaneously, namely the intervalley scattering (Fig. 33). Herring and Vogt [12] have shown that under certain conditions a separate Boltzmann equation can be written for each valley and that even in this case the relaxation-time approximation can be used³. Accordingly, the evaluation of the conductivity reduces to summation over all the ellipsoids in the conduction band. Of course, the contribution of each ellipsoid must be transformed to a common co-ordinate system.



FIG. 33. The types of scattering processes in the many-valuey model. (After Ziman, J., Electrons and Phonons, Oxford (1960)).

Let us denote the matrix which transforms the principal-axis system, say of the r-th ellipsoid, to the crystallographic co-ordinate system, by $T_{i\alpha}^{(t)}$. Then the contribution of this ellipsoid to the conductivity in the new system is given by

$$\sigma_{ij}^{(\mathbf{r})} = \sum_{\alpha\beta} T_{i\alpha}^{(\mathbf{r})} T_{j\beta}^{(\mathbf{r})} \sigma_{\alpha\beta}^{(\mathbf{r})}$$
(168)

which is, in general, markedly anisotropic.

Using expressions (165) and (168) the overall conductivity tensor can be written as follows:

$$\sigma_{ij} = Ne^2 \langle \tau \rangle \left[\frac{1}{s} \sum_{r}^{s} \sum_{\alpha\beta} T_{i\alpha}^{(r)} T_{j\beta}^{(r)} \frac{\delta_{\alpha\beta}}{m_{\alpha}^{(f)}} \right]$$
(169)

³ Those interested might consult the original paper by Herring and Vogt for details.

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Here s is the number of ellipsoids (Ge: s = 4, Si: s = 6) and N is now the total number of electrons per unit volume. $T_{i\alpha}^{(r)}$ can be easily found; e.g. when considering the [111] valley and choosing the y- and z-axis in the [110] and [112] direction, respectively, a simple calculation gives

$$\mathbf{T}_{i\alpha}^{[111]} = \begin{pmatrix} \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & 0 & \frac{2}{\sqrt{6}} \end{pmatrix}$$
(170)

Similarly we can get $T_{i\alpha}^{(r)}$ for all valleys. Substituting them into Eq.(169) we obtain

$$\sigma_{ij} = Ne^2 \langle \tau \rangle \left[\frac{1}{3} \quad \frac{1}{m_{\parallel}} + \frac{2}{m_{\perp}} \right] \delta_{ij}$$
(171)

When considering the set of ellipsoids in the <100> directions we find the same expression as can be obtained by simple consideration. Hence we may conclude that by measuring the conductivity we are not able to decide whether the ellipsoids are oriented along the <111> and <100> directions respectively. This results from the fact that the set of ellipsoids is arranged symmetrically in \vec{k} space and this is due to the symmetry of the diamond lattice. It is quite clear that when an external magnetic field or an uniaxial stress is applied, this symmetry is lost and different configurations of ellipsoids will give different results. We shall discuss both these problems later.

When calculating the contribution of holes in a degenerate valence band as in Ge to the conductivity the situation is considerably more complex. We have here two types of holes, namely light and heavy holes; moreover, the constant energy surfaces are warped surfaces. Finally, we have to consider both intraband and interband transitions in calculating the relaxation time. Unfortunately, the general treatment of this phenomenon is rather complicated and I am not going to enter into detail here (see Ref.[13]).

4.2. Piezoresistance

We shall show presently that the application of an appropriate uniaxial stress gives rise to a large change in resistivity, and that this effect is very sensitive to certain details of the energy band structure. It is thus clear that a study of the resistivity change as a function of the crystallographic orientation of the stress can be used to determine the location of the band extrema in the Brillouin zone. To be specific, I shall discuss in this section the many-valley conduction band of semiconductors typified by Ge and Si.

As a matter of fact, I shall not be interested in the piezoresistance effect, i.e. in the study of the resistivity change as a function of the applied stress which is usually measured. From the theoretical point ANTONČÍK

of view it seems to be more convenient to deal with the elastoresistance tensor $m_{ijk\ell}$ which relates the strain tensor $\epsilon_{k\ell}$ to the change in conductivity; for cubic crystals we can write

$$\sigma_{ij} = \sigma_0 \left[\delta_{ij} - \sum_{k\ell} m_{ijk\ell} \epsilon_{k\ell} \right]$$
(172)

The tensor $m_{ijk\ell}$ is thus defined as follows:

$$m_{ijk\ell} = -\frac{1}{\sigma_0} \frac{\partial \sigma_{ii}}{\partial \epsilon_{k\ell}}$$
(173)

It should be noted that the strains usually employed in experiments are of the order of 10^{-3} so that the linear dependence of σ_{ij} on $\epsilon_{k\ell}$ in Eq.(172) is quite satisfactory.



FIG. 34. The shift of the valleys due to the external stress. (After Ziman, J., Electrons and Phonons, Oxford (1960)).

We have shown at the beginning that in general a uniaxial stress can remove the degeneracy of some extrema in a many-valley model according to their orientation with respect to the applied stress. If the relative shift of different extrema is comparable with k_BT the electron population will be re-distributed: electrons migrate from the higher-energy to the lower-energy valleys. This is schematically shown in Fig. 34. Although this electron transfer is not the only effect due to the applied stress in this case, it is shown to be the most important at moderately low temperatures (see Ref.[14]).

We shall start with the conductivity tensor of a single valley as given for the unstrained crystal by Eq.(21).

$$\sigma_{ij}^{(r)} = N^{(r)} e \mu_{ij}^{(r)}$$
, $N^{(r)} = \frac{1}{s} N$ (174)

Then the change in conductivity produced by the strain is given by

$$\delta \sigma_{ij}^{(r)} = \delta N^{(r)} e \mu_{ij}^{(r)}$$
(175)

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where, following Eq.(152), the thermal distribution function $f_0^{(r)}$ becomes

$$f^{(r)} = f_0^{(r)} \exp\left[\frac{\delta \epsilon_F^{(r)} - \delta \epsilon_c^{(r)}}{k_B T}\right]$$
(176)

here $\delta \epsilon_F^{(r)}$ is the change of ϵ_F due to the strain and $\delta \epsilon_c^{(r)}$ is the shift of the extremum given by expression (62). As the exponential factor in Eq.(176) does not depend on the energy of electrons, $\delta N^{(r)}$ can be easily evaluated

$$\delta N^{(r)} = N^{(r)} \left[\exp\left(\frac{\delta \epsilon_{F}^{(r)} - \delta \epsilon_{C}^{(r)}}{k_{B}T}\right) - 1 \right]$$
(177)

In fact, the shift of the Fermi level must be independent of the valley; moreover it holds that

$$\sum_{\mathbf{r}} \delta \mathbf{N}^{(\mathbf{r})} = \mathbf{0} \tag{178}$$

This gives

$$\exp\left(-\frac{\delta \epsilon_{\rm F}}{k_{\rm B}T}\right) = \frac{1}{s} \sum_{\rm r} \exp\left(-\frac{\delta \epsilon_{\rm c}^{\rm (r)}}{k_{\rm B}T}\right)$$
(179)

The total change in conductivity is

$$\delta \sigma_{ij} = e \sum_{r} \delta N^{(r)} \mu^{(r)}_{ij}$$
(180)

Substituting expressions (177) and (179) into Eq.(180) we get

$$\delta \sigma_{ij} = N^{(r)} e \frac{\sum_{r} \mu_{ij}^{(r)} \exp\left(-\frac{\delta \epsilon_{c}^{(r)}}{k_{B}T}\right)}{\frac{1}{s} \sum_{r} \exp\left(-\frac{\delta \epsilon_{c}^{(r)}}{k_{B}T}\right)} - \sigma_{0} \delta_{ij}$$
(181)

Supposing that we are interested in small strains such that the exponential in Eq.(181) can be replaced by terms linear in $\delta \epsilon_c^{(n)} / k_B^{-T}$, we get

$$\delta \sigma_{ij} = N^{(r)} e \sum_{r} \mu_{ij}^{(r)} \left(-\frac{1}{k_B T} \right) \left[\delta \epsilon_c^{(r)} - \frac{1}{s} \sum_{r} \delta \epsilon_c^{(r)} \right]$$

$$= -\frac{N^{(r)} e}{k_B T} \sum_{r} \sum_{k\ell} \mu_{ij}^{(r)} \left[\Xi_{k\ell}^{(r)} - \frac{1}{s} \sum_{r} \Xi_{k\ell}^{(r)} \right] \epsilon_{k\ell}$$
(182)

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By comparing this expression with Eq.(172) we can immediately get the coefficients of the elastoresistance tensor. As an example let us consider two many-valley models as typified by the conduction band of Si and Ge. In fact, there would be no sense in calculating all the components of the elastoresistance tensor $m_{ijk\ell}$ (there are only three independent components with cubic lattices, namely m_{1111} , m_{1122} and m_{1212}) so I shall discuss only one or two of them.

Firstly, let us calculate the component m_{1111} with Si. We have shown in the previous section that the contributions of different valleys to the total mobility μ_{11} are as follows:

$$\begin{bmatrix} \pm 1, 0, 0 \end{bmatrix} \qquad \begin{bmatrix} 0, \pm 1, 0 \end{bmatrix} \qquad \begin{bmatrix} 0, 0, \pm 1 \end{bmatrix}$$

$$2\mu_{11} \qquad 2\mu_{1} \qquad 2\mu_{1}$$

The corresponding expressions $\Xi_{11}^{(r)}$ in (35) are given by (Eq.(63))

$$\Xi_d + \Xi_u \qquad \qquad \Xi_d \qquad \qquad \Xi_d$$

and the square bracket in Eq.(182) can be written as follows:

$$\frac{2}{3}\Xi_{u} \qquad -\frac{1}{3}\Xi_{u} \qquad -\frac{1}{3}\Xi_{u}$$

 m_{1111} takes the form

$$m_{1111} = \frac{2}{9} \frac{\Xi_{u}}{k_{B}T} \frac{\mu_{\parallel} - \mu_{\perp}}{\mu}$$
(183)

where, according to Eq.(171), $\mu = e \langle \tau \rangle \frac{1}{3} \left(\frac{1}{m_{\parallel}} + \frac{2}{m_{\perp}} \right)$

Similarly

$$m_{1122} = -\frac{1}{9} \frac{\Xi_{u}}{k_{\rm B} T} \frac{\mu_{\rm H} - \mu_{\rm I}}{\mu}$$
(184)

while

$$m_{1212} = 0$$
 (185)

The latter value results from Eq.(171).

On the other hand, when calculating the contributions of ellipsoids oriented in the <111> direction we get the same result from all valleys (see Eq.(24)): $(1/3)(\mu_{\parallel} + 2 \mu_{\perp})$. Accordingly when evaluating the summation in Eq.(182) we find that the (11) component is equal to zero for all ellipsoids. We can thus write

$$m_{1111} = 0$$
 (186)

and similarly

$$m_{1122} = 0$$
 (187)

while the third component can be shown to be

$$m_{1212} = \frac{1}{9} \frac{\Xi_{u}}{k_{B}T} \frac{\mu_{\parallel} - \mu_{\perp}}{\mu}$$
(188)

From the foregoing analysis it is clear that a large elastoresistance effect is produced if the applied stress destroys the symmetry of the set of ellipsoids because the transfer effect implies unequal weighting of the contribution of individual ellipsoids. If, for example, a silicon crystal is extended along, say, the [100] axis, then the degeneracy of the $[\pm 1, 0, 0]$ valleys with the $[0, \pm 1, 0]$ and $[0, 0, \pm 1]$ valleys is removed and this gives rise to a large effect. On the other hand, if Ge is extended in the same direction, the configuration of ellipsoids does not change and there is also no change in resistivity. Similarly, the extension of both crystals along the [111] direction gives rise to an opposite effect: There is a large change in conductivity with Ge but a negligible change with Si. As the components of the elastoresistance tensor $m_{ijk\ell}$ are of the order of 10^2 , relatively large changes in resistivity can be expected. This is shown in Fig. 35. Note that experimental measurements of this type enable us to estimate the value of the deformation potential Ξ_{u} if the ratio of μ_{I} and μ_{II} is known. On the other hand, the deformation potential constant Ξ_d (or better Tr Ξ) can be estimated by experiments using hydrostatic pressure.





It should be added that it is possible, in principle, to apply such large strains of proper symmetry as to transfer electrons from several equivalent valleys into one or two valleys only; in this case the conductivity anisotropy and other quantities can be measured directly.

The above discussion can be extended to holes as well but we shall not deal with this problem here. Those interested are referred to the original article by Picus and Bir [15]. 4.3. Magnetoresistance

Another method which enables us to obtain considerable information about the band structure of semiconductors is the study of the magnetoresistance effect. In fact, the many-valley structure of Si and Ge has been deduced in this way (Meiboom and Abeles, 1954). The formal treatment of this effect is very similar to that used with metals. First, I shall briefly summarize some well-known results.

As in the previous section I shall discuss the conductivity tensor. In the presence of a low magnetic field we can expand $\sigma_{ij}(\vec{H})$ in a Taylor series up to the second order in the components of the magnetic field

$$\sigma_{ij}(\vec{H}) = \sigma_{ij}(0) + \sum_{k} \sigma_{ijk} H_{k} + \sum_{k\ell} \sigma_{ijk\ell} H_{k} H_{\ell}$$
(189)

here

$$\sigma_{ijk} = \left[\frac{\partial \sigma_{ij}(\vec{H})}{\partial H_k}\right]_{\vec{H}=0}, \quad \sigma_{ijk\ell} = \sigma_{ij\ell k} = \frac{1}{2} \left[\frac{\partial^2 \sigma_{ij}(\vec{H})}{\partial H_k \partial H_\ell}\right]_{\vec{H}=0}$$
(190)

 $\sigma_{ij}(0)$ is the usual conductivity tensor (see Eq.(171)). $\sigma_{ij\ell}$ is the (third-rank) Hall effect tensor which defines the Hall constant

$$R = \frac{\sigma_{ij\ell}}{\sigma_0}$$
(191)

 $\sigma_{ijk\ell}$ is the (fourth-rank) magnetoconductivity tensor (in fact in cubic crystals only the components $\sigma_{i\neq j\neq k}$, σ_{iiii} , σ_{iijj} and σ_{ijij} are in general different from zero).

Supposing that the collision term in the Boltzman equation is unaffected by the magnetic field and using the usual relaxation-time approximation (149), Eq. (148) can be rewritten as follows:

$$-\frac{e}{\hbar}\left[\vec{E} + \frac{1}{\hbar c} \nabla_{\vec{k}} \epsilon \times \vec{H}\right] \nabla_{\vec{k}} f(\vec{k}) = -\frac{f_1(\vec{k})}{\tau(\epsilon)}$$
(192)

where f₁ is defined by

$$f(\vec{k}) = f_0(\vec{k}) + f_1(\vec{k})$$
 (193)

Substituting expression (193) into (192) we get the following equation to the first order in \vec{E} :

$$\frac{e}{\hbar} \vec{E} \cdot \nabla_{\vec{k}} f_0 + \frac{e}{\hbar^2 c} \left(\nabla_{\vec{k}} \epsilon \times \vec{H} \right) \cdot \nabla_{\vec{k}} f_1 = \frac{f_1}{\tau}$$
(194)

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Note the correction function f_1 in the magnetic term. This is due to the fact that the corresponding term involving f_0 is identically equal to zero. Equation (194) can be rewritten as

$$\left[1 - \tau \frac{e}{\hbar^2 c} \left(\nabla_{\vec{k}} \epsilon \times \vec{H}\right) \cdot \nabla_{\vec{k}}\right] f_1 = \frac{e}{\hbar} \tau \vec{E} \cdot \nabla_{\vec{k}} f_0$$
(195)

This equation is usually solved for f_1 using the inverse operator

$$\left[1 - \tau \frac{\mathrm{e}}{\hbar^2 \mathrm{c}} \left(\nabla_{\vec{k}} \epsilon \times \vec{H}\right) \cdot \nabla_{\vec{k}}\right]^{-1}$$
(196)

Expanding this inverse operator in a power series and retaining only terms up to the second order in components of the magnetic field we get

$$f_{1} = \left\{ 1 + \tau \frac{e}{\hbar^{2}c} \left(\nabla_{\vec{k}} \epsilon \times \vec{H} \right) \nabla_{\vec{k}} - \left[\tau \frac{e}{\hbar^{2}c} \left(\nabla_{\vec{k}} \epsilon \times \vec{H} \right) \nabla_{\vec{k}} \right]^{2} \right\} \left(\frac{e}{\hbar} \tau \vec{E} \cdot \nabla_{\vec{k}} \epsilon f_{0} \right)$$
(197)

Following Eq.(153), \vec{j} is given by

$$\vec{j} = -\frac{e}{4\pi^3} \int \vec{v} f_1 d^3 \vec{k}$$
(198)

In calculating $\sigma_{ij}(\vec{H})$ and using definitions (190) we get after a simple but tedious calculation

$$\sigma_{ijk} = \frac{e^3}{4\pi^3 c\hbar} \sum_{mn} \int \frac{\partial f_0}{\partial \epsilon} \tau v_i v_m \frac{\partial}{\partial k_n} (\tau v_j) d^3 \vec{k} \cdot \delta_{mnk}$$
(199)

$$\sigma_{ijk\ell} = -\frac{e^4}{4\pi^3 c^2 \hbar^2} \sum_{mnpq} \int \frac{\partial f_0}{\partial \epsilon} \tau v_i v_m \frac{\partial}{\partial k_n} \left[\tau v_p \frac{\partial}{\partial k_q} (\tau v_j) \right] d^3\vec{k} \frac{\delta_{kmn} \delta_{\ell pq} + \delta_{kpq} \delta_{\ell mn}}{2}$$
(200)

Here δ_{ijk} is the Levi-Cività tensor (δ_{ijk} vanishes if any of two subscripts are equal, and is +1 or -1 for even and odd permutations of the subscripts, respectively). Note that if τ depends on the energy only, then the relaxation times can be grouped together outside the differentials in Eqs (52) and (53). This is due to the fact that the operator

$$(\nabla_{\vec{k}} \epsilon \times \vec{H}) \cdot \nabla_{\vec{k}}$$
(201)

applied to a function of ϵ only is zero.

To proceed further we have to choose some special types of energy bands.

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4.3.1. Simple parabolic band

Let us discuss the simple parabolic band. Substituting expression (151) into Eqs (199) and (200) we get after a simple calculation (see also Eq. (158))

$$\sigma_{ijk} = -\frac{Ne^3}{m_e^2 c} \langle \tau^2 \rangle \delta_{ijk}$$
(202)

$$\sigma_{ijk\ell} = \frac{Ne^4}{m_e^3 c^2} \langle \tau^3 \rangle \sum_{p} \frac{\delta_{pki} \delta_{pj\ell} + \delta_{pjk} \delta_{p\ell i}}{2}$$
(203)

Note that owing to the properties of the Levi-Cività tensor the longitudinal magnetoconductivity corresponding to the σ_{iiii} components of (56) always vanishes.

4.3.2. Single ellipsoidal band

In this case we can proceed in a similar way as in section 4.1.2. Substituting expression (162) into Eqs (199) and (200) and using transformation (163) we get

$$\sigma_{ijk} = -\frac{Ne^3}{c} \langle \tau^2 \rangle \frac{\delta_{ijk}}{m_i m_j}$$
(204)

$$\sigma_{ijk\ell} = \frac{Ne^4}{c^2} \langle \tau^3 \rangle \sum_{p} \frac{\frac{\delta_{pki} \delta_{pj\ell} + \delta_{pjk} \delta_{p\ell i}}{2 m_i m_j m_p}$$
(205)

In this case, too, all components σ_{iiii} are equal to zero. Note that both these expressions can be generalized if we are dealing with an unisotropic relaxation time. In this case we simply use relation (167).

4.3.3. Many-valley band

To obtain the Hall effect tensor and the magnetoconductivity tensor for a many-valley band we have to sum all the contributions from all equivalent ellipsoids. Using the same method as in section 4.3 we can immediately write

$$\sigma_{ijk} = -\frac{Ne^3}{c} \langle \tau^2 \rangle \frac{1}{s} \sum_{r}^{s} \sum_{\alpha\beta\gamma} T_{i\alpha}^{(r)} T_{j\beta}^{(r)} T_{k\gamma}^{(r)} \frac{\delta_{\alpha\beta\gamma}}{m_{\alpha}^{(r)} m_{\beta}^{(r)}}$$
(206)

$$\sigma_{ijk\ell} = \frac{Ne^4}{c^2} \langle \tau^3 \rangle \frac{1}{s} \sum_{r}^{s} \sum_{\alpha\beta\gamma\lambda\nu} T_{i\alpha}^{(r)} T_{j\beta}^{(r)} T_{k\gamma}^{(r)} T_{\ell\lambda}^{(r)} \frac{\delta_{\nu\gamma\alpha} \delta_{\nu\beta\lambda} + \delta_{\nu\beta\gamma} \delta_{\nu\lambda\alpha}}{2 m_{\alpha}^{(r)} m_{\beta}^{(r)} m_{\nu}^{(r)}}$$
(207)

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As we are dealing with cubic crystals only, the components σ_{123} , σ_{1111} , σ_{1122} and σ_{1212} have to be calculated. After straightforward but tedious calculations we obtain for the <100> ellipsoids

$$\sigma_{123} = -\frac{\text{Ne}^3 \langle \tau^2 \rangle}{\text{c} m_0^2} \frac{3 \text{K} (2+\text{K})}{(1+2 \text{K})^2}$$
(208)

$$\sigma_{1111} = 0$$

$$\sigma_{1112} = -\frac{Ne^4 \langle \tau^3 \rangle}{c^2 m_0^2} - \frac{9 K (1 + K + K^2)}{(1 + 2 K)^2}$$

$$\sigma_{1212} = \frac{Ne^4 \langle \tau^3 \rangle}{c^2 m_0^3} - \frac{27 K^2}{2 (1 + 2 K)^3}$$
(209)

Here $\rm K=m_1/m_2$ and $\rm m_0$ is defined by Eq.(171). Similarly, for the <111> ellipsoids one gets

$$\sigma_{123} = -\frac{\text{Ne}^3 \langle \tau^2 \rangle}{\text{c } m_0^2} \frac{3 \text{ K} (2 + \text{K})}{(1 + 2 \text{ K})^2}$$
(210)

$$\sigma_{1111} = -\frac{Ne^4 \langle \tau^3 \rangle}{c^2 m_0^3} \frac{6 K (K-1)}{(1+2 K)^3}$$

$$\sigma_{1122} = -\frac{Ne^4 \langle \tau^3 \rangle}{c^2 m_0^3} \frac{3 K (2+K)}{(1+2 K)^2}$$

$$\sigma_{1212} = \frac{Ne^4 \langle \tau^3 \rangle}{c^2 m_0^3} \frac{3 K (2+K)}{2(1+2 K)^2}$$
(211)

When comparing the results for <100> and <111> ellipsoids we see that the Hall effect tensor is the same in both cases. Hence by measuring R we are not able to determine the orientation of the ellipsoids. On the other hand, following Eqs (209) and (211), measurements of the magnetoconductivity (or better magnetoresistance) coefficients make it possible to distinguish between the various arrangements of ellipsoids in the Brillouin zone. Figure 36 shows a typical variation of the magnetoresistance of n-type Si with the angle between \vec{j} and \vec{H} . We can see that Si has a negligibly small longitudinal magnetoresistance for current flow in the <100> directions. This fact implies that the principal axes of the ellipsoids are colinear with this direction and this condition is fulfilled for the set of <100> ellipsoids. On the other hand, similar measurement for Ge shows that σ_{1111} has quite a large value in this case. A more detailed analysis leads to the conclusion that the magnetoresistance measurements are in accordance with the model of <111> ellipsoids.

Finally, one can estimate the anisotropy coefficient K using the ratio of different tensor components (209) or (211). The values of K thus

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estimated (being 20 for n-type Ge and 5 for n-type Si) are in good agreement with the values determined from other experiments (e.g. cyclotron resonance).





Naturally, a similar analysis has been performed with different materials and under different conditions. Those interested are referred to the book by Beer [16] for further information.

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KOHN-ROSTOKER METHOD FOR ELECTRON ENERGY BANDS OF BERYLLIUM

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Abstract

Derivation of the method for simple Bravais lattices.
 Evaluation of structure constants.
 Kohn-Rostoker method for complex lattices.

1. DERIVATION OF THE METHOD FOR SIMPLE BRAVAIS LATTICES

To find the electronic band structure of a solid, we have to solve a one-electron Schrödinger equation where the potential is a suitably determined periodic potential $V(\vec{r})$ of the lattice. The equation to be solved is

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) + V(\vec{r})\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\psi_{\vec{k}}(\vec{r})$$
(1)

where \vec{k} is the propagation vector of the electron and $E(\vec{k})$ the corresponding value of the one-electron energy. For the sake of convenience we shall drop the suffix \vec{k} from wave function and energy, but shall always understand that these energies pertain to certain values of \vec{k} . We shall also drop $\hbar^2/2m$ either by choosing a proper unit of energy or by assuming that the new V(\vec{r}) and E(\vec{k}) are $2m/\hbar^2$ times the old ones. Thus, we write Eq.(1) as

$$-\nabla^{2}\psi(\vec{\mathbf{r}}) + \nabla(\vec{\mathbf{r}})\psi(\vec{\mathbf{r}}) = E\psi(\vec{\mathbf{r}})$$
(2)

This equation, along with its boundary conditions, can be converted into an integral equation

$$\psi(\vec{\mathbf{r}}) = \int_{\Omega} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') V(\vec{\mathbf{r}}') \psi(\vec{\mathbf{r}}') d\vec{\mathbf{r}}'$$
(3a)

where Ω is the volume of the lattice unit cell and $G(\vec{r}, \vec{r'})$ is the Green's function which depends on the chosen \vec{k} and E; it obeys the differential equation

$$(\nabla^2 + E) G(\vec{r}, \vec{r'}) = \delta(\vec{r} - \vec{r'})$$
(3b)

The Green's function can be written in reciprocal-space representation as

$$G_{\vec{k}}(E, \vec{r} - \vec{r'}) = G(\vec{r}, \vec{r'})$$
$$= -\frac{1}{\Omega} \sum_{\vec{k}_{n}} \frac{e^{i(\vec{k} + \vec{k}_{n}) \cdot \vec{(r' - r')}}}{(\vec{k} + \vec{k}_{n})^{2} - E}$$
(4)

if plane Bloch waves normalized in the unit cell volume i.e.

$$\frac{1}{\sqrt{\Omega}} e^{i(\vec{k}+\vec{K}_n)\cdot\vec{r}}$$
(5)

are used to expand the wave function $\psi(\vec{r})$ in Eq.(2). The Green's function defined in Eq.(4) has the properties

$$G(\vec{r}, \vec{r'}) = G^*(\vec{r'}, \vec{r})$$
(6)

and

$$G(\vec{r} + \vec{R}_i) = e^{i\vec{k}\cdot\vec{R}_i} G(\vec{r},\vec{r}')$$
(7)

The \vec{K}_n are the lattice vectors of the reciprocal space and the \vec{R}_i those of the crystal lattice. Integrating the right-hand side of Eq.(4) we obtain what is called the structural Green's function

$$\mathbf{G}_{\vec{k}}(\kappa, \mathbf{r} - \mathbf{r}') = \sum_{\substack{\vec{k} \\ \vec{k}_{i}}} \frac{\mathbf{e}^{i\kappa |\vec{r} - \vec{r}' + \vec{k}_{i}|}}{|\vec{r} - \vec{r}' + \vec{k}_{i}|} \mathbf{e}^{i\vec{k} \cdot \vec{k}_{i}}$$
(8)

where $\kappa = \sqrt{E}$ if E is positive and $i\sqrt{-E}$ if E is negative. This is the directspace representation of the Green's function used in Eq.(3) where the integration has been reduced to one over the unit cell only. Ziman [1] calls it a complete <u>Greenian</u>.

The method given by Kohn and Rostoker [2] is a variational method. They define a variational functional Λ whose variation gives the integral of Eq.(3a). Λ is given by

$$\Lambda = \int_{\Omega} d\vec{r} \psi^*(\vec{r}) V(\vec{r}) \left[\psi(\vec{r}) - \int_{\Omega'} G(\vec{r}, \vec{r'}) V(\vec{r'}) \psi(\vec{r'}) d\vec{r'} \right]$$
(9)

For $\delta\Lambda$ to be zero the variation with respect to $\psi^{*}\left(\vec{\mathbf{r}}\right)$ will yield the condition

$$\psi(\vec{\mathbf{r}}) = \int_{\Omega} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \, \nabla(\vec{\mathbf{r}}') \, \psi(\vec{\mathbf{r}}') \, d\vec{\mathbf{r}}'$$
(10)

which is Eq.(3a). It can be seen that $\Lambda = 0$ if in Eq.(9) $\psi(\vec{r})$ is the exact solution of the Schrödinger equation (2).

We have indicated that if $\psi(\vec{r})$ is the exact solution of the Schrödinger equation, then

$$\Lambda(\psi(\vec{\mathbf{r}}),\vec{\mathbf{k}},\mathbf{E}(\vec{\mathbf{k}})) = 0 \tag{11}$$

On the other hand, if we have a trial function $\psi_{\rm t}$ given by

$$\psi_{t} = \psi(\vec{r}) + \epsilon \chi(\vec{r})$$
(12)

where ϵ is a small real parameter, then

$$\begin{split} \Lambda(\psi_{i},\vec{k},\mathbf{E}_{i}) &= \int_{\Omega} d\vec{r} \left(\psi + \epsilon \chi\right)^{*} \nabla(\vec{r}) \left(\psi + \epsilon \chi\right) \\ &- \int_{\Omega} \int_{\Omega'} d\vec{r} d\vec{r}^{\dagger} \left(\psi + \epsilon \chi\right)^{*} \nabla(\vec{r}) G(\vec{r},\vec{r}^{\dagger}) \nabla(\vec{r}^{\dagger}) \left(\psi + \epsilon \chi\right) \\ &= \int_{\Omega} d\vec{r} \psi^{*} \left(\vec{r}\right) \nabla(\vec{r}) \psi(\vec{r}) - \int_{\Omega} \int_{\Omega'} d\vec{r} d\vec{r}^{\dagger} \psi^{*} \left(\vec{r}\right) \nabla(\vec{r}) G(\vec{r},\vec{r}^{\dagger}) \nabla(\vec{r}^{\dagger}) \psi(\vec{r}^{\dagger}) \\ &+ \epsilon \int_{\Omega} d\vec{r} \chi^{*} \left(\vec{r}\right) \nabla(\vec{r}) \left[\psi(\vec{r}) - \int_{\Omega'} d\vec{r}^{\dagger} G(\vec{r},\vec{r}^{\dagger}) \nabla(\vec{r}) \psi(\vec{r}) d\vec{r}^{\dagger} \right] \\ &+ \epsilon \int_{\Omega'} d\vec{r}^{\dagger} \nabla(\vec{r}^{\dagger}) \chi(\vec{r}^{\dagger}) \left[\psi^{*} \left(\vec{r}\right) - \int_{\Omega} G^{*} \left(\vec{r}^{\dagger},\vec{r}\right) \nabla(\vec{r}) \psi(\vec{r}) d\vec{r} \right] \\ &+ \epsilon^{2} \left[\int_{\Omega} \chi^{*} \left(\vec{r}\right) \nabla(\vec{r}) \chi(\vec{r}) d\vec{r} \right] \\ &- \int_{\Omega} \int_{\Omega'} \chi^{*} \left(\vec{r}\right) \nabla(\vec{r}) G(\vec{r},\vec{r}^{\dagger}) \nabla(\vec{r}^{\dagger}) \chi(\vec{r}^{\dagger}) d\vec{r} d\vec{r}^{\dagger} \right] \end{split}$$
(13)

In Eq.(13) the first term is zero as Λ is zero for exact $\psi(\vec{\mathbf{r}})$. The second and third terms are zero by virtue of Eq.(3) and its complex conjugate. Thus we have $\Lambda(\psi_t, \vec{\mathbf{k}}, \mathbf{E}_t) = \mathbf{0}(\epsilon^2)$ and for the eigenvalue \mathbf{E}_t we have, obviously:

$$\mathbf{E}_{t} - \mathbf{E} = \mathbf{O}(\boldsymbol{\epsilon}^{2}) \tag{14}$$

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Thus the error in energy is of the second order as compared to the error in the trial function. Similarly, if for a given E we calculate \vec{k}_t from the trial function by the condition $\Lambda(\psi_t, \vec{k}_t, E) = 0$ we have

$$\vec{k}_{t} - \vec{k} = O(\epsilon^{2})$$
(15)

Having now set up the variational principle $\delta \Lambda = 0$ we can use the Rayleigh-Ritz method. For this, we use a trial function of the form

$$\psi_{t}(\vec{r}) = \sum_{j=0}^{n} C_{j} \varphi_{j}(\vec{r})$$
(16)

to calculate Λ . Thus,

$$\Lambda = \int_{\Omega} \psi_{t}^{*}(\vec{\mathbf{r}}) \nabla(\vec{\mathbf{r}}) \psi_{t}(\vec{\mathbf{r}}) d\vec{\mathbf{r}} - \int_{\Omega} \int_{\Omega} d\vec{\mathbf{r}} d\vec{\mathbf{r}}' \psi_{t}^{*}(\vec{\mathbf{r}}) \nabla(\vec{\mathbf{r}}) G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \nabla(\vec{\mathbf{r}}') \psi_{t}(\vec{\mathbf{r}}')$$

$$= \sum_{i, j} C_{i}^{*} C_{j} \left[\int_{\Omega} d\vec{\mathbf{r}} \phi_{i}^{*}(\vec{\mathbf{r}}) \nabla(\vec{\mathbf{r}}) \phi_{j}(\vec{\mathbf{r}}) - \int_{\Omega} \int_{\Omega'} d\vec{\mathbf{r}}' d\vec{\mathbf{r}}' \phi_{i}^{*}(\vec{\mathbf{r}}) \nabla(\vec{\mathbf{r}}) G(\vec{\mathbf{r}}, \vec{\mathbf{r}}')$$

$$\times \phi_{j}(\vec{\mathbf{r}}') \nabla(\vec{\mathbf{r}}') \right] = \sum_{i, j} C_{i}^{*} C_{j} \Lambda_{ij}$$

$$(17)$$

The expansion coefficients in Eq.(17) may, in general, be complex. Now the variation of Λ with respect to one of the coefficients C_i^* yields the condition

 $\delta \Lambda = \sum_{j} \Lambda_{ij} C_{j}$ (18)

We have such a condition for each i and so we obtain n linear equations in C_j where the coefficients are Λ_{ij} . For a non-trivial solution of these equations to exist we must have

 $\left|\Lambda_{ii}\right| = 0 \tag{19}$

Since for a given set of functions φ_i the Λ_{ij} are functions of k and E only, the solution of Eq.(19) with the required stationary connection between E and k, thus, solves the problem we are faced with. Further, if one obtains the coefficients C_i after having found the eigenvalues of the matrix Λ_{ij} , the wave function ψ_t becomes known and can be used wherever required. The usefulness of the Kohn-Rostoker method depends upon how easily the Λ_{ij} can be calculated.

One way in which the form of the coefficients Λ_{ij} can be easily determined is to use plane Bloch waves of the form

$$\frac{1}{\sqrt{\Omega}} e^{\vec{i} \cdot \vec{k} + \vec{K}_{\vec{i}} \cdot \vec{r}}$$

Using these Bloch waves we obtain:

$$\Lambda = \sum_{i,j} C_{i}^{*} C_{j} \left[\frac{1}{\Omega} \int_{\Omega} d\vec{r} e^{-i(\vec{k}+\vec{K}_{i})\cdot\vec{r}} V(\vec{r}) e^{i(\vec{k}+\vec{K}_{j})\cdot\vec{r}} - \frac{1}{\Omega} \int_{\Omega} \int_{\Omega} d\vec{r} d\vec{r}' e^{-i(\vec{k}+\vec{K}_{i})\cdot\vec{r}} V(\vec{r}) G(\vec{r},\vec{r}') e^{i(\vec{k}+\vec{K}_{j})\cdot\vec{r}'} \right]$$
(20)

Since $V(\vec{r})$ is periodic in the lattice it can be expanded in the form

$$V(\vec{\mathbf{r}}) = \sum_{\vec{k}_{m}} V(\vec{k}_{m}) e^{i\vec{k}_{m}\cdot\vec{\mathbf{r}}}$$
(21)

If we now use Eq.(21) for $V(\vec{r})$ and Eq.(4) for $G(\vec{r}, \vec{r'})$ in Eq.(20), we obtain

$$\begin{split} \Lambda &= \sum_{i,j} C_{i}^{*} C_{j} \left[\frac{1}{\Omega} \int_{\Omega} d\vec{r} e^{-i(\vec{k}+\vec{K}_{j})\cdot\vec{r}} \sum_{\vec{k}_{m}} V(\vec{k}_{m}) e^{i\vec{k}_{m}\cdot\vec{r}} e^{i(\vec{k}+\vec{K}_{j})\cdot\vec{r}} \right] \\ &+ \frac{1}{\Omega^{2}} \int_{\Omega} d\vec{r} d\vec{r}' e^{-i(\vec{k}+\vec{K}_{j})\cdot\vec{r}} \sum_{\vec{k}_{m}} V(\vec{k}_{m}) e^{i\vec{k}_{m}\cdot\vec{r}} \\ &\times \sum_{\vec{k}_{m}} \frac{e^{i(\vec{k}+\vec{k}_{n})\cdot(\vec{r}-\vec{r}')}}{(\vec{k}+\vec{k}_{n})^{2}-\vec{E}} \sum_{\vec{k}_{s}} V(\vec{k}_{s}) e^{i\vec{k}_{s}\cdot\vec{r}} e^{i(\vec{k}+\vec{k}_{j})\cdot\vec{r}'} \\ &= \sum_{i,j} C_{i}^{*} C_{j} \left[\sum_{\vec{k}_{m}} V(\vec{k}_{m}) \frac{1}{\Omega} \int_{\Omega} d\vec{r} e^{i(\vec{k}_{m}-(\vec{k}_{i}-\vec{k}_{j}))\cdot\vec{r}} \\ &+ \sum_{\vec{k}_{n}} \sum_{\vec{k}_{m}} \sum_{\vec{k}_{s}} \frac{1}{(\vec{k}+\vec{k}_{n})^{2}-\vec{E}} V(\vec{k}_{m}) V(\vec{k}_{s}) \frac{1}{\Omega} \int_{\Omega} d\vec{r} e^{i(\vec{k}_{m}-(\vec{k}_{i}-\vec{k}_{j}))\cdot\vec{r}} \\ &\times \frac{1}{\Omega} \int_{\Omega'} d\vec{r}' e^{i(\vec{k}_{s}-(\vec{k}_{n}-\vec{k}_{j})\cdot\vec{r}'} \\ &= \sum_{i,j} C_{i}^{*} C_{j} \left[\sum_{\vec{k}_{m}} V(\vec{k}_{m}) \delta \left[\vec{k}_{m} - (\vec{k}_{i}-\vec{k}_{j}) \right] \end{split}$$

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$$+\sum_{\vec{k}_{n}}\sum_{\vec{k}_{m}}\sum_{\vec{k}_{s}}V(\vec{k}_{m})V(\vec{k}_{s})\frac{1}{(\vec{k}+\vec{k}_{n})^{2}-E}\delta\left[\vec{K}_{m}-(\vec{k}_{i}-\vec{k}_{n})\right]\delta\left[\vec{K}_{s}-(\vec{k}_{n}-\vec{K}_{j})\right]$$
$$=\sum_{i,j}C_{i}^{*}C_{j}\left[V(\vec{K}_{i}-\vec{K}_{j})+\sum_{\vec{k}_{n}}\frac{V(\vec{K}_{i}-\vec{K}_{n})V(\vec{K}_{n}-\vec{K}_{j})}{(\vec{k}+\vec{K}_{n})^{2}-E}\right]=\sum_{i}C_{i}^{*}C_{j}\Lambda_{ij}$$
(22)

where

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$$\Lambda_{ij} = V(\vec{K}_{i} - \vec{K}_{j}) + \sum_{\vec{K}_{n}} \frac{V(\vec{K}_{i} - \vec{K}_{n})V(\vec{K}_{n} - \vec{K}_{j})}{(\vec{k} + \vec{K}_{n})^{2} - E}$$
(23)

The secular equation to be solved in order to obtain a relation between \vec{k} and E is

$$\left| V(\vec{K}_{i} - \vec{K}_{j}) + \sum_{\vec{K}_{n}} \frac{V(\vec{K}_{i} - \vec{K}_{n}) V(\vec{K}_{n} - \vec{K}_{j})}{(\vec{k} + \vec{K}_{n})^{2} - E} \right| = 0$$
(24)

The secular equation of the form given by Eq. (24) may look very simple but in practice it is difficult to evaluate Λ_{ij} . This has two reasons: first, one must know the Fourier coefficients of the potential $V(\vec{r})$, which is not exactly known, and, secondly, one has to sum over \vec{K}_n which is not easy to carry out and yields an infinite sum. But the secular equation has one major role to play and this is that we can show that the Kohn-Rostoker method will fulfil the requirement of the empty-lattice test. We have seen before that Λ is zero for the exact solution. It can be seen that for $V(\vec{r})$ having a constant value over the lattice, the matrix element V(0) is the only one to survive. In this case the determinant $|\Lambda_{ij}|$ has only diagonal terms

$$\Lambda_{ii} = V(0) + \frac{V'(0)}{(\vec{k} + \vec{K}_i)^2 - E}$$
(25)

Then the solution of the scalar equation requires each $\Lambda_{i\,i}\,\text{to}$ be zero, giving

$$E(\vec{k}) = (\vec{k} + \vec{K}_{i})^{2} + V(0)$$
(26)

If V(0) = 0, the eigenvalues are

$$E(\vec{k}) = (\vec{k} + \vec{K}_i)^2$$
 (27)

In general, it is a formidable task to calculate Λ_{ij} as this involves first the calculation of the Green's function for various values of E and \vec{k} and then the evaluation of 6-dimensional integral occurring in

$$\Lambda_{ij} = \int_{\Omega} d\vec{r} \, \phi_i^* (\vec{r}) \nabla(\vec{r}) \, \phi_j(\vec{r}) - \int_{\Omega} \int_{\Omega'} d\vec{r} \, d\vec{r'} \, \phi_i^* (\vec{r}) \, \nabla(\vec{r}) \, G(\vec{r}, \vec{r'}) \, \nabla(\vec{r'}) \, \phi_2(\vec{r'})$$
(28)

The integration is complicated by the fact that the Green's function is singular for equal arguments \vec{r} and $\vec{r'}$ and the region of integration is a complex atomic polyhedron.

A great simplification was achieved by Kohn and Rostoker [2] by using a "muffin tin" potential with

$$V(\vec{r}) = V(r) \quad r < r_i$$
$$V(\vec{r}) = V_0 \qquad r \ge r_i$$
(29)

One can choose the zero of the energy scale such that $V(\vec{r})$ can be taken as zero for $r \ge r_i$. In this case the domain of integration is $r < r_i$ and the contribution to Λ comes from $r < r_i$ and $r' < r_i$. With the above form of potential chosen which means angular average in the domain of $r < r_i$ and space average in the domain of $r \ge r_i$ the solution inside the domain of $r < r_i$ can be written as

$$\psi(\vec{\mathbf{r}}) = \sum_{\ell m} C_{\ell m} Y_{\ell m}(\hat{\mathbf{r}}) R_{\ell}(\mathbf{E}, \mathbf{r})$$
(30)

The choice of a potential of this kind makes it possible to convert the expression for Λ into a form which does not depend explicitly on the potential but involves surface integrals over the sphere inscribed. In order to avoid trouble due to the singularity of the Green's function, the following procedure is adopted.



FIG. 1. Domains of integration over r and r'.

For the integration over r and r' new domains are defined as shown in Fig.1. One, for the integration over r', a sphere of radius $r_i - \epsilon$, and another one, for the integration over r, a sphere of radius $r_i - 2\epsilon$. Here ϵ is a small number which can be allowed to tend to zero after the final expression is obtained. Thus,

$$\Lambda = \lim_{\epsilon \to 0} \Lambda_{\epsilon}$$
(31)

where

$$\Lambda_{\epsilon} = \int_{\mathbf{r}' < \mathbf{r}_{i} - 2\epsilon} d\mathbf{\vec{r}} \psi^{*}(\mathbf{\vec{r}}) \nabla(\mathbf{\vec{r}}) \psi(\mathbf{\vec{r}})$$

-
$$\int_{\mathbf{r}' < \mathbf{r}_{i}^{-\epsilon} - \mathbf{r}} \int_{\mathbf{r}' < \mathbf{r}_{i}^{-2\epsilon}} \psi^{*}(\mathbf{\vec{r}}) \nabla(\mathbf{\vec{r}}) G(\mathbf{\vec{r}}, \mathbf{\vec{r}'}) \nabla(\mathbf{\vec{r}'}) \psi(\mathbf{\vec{r}'}) d\mathbf{\vec{r}} d\mathbf{\vec{r}'}$$
(32)

We shall now convert the integration over the volume to an integration over the surfaces of two spheres, one of a radius of $r_i - 2\epsilon$ and the other one of $r_i - \epsilon$. In this way, r and r' are different and so the singularity of the Green's function does not give rise to any difficulties. The limit $\epsilon \rightarrow 0$ is then taken in order to obtain Λ .

To do so, we use the Schrödinger equation

$$(\nabla^2 + \mathbf{E})\psi(\vec{\mathbf{r}}) = \mathbf{V}(\vec{\mathbf{r}})\psi(\vec{\mathbf{r}})$$
(33)

and replace $V(\vec{r}') \psi(\vec{r}')$ in the expression

$$\psi(\vec{\mathbf{r}}) - \int_{\mathbf{r}' < \mathbf{r}_{\mathbf{i}} - \epsilon} d\vec{\mathbf{r}'} G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) V(\vec{\mathbf{r}'}) \psi(\vec{\mathbf{r}'})$$
(34)

by $(\nabla'^2 + E)\psi(\vec{r'})$ to get a new expression

$$\psi(\vec{\mathbf{r}}) - \int_{\mathbf{r}' < \mathbf{r}_{i} - \epsilon} \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) (\nabla^{\prime 2} + \mathbf{E}) \psi(\vec{\mathbf{r}'}) d\vec{\mathbf{r}'}$$
(35)

If we now use Green's theorem we have

$$\int_{\mathbf{r}' < \mathbf{r}_{i}^{-\epsilon}} \left[G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) (\nabla^{'2} + E) \psi(\vec{\mathbf{r}'}) - \psi(\vec{\mathbf{r}}) (\nabla^{'2} + E) G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \right] d\vec{\mathbf{r}'}$$
$$= \int_{\mathbf{r}' < \mathbf{r}_{i}^{-\epsilon}} \left[G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \nabla^{'2} \psi(\vec{\mathbf{r}'}) - \psi(\vec{\mathbf{r}'}) \nabla^{2} G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \right] d\vec{\mathbf{r}'}$$
(36)

$$= \int_{\mathbf{S}'} d\mathbf{S}' \left[\mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \frac{\partial \psi(\vec{\mathbf{r}}')}{\partial n} - \psi(\vec{\mathbf{r}}') \frac{\partial \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}')}{\partial n} \right]$$
(37)

where $\partial/\partial n$ denotes the normal derivative over the surface S' of the sphere of radius $r_i - \epsilon$. In Eq.(37) we can put

$$(\nabla^{12} + E) G(\vec{r}, \vec{r}') = (\nabla^{12} + E) G^{*}(\vec{r}', \vec{r}) = \delta(\vec{r}' - \vec{r})$$

and, thus,

$$\int_{\mathbf{r}' < \mathbf{r}_{i}^{-\epsilon}} \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \, \mathbf{V}(\vec{\mathbf{r}'}) \, \psi(\vec{\mathbf{r}'}) \, d\vec{\mathbf{r}'} - \int_{\mathbf{r}' < \mathbf{r}_{i}^{-\epsilon}} d\vec{\mathbf{r}'} \, \psi(\vec{\mathbf{r}'}) \, \delta(\vec{\mathbf{r}'}, \vec{\mathbf{r}'})$$
$$= \int_{\mathbf{S}'(\mathbf{r}'=\mathbf{r}_{i}^{-\epsilon})} d\mathbf{S}' \left[\mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial n} - \psi(\vec{\mathbf{r}'}) \frac{\partial \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'})}{\partial n} \right]$$

which gives

$$\psi(\vec{\mathbf{r}}) - \int_{\mathbf{r}' < \mathbf{r}_{1} - \epsilon} d\vec{\mathbf{r}'} G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) V(\vec{\mathbf{r}'}) \psi(\vec{\mathbf{r}'})$$

$$= - \int_{\mathbf{S}'} d\mathbf{S}' \left[G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial n} - \psi(\vec{\mathbf{r}'}) \frac{\partial G(\vec{\mathbf{r}}, \vec{\mathbf{r}'})}{\partial n} \right]$$
(38)

We now introduce the right-hand side of Eq. (38) into Eq. (32) and obtain

$$\Lambda_{\epsilon} = -\int_{\mathbf{r} < \mathbf{r}_{i}^{-2}\epsilon} d\vec{\mathbf{r}} \psi^{*}(\vec{\mathbf{r}}) \nabla(\vec{\mathbf{r}}) \int_{\mathbf{S}'} d\mathbf{S}' \left[\mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} - \psi(\vec{\mathbf{r}'}) \frac{\partial \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'})}{\partial \mathbf{r}'} \right]$$
(39)

where we have put $\partial/\partial r'$ for $\partial/\partial n$. Λ_{ϵ} can be written as

$$\Lambda_{\epsilon} = -\int_{S'} dS' \int_{\mathbf{r} < \mathbf{r}_{i}^{-2}\epsilon} d\vec{\mathbf{r}} V(\vec{\mathbf{r}}) \psi^{*}(\vec{\mathbf{r}}) G(\vec{\mathbf{r}}, \vec{\mathbf{r}}^{\prime}) \frac{\partial \psi(\vec{\mathbf{r}}^{\prime})}{\partial \mathbf{r}^{\prime}} + \int_{S'} dS' \int_{\mathbf{r} < \mathbf{r}_{i}^{-2}\epsilon} d\vec{\mathbf{r}} V(\vec{\mathbf{r}}) \psi^{*}(\vec{\mathbf{r}}) \frac{\partial G(\vec{\mathbf{r}}, \vec{\mathbf{r}}^{\prime})}{\partial \mathbf{r}^{\prime}} \psi(\vec{\mathbf{r}}^{\prime})$$
(40)

Using Eq. (38) we can write Eq. (40) in the form

$$\Lambda_{\epsilon} = \int_{\mathbf{S}'(\mathbf{r}'=\mathbf{r}_{i}^{-\epsilon})} d\mathbf{S}' \int_{\mathbf{r}'=\mathbf{r}_{i}^{-2\epsilon}} d\mathbf{\vec{r}}(\nabla^{2} + \mathbf{E})\psi^{*}(\mathbf{\vec{r}}) \mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'}) \frac{\partial\psi(\mathbf{\vec{r}'})}{\partial\mathbf{r}'} + \int_{\mathbf{S}'(\mathbf{r}'=\mathbf{r}_{i}^{-\epsilon})} d\mathbf{S}' \int_{\mathbf{r}'=\mathbf{r}_{i}^{-2\epsilon}} d\mathbf{\vec{r}}(\nabla^{2} + \mathbf{E})\psi^{*}(\mathbf{\vec{r}}) \frac{\partial\mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'})}{\partial\mathbf{r}'}\psi(\mathbf{\vec{r}'})$$
(41)

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We again use Green's theorem for the two integrals in Eq.(40). The first integral over \vec{r} is obtained by making use of

$$\int_{\mathbf{r}<\mathbf{r}_{i}-\epsilon} d\mathbf{\vec{r}} \left[(\nabla^{2} + \mathbf{E})\psi^{*}(\mathbf{\vec{r}}) \mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'}) - (\nabla^{2} + \mathbf{E}) \mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'})\psi^{*}(\mathbf{\vec{r}}) \right]$$
$$= \int_{\mathbf{r}<\mathbf{r}_{i}-\epsilon} d\mathbf{\vec{r}} \left[\nabla^{2}\psi^{*}(\mathbf{\vec{r}}) \mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'}) - \nabla^{2} \mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'})\psi^{*}(\mathbf{\vec{r}}) \right]$$
$$= \int_{\mathbf{S}(\mathbf{r}=\mathbf{r}_{i}-2\epsilon)} d\mathbf{S} \left[\mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'}) \frac{\partial\psi^{*}(\mathbf{\vec{r}})}{\partial\mathbf{r}} - \psi^{*}(\mathbf{\vec{r}}) \frac{\partial\mathbf{G}(\mathbf{\vec{r}}, \mathbf{\vec{r}'})}{\partial\mathbf{r}} \right]$$

or

$$\int_{\mathbf{r}<\mathbf{r}_{i}-2\epsilon} d\vec{r} \psi^{*}(\vec{r}) \nabla(\vec{r}) G(\vec{r},\vec{r}') - \psi^{*}(\vec{r}')$$
$$= \int_{S(\mathbf{r}=\mathbf{r}_{i}-2\epsilon)} dS \left[G(\vec{r},\vec{r}') \frac{\partial \psi^{*}(\vec{r})}{\partial \mathbf{r}} - \psi^{*}(\vec{r}) \frac{\partial G(\vec{r},\vec{r}')}{\partial \mathbf{r}} \right]$$

which yields

$$\int d\vec{r} \psi^* (\vec{r}) \nabla(\vec{r}) G(\vec{r}, \vec{r'})$$

$$= \psi^* (\vec{r'}) + \int_{S(r=r_i-2\epsilon)} dS \left[G(\vec{r}, \vec{r'}) \frac{\partial \psi^* (\vec{r})}{\partial r} - \psi^* (\vec{r}) \frac{\partial G(\vec{r}, \vec{r'})}{\partial r} \right]$$
(42)

The first integral in Eq. (40) thus becomes

$$-\int_{\mathbf{r}'=\mathbf{r}_{i}-\epsilon} d\mathbf{S}' \left\{ \psi^{*}(\vec{\mathbf{r}'}) + \int_{\mathbf{r}=\mathbf{r}_{i}-2\epsilon} d\mathbf{S} \left[\mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'}) \frac{\partial \psi^{*}(\vec{\mathbf{r}})}{\partial \mathbf{r}} - \psi^{*}(\vec{\mathbf{r}}) \frac{\partial \mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'})}{\partial \mathbf{r}} \right] \right\} \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial \mathbf{r}'}$$

$$= -\int_{\mathbf{r}'=\mathbf{r}_{i}-\epsilon} d\mathbf{S}' \psi^{*}(\vec{\mathbf{r}}) \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} + \int_{\mathbf{r}'=\mathbf{r}_{i}-\epsilon} \int_{\mathbf{r}=\mathbf{r}_{i}-2\epsilon} d\mathbf{S}' d\mathbf{S}$$

$$\times \left[-\mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'}) \frac{\partial \psi^{*}(\vec{\mathbf{r}})}{\partial \mathbf{r}} \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} + \psi^{*}(\vec{\mathbf{r}}) \frac{\partial \mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'})}{\partial \mathbf{r}} \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} \right]$$
(43)

In the same manner, the second integral in Eq.(40) can be shown to be

$$\int_{\mathbf{r}'=\mathbf{r}_{i}-\epsilon} d\mathbf{S}' \left\{ \frac{\partial \psi^{*}(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} + \int_{\mathbf{r}=\mathbf{r}_{i}-2\epsilon} d\mathbf{S} \left[\frac{\partial \mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'})}{\partial \mathbf{r}'} \frac{\partial \psi^{*}(\vec{\mathbf{r}})}{\partial \mathbf{r}} - \psi(\vec{\mathbf{r}}) \frac{\partial^{2} \mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'})}{\partial \mathbf{r}\partial \mathbf{r}'} \right] \right\} \psi(\vec{\mathbf{r}'})$$

$$= \int_{\mathbf{r}'=\mathbf{r}_{i}-\epsilon} d\mathbf{S}' \frac{\partial \psi^{*}(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} \psi(\vec{\mathbf{r}'})$$

$$+ \int_{\mathbf{r}'=\mathbf{r}_{i}-\epsilon} \int_{\mathbf{r}=\mathbf{r}_{i}-2\epsilon} d\mathbf{S} d\mathbf{S}' \left[\frac{\partial \mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'})}{\partial \mathbf{r}'} \frac{\partial \psi^{*}(\vec{\mathbf{r}})}{\partial \mathbf{r}} - \psi(\vec{\mathbf{r}}) \frac{\partial^{2} \mathbf{G}(\vec{\mathbf{r}},\vec{\mathbf{r}'})}{\partial \mathbf{r}\partial \mathbf{r}'} \right] \psi(\vec{\mathbf{r}'})$$
(44)

Putting Eqs (43) and (44) together, we obtain

$$\Lambda_{\epsilon} = \int_{\mathbf{r}'=\mathbf{r}_{\mathbf{i}}-\epsilon} d\mathbf{S}' \left[\psi^{*}(\vec{\mathbf{r}'}) \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} - \psi(\vec{\mathbf{r}'}) \frac{\partial \psi^{*}(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} \right] + \int_{\mathbf{r}'=\mathbf{r}_{\mathbf{i}}-\epsilon} \int_{\mathbf{r}=\mathbf{r}_{\mathbf{i}}-2\epsilon} d\mathbf{S}' d\mathbf{S} \left[\frac{\partial \psi^{*}(\vec{\mathbf{r}})}{\partial \mathbf{r}} - \psi^{*}(\vec{\mathbf{r}}) \frac{\partial}{\partial \mathbf{r}} \right] \times \left[\psi(\vec{\mathbf{r}'}) \frac{\partial}{\partial \mathbf{r}} \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) - \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \frac{\partial \psi(\vec{\mathbf{r}'})}{\partial \mathbf{r}'} \right]$$
(45)

In this equation the first term vanishes as the radial parts of $\psi(\vec{r}')$ and $\psi^*(\vec{r}')$ are identical. This reduces Λ_{ϵ} to

$$\Lambda_{\epsilon} = \int_{\mathbf{r}'=\mathbf{r}_{\mathbf{i}}-\epsilon} d\mathbf{S}' \int d\mathbf{S} \left[\frac{\partial \psi^{*}(\vec{\mathbf{r}})}{\partial \mathbf{r}} - \psi^{*}(\vec{\mathbf{r}}) \frac{\partial}{\partial \mathbf{r}} \right] \\ \times \left[\psi(\vec{\mathbf{r}'}) \frac{\partial}{\partial \mathbf{r}'} G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) - G(\vec{\mathbf{r}}, \vec{\mathbf{r}'}) \frac{\partial}{\partial \mathbf{r}'} \psi(\vec{\mathbf{r}'}) \right]$$
(46)

To be able to use Eq.(46) we must have an expansion of the Green's function in terms of spherical harmonics. For r < r' this expansion is well known:

$$G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') = -\frac{1}{4\pi} \frac{e^{i\kappa|\mathbf{r}-\mathbf{r}'|}}{|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|}$$
$$= \kappa \sum_{\ell m} j_{\ell}(\kappa \mathbf{r}) \left[n_{\ell}(\kappa \mathbf{r}') - i j_{\ell}(\kappa \mathbf{r}') \right] Y_{\ell m}(\hat{\mathbf{r}}) Y_{\ell'm'}^{*}(\hat{\mathbf{r}}')$$
(47)

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In the evaluation of Λ_ϵ we shall use the Green's function expansion in the form

$$G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') = \sum_{\ell m, \ell'm'} \left[A_{\ell m, \ell'm'} \mathbf{j}_{\ell}(\kappa \mathbf{r}) \mathbf{j}_{\ell'}(\kappa \mathbf{r}') + \kappa \delta_{\ell \ell} \delta_{mm'} \mathbf{j}_{\ell}(\kappa \mathbf{r}) \mathbf{n}_{\ell}(\kappa \mathbf{r}') \right] \mathbf{Y}_{\ell m}(\mathbf{\hat{r}}) \mathbf{Y}_{\ell'm'}(\mathbf{\hat{r}'})$$
(57)

We have now to substitute the above expansion for G($\vec{r}, \vec{r'}$) and $\psi(\vec{r})$ in the form

$$\psi(\vec{\mathbf{r}}) = \sum_{\ell,m} C_{\ell m} R_{\ell}(\mathbf{E}, \mathbf{r}) Y_{\ell m}(\mathbf{\hat{r}})$$
(58)

and carry out the integration over the surfaces in Eq. (46) and obtain after letting $\epsilon \rightarrow 0$

$$\Lambda = \sum_{\ell,m} \sum_{\ell',m'} C_{\ell m}^* C_{\ell'm'} \Lambda_{\ell m,\ell'm'}$$

where

$$\Lambda_{\ell m, \ell'm'} = R_{\ell}R_{\ell'}(L_{\ell}j_{\ell} - j_{\ell}')(j_{\ell}' - j_{\ell'}L_{\ell'}) \times \left[A_{\ell m, \ell'm'} + \kappa \delta_{\ell\ell'} \delta_{mm'}, \frac{n_{\ell'} - n_{\ell'}L_{\ell'}}{j_{\ell'}' - j_{\ell'}L_{\ell'}} \right]$$
(59)

where all the functions have their values for $r' = r = r_i$, and L_{ℓ} and $L_{\ell'}$ are the logarithmic derivatives of the radial functions R_{ℓ} and $R_{\ell'}$ on the surface of the sphere of radius r_i . Our problem to be solved is

$$\left| \Lambda_{\ell m, \ell' m} \right| = 0 \tag{60}$$

which can be further simplified by noticing that the expression

 $\mathbf{R}_{\boldsymbol{\ell}}\mathbf{R}_{\boldsymbol{\ell}'}(\mathbf{L}_{\boldsymbol{\ell}}\mathbf{j}_{\boldsymbol{\ell}}-\mathbf{j}_{\boldsymbol{\ell}}')(\mathbf{j}_{\boldsymbol{\ell}}',-\mathbf{j}_{\boldsymbol{\ell}},\mathbf{L}_{\boldsymbol{\ell}},)$

depends only on functions and their derivatives at ${\bf r}_{\rm i}$ so that the secular equation reduces to

$$\left|A_{\ell m, \ell'm'} + \kappa \delta_{\ell \ell} \delta_{mm'} \frac{n_{\ell'} - n_{\ell'} L_{\ell'}}{j_{\ell'} - j_{\ell'} L_{\ell'}}\right| = 0$$
(61)

From scattering theory we know that phase shift δ_{ℓ} is defined by

$$\cot \delta_{\ell'} = \frac{n'_{\ell'} - n_{\ell'} L_{\ell'}}{j'_{\ell'} - j'_{\ell'} L_{\ell'}}$$
(62)

such that Eq. (61) can be written in the form

$$\left|A_{\ell m, \ell'm'} + \kappa \cot \delta_{\ell}, \delta_{\ell \ell'}, \delta_{m m'}\right| = 0$$
(63)

This is the Korringa form which he derived earlier. It can also be written in terms of $B_{\ell m, \ell'm'}$ defined in Eq. (60) as

$$\left| \mathbf{B}_{\ell \mathbf{m}, \ell' \mathbf{m}'} + \kappa \delta_{\ell \ell'} \delta_{\mathbf{m} \mathbf{m}'} \frac{\mathrm{e}^{-\mathrm{i} \delta_{\ell'}}}{\sin \delta_{\epsilon'}} \right| = 0 \tag{64}$$

The solution of the secular Eq. (61) depends on the evaluation of the structure constants $A_{\ell m, \ell'm'}$ which depend on chosen values of E and \vec{k} and also on the logarithmic derivative of the radial function on the spherical boundary of the muffin-tin potential. The $A_{\ell m, \ell'm'}$ are not all independent. Firstly they satisfy the relation

$$A_{\ell m, \ell'm'} = A_{\ell'm', \ell m}^{*}$$
 (65)

2. EVALUATION OF STRUCTURE CONSTANTS

Apart from the Hermitian relation (65), the structure constants $A_{\ell m, \ell'm'}$ are not all independent but can be derived from a smaller number of independent constants. We can write $G(\vec{r}, \vec{r'})$ as a function of a single vector $\vec{R} = \vec{r} - \vec{r'}$. Thus

$$G(\vec{r}, \vec{r'}) = G(R) = -\frac{1}{\Omega} \sum_{\vec{k}} \frac{e^{i(\vec{k} + \vec{K}_n) \cdot \vec{R}}}{(\vec{k} + \vec{K}_n)^2 - E} = -\frac{1}{4\pi} \frac{e^{i\kappa R}}{R}$$
(66)

which we put again in terms of real and imaginary parts. Thus

$$G(R) = G_{o}(R) + D(R)$$
 for $R < R$

The function $G_0(R) = -(1/4\pi)[(\cos \kappa R)/R]$ and is singular at R = 0 while D(R) is regular. We can again expand D(R) in the following form:

$$D(R) = \sum_{L, M} D_{LM} j_{L}(\kappa R) Y_{LM}(\hat{R})$$
(67)

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where \hat{R} indicates the (θ,ϕ) polar angles of \vec{R} . Making use of the above forms of $G_0(R)$ and D(R) the Green's function can be written as

$$G(\mathbf{R}) = \sum_{\mathrm{L,M}} \left[-\frac{\kappa}{4\pi} \frac{\cos\kappa \mathbf{R}}{\kappa \mathbf{R}} \delta_{\mathrm{L0}} \delta_{\mathrm{M0}} + D_{\mathrm{LM}} \mathbf{j}_{\mathrm{L}}(\kappa \mathbf{R}) \mathbf{Y}_{\mathrm{LM}}(\mathbf{\widehat{R}}) \right]$$
(68)

It can also be written as

$$G(\mathbf{R}) = -\frac{1}{\Omega} \sum_{\vec{k}_{n}} \frac{e^{i(\vec{k}+\vec{k}_{n})\cdot\vec{R}}}{(\vec{k}+\vec{k}_{n})^{2}-\mathbf{E}}$$
$$= -\sum_{\mathbf{L},\mathbf{M}} \frac{4\pi}{\Omega} \sum_{\vec{k}_{n}} i^{\mathbf{L}} \frac{\mathbf{j}_{\mathbf{L}}(|\vec{k}+\vec{k}_{n}|\mathbf{R})}{(\vec{k}+\vec{k}_{n})^{2}-\mathbf{E}} Y_{\mathbf{LM}}(\hat{\mathbf{R}}) Y_{\mathbf{LM}}^{*}(\hat{\mathbf{k}})$$
(69)

Comparing Eqs (68) and (69) we obtain

$$D_{LM} = -\frac{4\pi}{\Omega} \frac{i^{L}}{j_{L}(\kappa R)} \sum_{\vec{k}_{n}} \frac{j_{L}(|\vec{k} + \vec{k}_{n}|R)}{(\vec{k} + \vec{k}_{n})^{2} - E} Y_{LM}^{*}(\hat{k})$$

$$+ \frac{\kappa}{4\pi} \frac{\cos \kappa R}{\kappa R} \frac{1}{j_{L}(\kappa R)} \frac{1}{Y_{LM}(\hat{R})} \delta_{L0} \delta_{M0} \qquad (70)$$

$$= -\frac{4\pi}{\Omega} i^{L} \left[j_{L}(\kappa R) \right]^{-1} \sum_{\vec{k}_{n}} \frac{j_{L}(|\vec{k} + \vec{k}_{n}|R) Y_{LM}^{*}(\hat{R})}{(\vec{k} + \vec{k}_{n})^{2} - E}$$

$$+ \frac{\kappa}{(4\pi)^{\frac{1}{2}}} \cot \kappa R \delta_{L0} \delta_{M0} \qquad (71)$$

where the last term in Eq. (71) is obtained by replacing $j_L(\kappa R)$ by $j_0(\kappa R) = (\sin \kappa R)/\kappa R$ and $Y_{LM}(\hat{R})$ by $Y_{00}(\hat{R}) = (1/4\pi)^{\frac{1}{2}}$. A relation between the coefficients $A_{\ell m, \ell'm'}$ and D_{LM} can be derived

the equation

$$\sum_{\ell,m} \sum_{\ell'm'} A_{\ell m,\ell'm'} j_{\ell}(\kappa \mathbf{r}) j_{\ell}(\kappa \mathbf{r'}) Y_{\ell m}(\hat{\mathbf{r}}) Y_{\ell'm'}^{*} (\hat{\mathbf{r'}})$$
$$= \sum_{L,M} D_{LM} j_{L}(\kappa R) Y_{LM}(\hat{R})$$
(72)

by making use of the well-known formulae

$$j_{L}(\kappa R) Y_{LM}(\hat{R}) = \frac{1}{4\pi i^{L}} \int e^{i\vec{K}\cdot\vec{R}} Y_{LM}(\hat{K}) d\Omega_{\vec{K}}$$
$$= \frac{1}{4\pi i^{L}} \int e^{i\vec{K}\cdot\vec{r}\cdot\vec{K}\cdot\vec{r}} Y_{LM}(\hat{K}) d\Omega_{\vec{K}}$$
(73)

We can thus write

$$\sum_{\ell m} \sum_{\ell'm'} A_{\ell m, \ell'm'} j_{\ell}(\kappa \mathbf{r}) j_{\ell'}(\kappa \mathbf{r}') Y_{\ell m}(\hat{\mathbf{r}}) Y_{\ell'm'}^{*}(\hat{\mathbf{r}}')$$

$$= \sum_{LM} D_{LM} \int \sum_{\ell m} \sum_{\ell'm'} \frac{4\pi}{i^{L}} i^{\ell'\ell'} j_{\ell}(\kappa \mathbf{r}) j_{\ell'}(\kappa \mathbf{r}')$$

$$\times Y_{LM}(\hat{\mathbf{K}}) Y_{\ell m}(\hat{\mathbf{r}}) Y_{\ell'm'}^{*}(\hat{\mathbf{r}}') Y_{\ell m}^{\bullet}(\hat{\mathbf{K}}) Y_{\ell'm'}(\hat{\mathbf{K}}) d\Omega_{\vec{\mathbf{K}}}$$

$$= \sum_{LM} D_{LM} \frac{4\pi}{i^{L}} \sum_{\ell m} \sum_{\ell'm'} i^{\ell'\ell'} C_{LM, \ell m, \ell'm'} j_{\ell}(\kappa \mathbf{r}) j_{\ell'}(\kappa \mathbf{r}')$$

$$\times Y_{\ell m}(\hat{\mathbf{r}}) Y_{\ell'm'}^{*}(\hat{\mathbf{r}}') \qquad (74)$$

where

$$C_{LM, \ell m, \ell'm'} = \int Y_{LM}(\hat{K}) Y_{\ell m}^{*}(\hat{K}) Y_{\ell'm'}(\hat{K}) d\Omega_{\vec{K}}$$

Equation (74) gives

$$A_{\ell m, \ell'm'} = 4\pi i^{\ell'\ell'} \sum_{L} i^{-L} D_{L, m-m'} C_{L, m-m', \ell m, \ell'm'}$$
(75)

because $C_{LM,\,\ell m,\,\ell'm'}$ are zero unless M = m - $m^{\,\prime}$. The sum over L runs only over the values

$$\mathbf{L} = \left| \boldsymbol{\ell} - \boldsymbol{\ell}^{\dagger} \right|, \quad \left| \boldsymbol{\ell} - \boldsymbol{\ell}^{\dagger} \right| + 2, \dots, \quad \left| \boldsymbol{\ell} + \boldsymbol{\ell}^{\dagger} \right|$$

and the C vanish for all other L. In this way, we must calculate a smaller number of constants D_{LM} from Eq.(70) and then use Eq.(75) to obtain $A_{\ell m, \ell' m'}$. The C coefficients are well-known Wigner coefficients.

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It is possible to obtain another form of the structure constant $\rm D_{LM}$ by using the equivalent form of the Green's function

$$\begin{split} G(R) &= -\frac{1}{4\pi} \sum_{\vec{k}_{n}} e^{i\vec{k}\cdot\vec{R}_{n}} \frac{e^{i\kappa(\vec{R}-\vec{R}_{n})}}{|\vec{R}-\vec{R}_{n}|} \\ &= -\frac{1}{4\pi} \frac{e^{i\kappa R}}{R} - \frac{1}{4\pi} \sum_{\vec{k}_{n}\neq 0} e^{i\vec{k}\cdot\vec{R}_{n}} \frac{e^{i\kappa(\vec{R}-\vec{R}_{n})}}{|\vec{R}-\vec{R}_{n}|} \\ &= -\frac{\kappa}{4\pi} \frac{\cos\kappa R}{\kappa R} - \frac{i\kappa\sin\kappa R}{4\pi\kappa R} + \kappa}{\vec{R}_{n}+\kappa} \sum_{\vec{R}_{n}\neq 0} e^{i\vec{k}\cdot\vec{R}_{n}} \\ &\times \sum_{LM} j_{L}(\kappa R) \left[n_{L}(\kappa R_{n}) - ij_{L}(\kappa R_{n}) \right] Y_{LM}(\hat{R}) Y_{LM}(\hat{R}_{n}) \\ &= -\frac{\kappa}{4\pi} \frac{\cos\kappa R}{\kappa R} - \frac{i\kappa}{4\pi} j_{0}(\kappa R) + \kappa}{\sum_{\vec{R}_{n}\neq 0} e^{i\vec{k}\cdot\vec{R}_{n}}} \sum_{LM} j_{L}(\kappa R) \left[n_{L}(\kappa R_{n}) - ij_{L}(\kappa R_{n}) \right] \\ &- ij_{L}(\kappa R_{n}) \right] Y_{LM}(\hat{R}) Y_{LM}(\hat{R}_{n}) \\ &= -\frac{\kappa}{4\pi} \frac{\cos\kappa R}{\kappa R} + \sum_{LM} \left[-\frac{i\kappa}{4\pi} j_{L}(\kappa R) \delta_{L0} \delta_{M0} + \kappa \sum_{\vec{R}_{n}\neq 0} e^{i\vec{k}\cdot\vec{R}_{n}} j_{L}(\kappa R) \right] \\ &\times \left[n_{L}(\kappa R_{n}) - ij_{L}(\kappa R_{n}) \right] \times Y_{LM}(\hat{R}) Y_{LM}(\hat{R}) \\ &\times \left[n_{L}(\kappa R_{n}) - ij_{L}(\kappa R_{n}) \right] \times Y_{LM}(\hat{R}) Y_{LM}(\hat{R}) \end{split}$$
(76)

Hence

$$D_{LM} = \kappa \sum_{\vec{R}_n \neq 0} e^{i\vec{k}\cdot\vec{R}_n} \left[n_L(\kappa R_n) - ij_L(\kappa R_n) \right] Y_{LM}^* (\hat{R}_n) - \frac{i\kappa}{4\pi} \delta_{L0} \delta_{M0}$$
(77)

This form demonstrates that for $\mathrm{E}<0$ the series rapidly converges since

$$n_{L}(i\kappa R) - ij_{L}(i\kappa R) = -\frac{e^{-\kappa R}}{\kappa R}$$
(78)

for large R.

The calculation of structure constants by Ewald's method has been formulated by Ham and Segall [3] for simple monatomic lattices. The number of the D_{LM} can be reduced further by symmetry considerations for G(R) for a given \vec{k} . [G(SR) = G(R) where S is any symmetry operation belonging to the group of wave vector \vec{k}].

3. KOHN-ROSTOKER METHOD FOR COMPLEX LATTICES [4]

In a complex lattice the unit cell contains more than one atom; these atoms may be either of the same kind, as in pure elemental solids, or of different kinds, as in compound solids. In this situation we again prescribe a muffin-tin form of the potential where the potential is spherically symmetric in each muffin-tin and zero outside owing to a suitable choice of the energy scale. Thus, we write the form of potential as

$$V(\vec{r}) = \begin{cases} V^{(i)} (|\vec{r} - \vec{R}_n - \vec{\tau}_i|) \\ & \text{for } |\vec{r} - \vec{R}_n - \vec{\tau}_i| < R_i \end{cases}$$
(79)
0 elsewhere

where R_i is the radius of ith muffin tin and $V^{(i)}$ ($|\vec{r} \cdot \vec{R}_n - \vec{\tau}_i|$) is the potential inside this muffin tin; τ_i is the vector position of the ith atom in the unit cell with $\vec{R}_n = 0$. For beryllium we have i = 0 and 1.

We again write down the Kohn-Rostoker variational principle $\delta\Lambda$ = 0 with

$$\Lambda = \int_{\Omega} \psi^{*}(\vec{\mathbf{r}}) \nabla(\vec{\mathbf{r}}) d\vec{\mathbf{r}} \left[\psi(\vec{\mathbf{r}}) - \int_{\Omega'} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \nabla(\vec{\mathbf{r}}') \psi(\vec{\mathbf{r}}') d\vec{\mathbf{r}} \right]$$
(80)

where the integration is over only the unit cell with $\vec{R}_{p} = 0$.

The term
$$\int_{\Omega'} G(\vec{r}, \vec{r}') V(\vec{r}') \psi(\vec{r}') d\vec{r}' \text{ in Eq. (80)}$$

can be written as

$$\sum_{j} \int_{\Omega_{j}} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \, V^{(j)}(\vec{\mathbf{r}}'_{j}) \, \psi^{(j)}(\vec{\mathbf{r}}'_{j}) \, d\vec{\mathbf{r}}'_{j}$$

where integral is over volume Ω_j of the jth muffin tin. The potentials of different muffin thus are assumed not to overlap. In the jth muffin tin we

define the position as $\vec{r}_j = \vec{r} \cdot - \vec{\tau}_j$. So we have

$$\int_{\Omega'} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}') V(\vec{\mathbf{r}}') \psi(\vec{\mathbf{r}}') d\vec{\mathbf{r}}' = \sum_{j \ \Omega'} \int_{\Omega'} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}') V(|\vec{\mathbf{r}}_{j}'|) \psi(\vec{\mathbf{r}}_{j}') d\vec{\mathbf{r}}'_{j}.$$
 (81)

Again $\psi(\vec{r'}_j)$ satisfies the Schrödinger equation

$$(\nabla^{!2} + \mathbf{E}) \,\psi(\vec{\mathbf{r}_{j}^{!}}) = \mathbf{V}(\vec{\mathbf{r}_{j}^{!}}) \,\psi(\vec{\mathbf{r}_{j}^{!}})$$

So we have

$$\begin{split} \sum_{j} \int_{\Omega_{j}(\mathbf{r}_{j}^{\prime} < R_{j}^{-} \epsilon)} & \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime}) \, \mathbf{V}(\vec{\mathbf{r}}_{j}^{\prime}) \, \psi(\vec{\mathbf{r}}_{j}^{\prime}) \, d\vec{\mathbf{r}}_{j}^{\prime} \\ &= \sum_{j} \int_{\Omega_{j}(\mathbf{r}_{j}^{\prime} < R_{j}^{-} \epsilon)} & \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime}) \, (\nabla^{\prime 2} + \mathbf{E}) \, \psi(\vec{\mathbf{r}}_{j}^{\prime}) \, d\vec{\mathbf{r}}_{j}^{\prime} \\ &= \psi(\vec{\mathbf{r}}) + \sum_{j} \int_{S_{j}^{\prime}} & \mathbf{dS}_{j}^{\prime} \left[\mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime}) \, \frac{\partial \psi(\vec{\mathbf{r}}_{j}^{\prime})}{\partial \mathbf{r}_{j}^{\prime}} - \psi(\vec{\mathbf{r}}_{j}^{\prime}) \, \frac{\partial \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime})}{\partial \mathbf{r}_{j}^{\prime}} \right] \end{split}$$

Thus

$$\begin{bmatrix} \psi(\vec{\mathbf{r}}) - \sum_{j} \int_{\mathbf{r}_{j}^{\prime} < R_{j}^{-} \epsilon} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime}) V(\vec{\mathbf{r}}_{j}^{\prime}) \psi(\vec{\mathbf{r}}_{j}^{\prime}) d\vec{\mathbf{r}}_{j}^{\prime} \end{bmatrix}$$

= $-\sum_{j} \int_{\mathbf{s}_{j}^{\prime}} d\mathbf{S}_{j}^{\prime} \begin{bmatrix} G(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime}) \frac{\partial \psi(\vec{\mathbf{r}}_{j}^{\prime})}{\partial \mathbf{r}_{j}^{\prime}} - \psi(\vec{\mathbf{r}}_{j}^{\prime}) \frac{\partial G}{\partial \mathbf{r}_{j}}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime}) \end{bmatrix}$ (83)

We substitute Eq. (83) into Eq. (8) and obtain:

$$\Lambda_{\epsilon} = \int_{\Omega} \psi^{*}(\vec{\mathbf{r}}) \, \mathbf{V}(\vec{\mathbf{r}}) \, d\vec{\mathbf{r}} \sum_{j} - \int_{\mathbf{S}_{j}^{i}} d\mathbf{S}_{j}^{i} \left[\mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{i}) \, \frac{\partial \psi(\vec{\mathbf{r}}_{j}^{i})}{\partial \mathbf{r}_{j}^{i}} - \psi(\vec{\mathbf{r}}_{j}^{i}) \, \frac{\partial \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{i})}{\partial \mathbf{r}_{j}^{i}} \right]$$
$$= -\sum_{j} \int_{\mathbf{S}_{j}^{i}} d\mathbf{S}_{j}^{i} \left[\int_{\Omega} \psi^{*}(\vec{\mathbf{r}}) \mathbf{V}(\vec{\mathbf{r}}) \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{i}) \, d\vec{\mathbf{r}} \right] \frac{\partial \psi(\vec{\mathbf{r}}_{j}^{i})}{\partial \mathbf{r}_{j}^{i}}$$
$$+ \sum_{j} \int_{\mathbf{S}_{j}^{i}} d\mathbf{S}_{j}^{i} \left[\int_{\Omega} \psi^{*}(\vec{\mathbf{r}}) \, \mathbf{V}(\vec{\mathbf{r}}) \, \frac{\partial \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{i})}{\partial \mathbf{r}_{j}^{i}} \, d\vec{\mathbf{r}} \right] \psi(\vec{\mathbf{r}}_{j}^{i})$$
(84)

We again replace the integration over $\,\Omega$ by an integration over the muffin tins. Thus

$$\int_{\Omega} \mathbf{V}(\vec{\mathbf{r}}) \psi^*(\vec{\mathbf{r}}) \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_j) d\vec{\mathbf{r}} = \sum_{\mathbf{k}} \int_{\Omega_{\mathbf{k}}} \mathbf{V}^{(\mathbf{k})}(\vec{\mathbf{r}}) \psi^*(\vec{\mathbf{r}}) \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_j) d\vec{\mathbf{r}}$$
(85)

If we again indicate the position in each muffin tin relative to its own centre we have

$$\int_{\Omega} \mathbf{V}(\vec{\mathbf{r}}) \psi^*(\vec{\mathbf{r}}) \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_j!) d\vec{\mathbf{r}} = \sum_{\mathbf{k}} \int_{\Omega_{\mathbf{k}}} \mathbf{V}^{(\mathbf{k})}(\vec{\mathbf{r}}_k) \psi^*(\vec{\mathbf{r}}_k) \mathbf{G}(\vec{\mathbf{r}}_k, \vec{\mathbf{r}}_j!) d\vec{\mathbf{r}}_k$$

where $\vec{r}_k = \vec{r} - \vec{\tau}_k$. As before,

$$\int_{\Omega_{k}} \nabla^{(k)}(\vec{\mathbf{r}}_{k})\psi^{*}(\vec{\mathbf{r}}_{k}) G(\vec{\mathbf{r}}_{k},\vec{\mathbf{r}}_{j}) d\vec{\mathbf{r}}_{k}$$

$$=\psi^{*}(\vec{\mathbf{r}}_{j}) \delta_{kj} + \int_{S_{k}} dS_{k} \left[G(\vec{\mathbf{r}}_{k},\vec{\mathbf{r}}_{j}) \frac{\partial\psi^{*}(\vec{\mathbf{r}}_{k})}{\partial \mathbf{r}_{k}} - \psi^{*}(\vec{\mathbf{r}}_{k}) \frac{\partial G(\vec{\mathbf{r}}_{k},\vec{\mathbf{r}}_{j})}{\partial \mathbf{r}_{k}} \right]$$
(86)

This gives

$$\int_{\Omega} \psi^{*}(\vec{\mathbf{r}}) \, \mathbf{V}(\vec{\mathbf{r}}) \, \mathbf{G}(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{*}) \, d\vec{\mathbf{r}}$$

$$= \sum_{k} \psi^{*}(\vec{\mathbf{r}}_{j}^{*}) \, \delta_{kj} + \sum_{k} \int_{\mathbf{S}_{k}} d\mathbf{S}_{k} \left[\mathbf{G}(\vec{\mathbf{r}}_{k}, \vec{\mathbf{r}}_{j}^{*}) \frac{\partial \psi^{*}(\vec{\mathbf{r}}_{k})}{\partial \mathbf{r}_{k}} - \psi^{*}(\vec{\mathbf{r}}_{k}) \frac{\partial \mathbf{G}(\vec{\mathbf{r}}_{k}, \vec{\mathbf{r}}_{j}^{*})}{\partial \mathbf{r}_{k}} \right]$$

$$(87)$$

and, similarly,

$$\int_{\Omega} \psi^{*}(\vec{\mathbf{r}}) \nabla(\vec{\mathbf{r}}) \frac{\partial G(\vec{\mathbf{r}}, \vec{\mathbf{r}}_{j}^{\prime})}{\partial \mathbf{r}_{j}^{\prime}} d\vec{\mathbf{r}}$$

$$= \sum \frac{\partial \psi^{*}(\vec{\mathbf{r}}_{j}^{\prime})}{\partial \mathbf{r}_{j}^{\prime}} \delta_{kj} + \sum_{k} \int_{S_{k}} dS_{k} \left[\frac{\partial G(\vec{\mathbf{r}}_{k}, \vec{\mathbf{r}}_{j}^{\prime})}{\partial \mathbf{r}_{j}^{\prime}} \frac{\partial \psi^{*}(\vec{\mathbf{r}}_{k})}{\partial \mathbf{r}_{k}} - \psi^{*}(\vec{\mathbf{r}}_{k}) \frac{\partial^{2} G(\vec{\mathbf{r}}_{k}, \vec{\mathbf{r}}_{j}^{\prime})}{\partial \mathbf{r}_{k} \partial \mathbf{r}_{j}^{\prime}} \right]$$

Now substitute Eqs (87) and (88) into (84) and obtain:

$$\Lambda_{\epsilon} = -\sum_{j} \int_{S_{j}} dS_{j}' \left\{ \psi^{*}(\vec{r_{j}}) + \sum_{k} \int_{S_{k}} dS_{k} \left[G(r_{k}, r_{j}) \frac{\partial \psi^{*}(r_{k})}{\partial r_{k}} \right] \right\}$$

(88)

$$-\psi^{*}(\vec{r}_{k})\frac{\partial G(\vec{r}_{k},\vec{r}_{j}^{\dagger})}{\partial r_{k}}\Bigg]\Bigg\} \frac{\partial\psi^{*}(\vec{r}_{j}^{\dagger})}{\partial r_{j}^{\dagger}}$$

$$+\sum_{j}\int_{S_{j}^{\dagger}} dS_{j}^{\dagger} \left\{\frac{\partial\psi^{*}(\vec{r}_{j}^{\dagger})}{\partial r_{j}^{\dagger}} + \sum_{k}\int_{S_{k}} dS_{k} \left[\frac{\partial G(\vec{r}_{k},\vec{r}_{j}^{\dagger})}{\partial r_{j}} \frac{\partial\psi^{*}(\vec{r}_{k})}{\partial r_{k}}\right]$$

$$-\psi^{*}(\vec{r}_{k})\frac{\partial^{2}G(\vec{r}_{k},\vec{r}_{j}^{\dagger})}{\partial r_{k}\partial r_{j}^{\dagger}}\Bigg]\Bigg\}\psi(\vec{r}_{j}^{\dagger})$$

$$=\sum_{j}\int_{S_{j}^{\dagger}} dS_{j}^{\dagger} \left(\frac{\partial\psi^{*}(\vec{r}_{j})}{\partial r_{j}^{\dagger}}\psi(\vec{r}_{j}) - \psi^{*}(\vec{r}_{j})\frac{\partial\psi(\vec{r}_{j}^{\dagger})}{\partial r_{j}^{\dagger}}\right)$$

$$+\sum_{k}\int_{S_{k}} dS_{k} \left[-\psi^{*}(\vec{r}_{k})\frac{\partial}{\partial r_{k}} + \frac{\partial}{\partial r_{k}}\psi^{*}(\vec{r}_{k})\right]$$

$$\times\sum_{j}\int_{S_{j}^{\dagger}} dS_{j}^{\dagger} \left[-G(\vec{r}_{k},\vec{r}_{j}^{\dagger})\frac{\partial}{\partial r_{j}^{\dagger}}\psi(\vec{r}_{j}^{\dagger}) + \psi(\vec{r}_{j}^{\dagger})\frac{\partial}{\partial r_{j}^{\dagger}}G(\vec{r}_{k},\vec{r}_{j}^{\dagger})\right]$$
(89)

Again, since $\psi(\vec{r}_j)$ has real radial part the first term on the righthand side of Eq.(89) is zero, such that

$$\Lambda_{\epsilon} = \sum_{k} \int_{S_{k}} dS_{k} \left[\frac{\partial}{\partial r_{k}} \psi^{*}(\vec{r}_{k}) - \psi^{*}(\vec{r}_{k}) \frac{\partial}{\partial r_{k}} \right]$$
$$\times \sum_{j} \int_{S_{j}'} dS_{j}' \left[\psi(\vec{r}_{j}') \frac{\partial}{\partial r_{j}'} G(\vec{r}_{k}, \vec{r}_{j}') - G(\vec{r}_{k}, \vec{r}_{j}') \frac{\partial}{\partial r_{j}'} \psi(\vec{r}_{j}') \right]$$
(90)

We have two kinds of terms in Eq. (90). The first kind is the same for a simple lattice and the integration goes over the spherical surfaces centred at one muffin tin. In addition, we have terms where one integration is carried out over the surface centred at one muffin tin and the other one centred at the other muffin tin. Thus we have what we call diagonal and non-diagonal terms.

For the case of spherical surfaces centred at the same nucleus or muffin tin the Green's function can be written as before for $r < r' < R_i$

$$G(\vec{r}_{j}, \vec{r}_{j}) = \sum_{\ell m} \sum_{\ell' m'} \left[A_{\ell m, \ell' m}^{(j, j)}, j_{\ell}(\kappa r_{j}) j_{\ell}(\kappa r_{j}') + \kappa \delta_{\ell \ell'}, \delta_{m m'}, j_{\ell}(\kappa r_{j}) n_{\ell'}, (\kappa r_{j}') \right] Y_{\ell m}(\hat{r}_{j}) Y_{\ell' m'}(\hat{r}_{j}')$$

$$(91)$$

If we substitute the above expression for $G(\vec{r}_i, \vec{r}_i^{\prime})$ and

$$\psi(\vec{r}_{j}) = \sum_{\ell=0}^{\ell} \sum_{m=-\ell}^{+\ell} C_{\ell m}^{j} R_{\ell}(E, r_{j}') Y_{\ell m}(\hat{r}_{j}')$$
(92)

we obtain after integration over the surfaces the diagonal terms at the centres in Eq. (90) in the following form:

$$\sum_{\ell m} \sum_{\ell' m'} C_{\ell m}^{*(i)} C_{\ell' m'}^{(i)} \left[j_{\ell} (\kappa \mathbf{r}_{j}) \mathbf{R}_{\ell}^{(j)} - j_{\ell} (\kappa \mathbf{r}_{j}) \mathbf{R}_{\ell}^{(j)} \right] \times \left\{ \mathbf{A}_{\ell m, \ell' m'}^{(i)} \left(j_{\ell'} (\kappa \mathbf{r}_{j}) \mathbf{R}_{\ell'}^{(j)} - j_{\ell'} (\kappa \mathbf{r}_{j}) \mathbf{R}_{\ell'}^{(j)} \right) + \kappa \delta_{\ell \ell}, \delta_{m m'} \left[\mathbf{n}_{\ell'} \mathbf{R}_{\ell'}^{(j)} - \mathbf{n}_{\ell'} \mathbf{R}_{\ell'}^{(j)} \right] \right\}$$
(93)

where

$$R_{\ell}^{(i)} = \frac{dR_{\ell}^{(i)}}{dr_{j}'} \text{ and } j_{\ell}' = \frac{d}{dr_{j}'} j_{\ell}(\kappa r_{j}')$$

...

The terms which are off-diagonal in the centres involving products of surface integrals over different spheres are somewhat more complicated because the natural co-ordinate systems for r_k and r'_l have their origins at different points. But in our final form for the Green's function these non-diagonal terms are no more difficult to evaluate than the diagonal ones. The Green's function $G(\vec{r}_k, \vec{r}'_l)$ satisfies the homogeneous equation

$$(\nabla^2 + \mathbf{E}) \mathbf{G}(\vec{\mathbf{r}}_k, \vec{\mathbf{r}}_j) = \delta(\vec{\mathbf{r}}_k - \vec{\mathbf{r}}_j).$$
(94)

both in \vec{r}_k and \vec{r}'_j since $G(\vec{r}_k, \vec{r}'_j)$ is finite about both the origins $\vec{\tau}_k$ and $\vec{\tau}_j$. Thus it must be expressible in the form of a series:

$$\mathbf{G}(\vec{\mathbf{r}}_{k},\vec{\mathbf{r}}_{j}') = \sum_{\ell,m} \sum_{\ell'm'} \mathbf{A}_{\ell m,\ell'm'}^{(k,j)} \mathbf{j}_{\ell}(\kappa \mathbf{r}_{k}) \mathbf{j} \ (\kappa \mathbf{r}_{\ell}') \mathbf{Y}_{\ell m}(\hat{\mathbf{r}}_{k}) \mathbf{Y}_{\ell'm'}^{*} (\hat{\mathbf{r}}_{j}')$$
(95)

for $(r_k + r_j^t) < |\vec{\tau}_k - \vec{\tau}_j|$. The contribution to Λ of the term with \vec{r}_k centred about k^{th} nucleus and \vec{r}'_j centred about j^{th} nucleus can be shown to be

$$\sum_{\ell m} \sum_{\ell' m'} A_{\ell m, \ell' m'}^{(k, j)} C_{\ell m}^{*(k)} C_{\ell' m'}^{(j)} \left[j_{\ell}^{\dagger} R_{\ell}^{(k)} - j_{\ell} R_{\ell}^{'(j)} \right]_{r_{k} = R_{k}} \times \left[j_{\ell}, R_{\ell'}^{\dagger} - j_{\ell'}, R_{\ell'}^{(j)} \right]_{r_{j}^{\dagger} = R_{j}}$$
(96)
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The quantity Λ which is the sum of all the diagonal terms (93) and all the non diagonal terms (96) is

$$\Lambda = \sum_{k, j} \sum_{\ell, m} \sum_{\ell', m'} C_{\ell m}^{*(k)} C_{\ell' m'}^{(j)} \left\{ A_{\ell m, \ell' m'}^{(k, j)} \left[j_{\ell}^{*} R_{\ell}^{(k)} - j_{\ell} R_{\ell}^{*(k)} \right]_{r_{k}^{*} = R_{k}} \right. \\
\times \left[j_{\ell}^{*}, R_{\ell'}^{(j)} - j_{\ell'}^{*}, R_{\ell'}^{(j)} \right]_{r_{j}^{*} = R_{j}} \\
+ \kappa \delta_{\ell \ell'} \delta_{mm'} \delta_{jj'} \left[j_{\ell}^{*} R_{\ell'}^{(k)} - j_{\ell} R_{\ell'}^{*(k)} \right]_{r_{k}^{*} = R_{k}} \left[n_{\ell'}^{*}, R_{\ell'}^{*(j)} - n_{\ell'}^{*}, R_{\ell'}^{(j)} \right]_{r_{j}^{*} = R_{j}} \right\}$$
(97)

By taking the variation of Λ with respect to the variational coefficient and putting it equal to zero we obtain the equations

$$\sum_{\ell'm'j} \left\{ A_{\ell m,\ell'm'}^{(k,j)} \left[j_{\ell'}, R_{\ell'}^{(j)} - j_{\ell'}, R_{\ell'}^{(j)} \right]_{r_{j}' = R_{j}} + \kappa \delta_{\ell\ell'} \delta_{mm'} \delta_{kj} \left[n_{\ell'}, R_{\ell'}^{(j)} - n_{\ell'}', R_{\ell}^{(j)} \right]_{r = R_{j}} C_{\ell'm'}^{(j)} = 0$$
(98)

For a non trivial solution of Eq. (98) we must have the condition

$$\begin{vmatrix} A_{\ell m,\ell'm'}^{(k,j)} \left[j_{\ell'} R_{\ell'}^{(j)} - j_{\ell'}^{t} R_{\ell'}^{(j)} \right]_{r_{j}^{t} = R_{j}} \\ + \kappa \delta_{\ell \ell'} \delta_{mm'} \delta_{kj} \left[n_{\ell'} R_{\ell'}^{(j)} - n_{\ell'}^{t} R_{\ell'}^{(j)} \right]_{r_{j}^{t} = R_{j}} = 0$$
(99)

or, dividing each column by

$$\left[\mathbf{j}_{\boldsymbol{\ell}'} \mathbf{R}_{\boldsymbol{\ell}'}^{\dagger(j)} - \mathbf{j}_{\boldsymbol{\ell}'}^{\dagger} \mathbf{R}_{\boldsymbol{\ell}'}^{(j)} \right]_{r_{j} = R_{j}}$$

we obtain the secular equation

$$\left| A_{\ell m, \ell' m'}^{(k, j)} + \kappa \delta_{\ell \ell'} \delta_{m m'} \delta_{k j} \times \left\{ \frac{n_{\ell'}^{i} - n_{\ell'} L_{\ell'}^{(j)}}{j_{\ell'}^{i} - j_{\ell'} L_{\ell'}^{(j)}} \right\}_{r_{j}^{i} = R_{j}^{i}} = 0$$
(100)

where

$$L_{\ell'}^{(j)} = \frac{1}{R_{\ell'}^{(j)}(r'_j)} \frac{d}{dr'_j} R_{\ell'}^{(j)} (r'_j)$$

ELECTRON ENERGY BANDS

In general, the calculation of the diagonal structure constants in muffin tin centres $A_{\ell m,\ell'm'}^{(k,k)}$ is identical with those for simple lattices with the same translational symmetry. We shall here discuss the off-diagonal structure constants $A_{\ell m,\ell'm'}^{(k,j)}$. One important property of these constants results from the hermiticity of the Green's function, i.e.,

$$G^{(k,j)}(\vec{r}_{k},\vec{r}_{j}) = G^{*(j,k)}(\vec{r}_{j},\vec{r}_{k})$$
(101)

which leads to

$$A_{\ell m, \ell'm'}^{(k, j)} = A_{\ell'm', \ell m}^{* (j, k)}$$
(102)

if one uses the expansion for the Green's function

$$\mathbf{G}^{(\mathbf{k},\mathbf{j})}\left(\vec{\mathbf{r}}_{\mathbf{k}},\vec{\mathbf{r}}_{\mathbf{j}}^{\prime}\right) = \sum_{\ell m} \sum_{\ell' m'} \mathbf{A}_{\ell m,\ell' m'}^{(\mathbf{k},\mathbf{j})} \mathbf{j}_{\ell}(\kappa \mathbf{r}_{\mathbf{k}}) \mathbf{j}_{\ell'}(\kappa \mathbf{r}_{\mathbf{j}}^{\prime}) \mathbf{Y}_{\ell m}(\hat{\mathbf{r}}_{\mathbf{k}}) \mathbf{Y}_{\ell' m'}(\hat{\mathbf{r}}_{\mathbf{j}})$$

for $(k \neq j)$

as given in Eq. (95). The Green's function can also be written as

$$G^{(k, j)}(\vec{r}_{k}, \vec{r}_{j}) = -\frac{1}{\Omega} \sum_{\vec{k}_{n}} \frac{1}{(\vec{k} + \vec{K}_{n})^{2} - E} e^{i(\vec{k} + \vec{K}_{n}) \cdot (\vec{r}_{k} - \vec{r}_{j})} \times e^{i(\vec{k} + \vec{K}_{n}) \cdot (\vec{r}_{k} - \vec{r}_{j})}$$
(103)

Expansion of exp $[i(\vec{k} + \vec{K}_n) \cdot (\vec{r}_k - \vec{r'_j})]$ in spherical harmonics and comparison with Eq.(95) gives the structure constants:

$$A_{\ell m, \ell' m'}^{(k, j)} = -\frac{(4\pi)^2}{\Omega} \frac{i^{\ell-\ell'}}{j_{\ell}(\kappa r_k)j_{\ell'}(\kappa r_j')} \sum_{\vec{k}_n} \frac{e^{i(\vec{k}+\vec{k}_n)\cdot(\vec{r}_k-\vec{\tau}_j)}}{(\vec{k}+\vec{k}_n)^2 - E} \times j_{\ell}(|\vec{k}+\vec{k}_n|r_k)j_{\ell'}(|\vec{k}+\vec{k}_n|r_j') \times Y_{\ell m}(\vec{k}) Y_{\ell'm'}(\vec{k})$$
(104)

where \hat{k} has now been used to indicate the directional angles of the vector $\vec{k}+\vec{K}_{n}.$

We can also write the Green's function in the form

$$G(\vec{r}_{k},\vec{r}_{j}) = -\frac{1}{\Omega} \sum_{\vec{k}_{n}} \frac{e^{i(\vec{k}+\vec{K}_{n})\cdot(\vec{r}_{k}-\vec{r}_{j})}}{(\vec{k}+\vec{K}_{n})^{2}-E} e^{i(\vec{k}+\vec{K}_{n})\cdot\vec{R}_{kj}}$$

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$$= -\frac{4\pi}{\Omega} \sum_{\vec{k}_{n}} \frac{1}{(\vec{k} + \vec{k}_{n})^{2} - E} e^{i(\vec{k} + \vec{k}_{n}) \cdot (\vec{r}_{k} - \vec{\tau}_{j})} \times \sum_{LM} i^{L} j_{L} (|\vec{k} + \vec{K}_{n}| R_{kj}) \times Y_{LM} (\hat{R}_{kj}) Y_{LM}^{*} (\hat{k})$$
(105)

$$G(\vec{r}_{k},\vec{r}_{j}) = \sum_{LM} D_{LM}^{(k,j)} j_{L}(|\vec{k}+\vec{K}_{n}|R_{kj}) Y_{LM}(\hat{R}_{kj})$$
(106)

Comparing Eqs (105) and (106) we have

$$D_{LM}^{(k,j)} = -\frac{4\pi}{\Omega} \sum_{\vec{k}_n} i^L \frac{1}{(\vec{k} + \vec{k}_n)^2 - E} e^{i(\vec{k} + \vec{k}_n) \cdot (\tau_k - \vec{\tau}_j)} Y_{LM}^*(\hat{k})$$
(107)

It can be shown, as in the case of simple lattices, that the structure constants $A^{(k, j)}$ are related to the $D^{(k, j)}$ by the relation

$$A_{\ell m, \ell'm'}^{(k, j)} = 4\pi i \sum_{LM}^{\ell'\ell'} \sum_{LM, i} i^{-L} C_{L, m-m'; \ell m; \ell'm'} D_{L, m-m'}^{(k, j)}$$
(108)

where

$$C_{L,\,m^{-}m^{\prime};\,\ell m,\,\ell^{\prime}m^{\prime}} = \int Y_{LM}(\widehat{k}) Y_{\ell m}^{*}(\widehat{k}) Y_{\ell^{\prime}m^{*}}(\widehat{k}) \, d\,\Omega_{\overline{k}}^{*}$$

Except when the maximum number of ℓ chosen is small the number of the D required in a particular calculation is considerably smaller than the number of the A.

Another representation for the structure constants $D_{LM}^{(k,j)}$ can be obtained by starting with the Green's function in the form

$$G(\vec{r}_{k},\vec{r}_{j}) = -\frac{1}{4\pi} \sum_{\vec{R}_{n}} e^{i\vec{k}\cdot\vec{R}_{n}} \frac{e^{i\vec{k}\cdot\vec{R}_{n}} - \frac{e^{i\vec{k}\cdot\vec{R}_{k}-\vec{r}_{k}+\vec{\tau}_{j}}}{|\vec{R}_{kj}-(\vec{R}_{n}-\tau_{k}+\vec{\tau}_{j})|} = -\frac{1}{4\pi} e^{i\vec{k}\cdot(\vec{r}_{k}-\vec{r}_{j})}$$

$$\times \sum_{\vec{k},n} e^{i\vec{k}\cdot\vec{s}_{kj,n}} \frac{e^{i\kappa(\vec{R}_{kj}-\vec{s}_{kj,n})}}{|\vec{R}_{kj}-\vec{s}_{kj,n}|}$$
(109)

The sum $\vec{s}_{k,i,n}$ runs over the whole lattice.

Using this form it can be easily shown, as before, that

$$D_{LM}^{(k,j)} = \kappa e^{\vec{i}\vec{k}\cdot(\vec{\tau}_{k}-\vec{\tau}_{j})} \sum_{s_{kj,n}} e^{\vec{i}\vec{k}\cdot\vec{s}_{kj,n}}$$

$$\times \left[n_{L}(\kappa s_{kj,n}) - ij_{L}(\kappa s_{kj,n}) \right] Y_{LM}^{*}(\vec{s}_{kj,n})$$
(110)

The Ewald method again enables us to calculate $D_{LM}^{(k,\,j)}$ in the three parts for better convergence. Thus, we write

$$D_{LM}^{(k, j)} = D_{LM}^{(k, j)} (1) + D_{LM}^{(k, j)} (2) + D_{00}^{(k, j)} (3) \delta_{L0} \delta_{M0}$$

where

$$D_{LM}^{(k,j)}(1) = -\frac{4\pi}{\Omega} \frac{i}{\kappa^{L}} \sum_{\vec{k}_{n}} \frac{e^{i(\vec{k}+\vec{K}_{n})\cdot(\vec{\tau}_{k}-\vec{\tau}_{j})}}{(\vec{k}+\vec{K}_{n})^{2} - E} \times |\vec{k}+\vec{K}_{n}|^{L} \mathscr{Y}_{LM}^{*}(\vec{k}+\vec{K}_{n})e^{-\frac{(\vec{k}+\vec{K}_{n})^{2} + E}{\eta}}$$
(111)

$$D_{LM}^{(k,j)}(2) = -\frac{1}{\sqrt{\pi}} \frac{2^{L+1}}{\kappa^{L}} \sum_{\vec{R}_{n} \neq 0} e^{\vec{i}\vec{k}\cdot\vec{R}_{n}} |\vec{R}_{n} - \vec{\tau}_{k} + \vec{\tau}_{j}|^{L} \mathscr{G}_{LM}(\vec{R}_{n} - \vec{\tau}_{k} + \vec{\tau}_{j})$$

$$\times \int_{\frac{\sqrt{\eta}}{2}}^{\infty} e^{-(\vec{R}_{n} - \vec{\tau}_{k} + \vec{\tau}_{j})^{2}\xi^{2} + \frac{E}{4\xi^{2}}} \xi^{2L} d\xi \qquad (112)$$

$$D_{00}(3) = -\frac{\sqrt{\eta}}{2\pi} \sum_{n=0}^{\infty} \frac{\left(\frac{E}{\eta}\right)^n}{n! (2n-1)!}$$
(113)

In the above \mathscr{Y}_{LM} denote the hexagonal harmonics. The parameter η can be chosen for reasonable convergence of Eqs (111), (112), and (113).

For the case of beryllium, in particular, we shall have the structure constants $D_{LM}^{(j,k)}$ of the type $D_{LM}^{(0,0)}$, $D_{LM}^{(1,1)}$ and $D_{LM}^{(0,1)}$ which are to be computed by using Eqs (111), (112) and (113). For the diagonal structure constants these equations reduce to those for simple lattices.

The space group of beryllium is $P(6_3/m)mc$. The lattice parameters for beryllium are the following:

a = 4.32109 Bohr units b = 6.77152 Bohr units The volume of the unit cell is

$$\frac{\sqrt{3}}{2} a^2 c = 109.5 a_0^3$$

As we have indicated earlier, a considerable amount of computation time can be saved if the wave function in Eq. (92) is expanded in hexagonal harmonics $\mathscr{G}_{\ell'm}(\hat{r})$ rather than spherical harmonics. This helps us to reduce the number of $C_{\ell m}$ for the same number of ℓ values taken. In the evaluation of structure constants, again the number of $D_{\rm LM}$ can be reduced by using hexagonal harmonics in Eqs (111), (112) and (113) as we have done. The construction of hexagonal harmonics has been discussed by several workers [5-9] using the necessary group-theoretical considerations (see also Ref. [12]).

The energy band structure of beryllium has been calculated by Herring [5] (OPW), Loucks and Cutler [10] (OPW) and Terrell [11] (APW) besides a few other calculations which are not so extensive. It is proposed to make use of some of the quantities used in the calculation given above in order to carry out Kohn-Rostoker type calculations.

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ELECTRIC FIELD EFFECTS ON INTERBAND TRANSITIONS

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Abstract

1. Introduction. 2. General theory. 3. Electric field effect at a point \vec{k}_c of the Brillouin zone. 4. Electric field effect at a critical point. 5. Critical point at $\vec{k}_c \neq 0$. Effect of the direction of the electric field and of the polarization of light.

1. INTRODUCTION

From a historical point of view, the first effect of an electric field on interband transitions which was investigated both theoretically and experimentally is the well known Franz-Keldysh effect. Franz [1] and Keldysh [2] in 1958 independently showed that the absorption coefficient of a semiconductor, in the region of the fundamental edge, is shifted by an electric field toward lower energies. In the following years this theoretical prediction was confirmed by experimental measurements performed by many authors [3], on various semiconductors.

In 1965 Seraphin [4] found that an external electric field strongly modifies the reflectivity of a semiconductor also at energies higher than the energy gap. In the last years this effect, which is of the same nature as the Franz-Keldysh effect, helped us to study the energy levels of an electron in a crystal. A number of theoretical [5] and experimental [6] papers have recently been published on the effect of an electric field on interband transitions. We recall the papers by Aspnes [7,8] who has shown, in the effective-mass approximation, how to compute the dielectric function due to direct interband transitions at a critical point in presence of an electric field.

We shall give here the main steps of a general treatment of the effect of an electric field on direct interband transitions at every point of the Brillouin Zone, by following an approach used in a previous paper by Bassani and myself [9].

2. GENERAL THEORY

To study the influence of an electric field on optical properties we must calculate the imaginary part of the dielectric function. From $\epsilon_2(\omega)$ we obtain all the optical constants.

The imaginary part of the dielectric function due to the optical transitions from an initial state i to a final state f is given, in the dipole approximation [10], by:

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$$\epsilon_{2}(\omega) = \frac{4\pi\hbar}{\omega^{2}} \left| \frac{e}{m} \right|^{2} \sum_{\substack{\text{all states in} \\ \text{the unit volume}}} \frac{1}{T} \left| \int_{0}^{T} dt \int_{V\infty} d\vec{r} \, \phi_{f}^{*}(\vec{r}, t) \vec{e} \cdot \vec{\nabla} \, \phi_{i}(\vec{r}, t) \right|^{2}$$
(1)

In our case $\phi(\vec{r},t)$ is a solution of the time-dependent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{\mathbf{r}}) + \mathbf{e}\cdot\vec{\mathbf{F}}\cdot\vec{\mathbf{r}}\right]\phi(\vec{\mathbf{r}},t) = -i\hbar\frac{\partial}{\partial t}\phi(\vec{\mathbf{r}},t)$$
(2)

We can obtain the time-dependent wave functions by solving the stationary problem associated with this equation. This approach was followed previously by Callaway[11], who obtained the absorption coefficient near the fundamental edge, and more recently by Aspnes, Handler and Blossey [12] who obtained $\epsilon_2(\omega)$ at any point of the Brillouin Zone.

We follow here the approach developed by Franz and Keldysh and used in Reference [9]. As the time-dependent wave functions we take the Houston [13] wave functions:

$$\varphi(\vec{r}, t) = b(\vec{r}, \vec{k}) \exp\left[-\frac{i}{\hbar} \int_{0}^{t} E(\vec{k}') dt'\right]$$
(3)

where $b(\vec{r}, \vec{k})$ is a Bloch function of wave vector \vec{k} , $E(\vec{k})$ is the dispersion law of the energy band which we are considering, and \vec{k} is a time-dependent vector. The reason for which \vec{k} can be regarded as a time-dependent wave vector is that the translation operators of the lattice are no longer constants of motion of our problem, but the time derivatives of these operators are diagonal in a representation in which these operators are diagonal. The function (3) is written in this representation and the time dependence of \vec{k} is given by (see Ref.[14]):

$$\vec{k} = \vec{k}_0 + \frac{e\vec{F}t}{\hbar}$$
(4)

We notice that the original wave vector is restored after a time

$$T = \frac{\hbar a^*}{eF}$$
(5)

where a* is the dimension of the Brillouin Zone in the direction of the external electric field. It has been shown by Callaway [11] that the Stark effect of Bloch electrons is very small compared to the Franz-Keldysh effect, and we shall neglect the Stark effect by taking the following approximate wave function:

$$\varphi(\vec{\mathbf{r}},t) \simeq b(\vec{\mathbf{r}},\vec{\mathbf{k}}_0) \exp\left[-\frac{i}{\hbar} \int_{0}^{t} E(\vec{\mathbf{k}'}) dt'\right]$$
 (3a)

By substituting this function into Eq.(9) we obtain an expression for $\epsilon_2(\omega)$ which is valid at every point of the Brillouin Zone.

In the case of allowed transition between a fully occupied valence band and an empty conduction band, we obtain from Eqs (1) and (3a):

$$\epsilon_{2}(\omega, \vec{F}) = \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \left| \vec{e} \cdot \vec{M}_{vc} \right|^{2} \frac{eF}{\hbar a^{3}} \int \frac{d\vec{k}_{0}}{8\pi^{3}} \left| \int dt \exp\left\{\frac{i}{\hbar} \int (E_{c}(\vec{k}') - E_{v}(k') - \hbar\omega\right] dt' \right\} \right|^{2}$$
(6)

where we have used the usual approximation of taking constant the dipole matrix element between Bloch states, and we have chosen T given by expression (5).

If we know the band structure of a semiconductor, we can evaluate the effect of an external electric field on interband transitions by performing the integrals in Eq.(6).

3. ELECTRIC FIELD EFFECT AT A POINT \vec{k}_c OF THE BRILLOUIN ZONE

What we can do in general in order to evaluate expression (6) is to expand E_c - E_v in the time-dependent exponential in power terms of $(\vec{k} - \vec{k}_c)$, if \vec{k}_c is the value of \vec{k} about which we consider the transitions.

Let us first consider the cases where the energy expansion contains one or more linear terms and then the case where the energy expansion contains only quadratic terms.

a) <u>Three linear terms</u>: If, in a volume $-R \leq \alpha_x k_x, \alpha_y k_y, \alpha_z k_z \leq R$ the energy expansion contains three dominant linear terms, we can write:

$$E_{c} - E_{v} = E_{0} + \alpha_{x} k_{x} + \alpha_{y} k_{y} + \alpha_{z} k_{z}$$
(7)

By taking the electric field in the x direction, and recalling Eq.(4), we have: $k + 2^*$

$$\epsilon_{2}(\omega, \vec{F}) = \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \left| \vec{e} \cdot \vec{M}_{vc} \right|^{2} \frac{eF}{\hbar a^{*}} \int \frac{d\vec{k}_{0}}{8\pi^{3}} \left| \int dk_{x} \frac{\hbar}{eF} \exp\left\{\frac{i}{eF}\right\} \\ = \frac{4\pi\hbar}{\omega^{2}} \left(E_{0} - \hbar\omega + \alpha_{z} k_{0z} + \alpha_{y} k_{0y} + \alpha_{x} k_{x}^{\dagger} \right) dk_{x}^{\dagger} \right\} \right|^{2} \\ = \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left| \vec{e} \cdot \vec{M}_{vc} \right|^{2} \hbar}{a^{*}eF} \int_{B.z.} \frac{d\vec{k}_{0}}{8\pi^{3}} \\ = \frac{4\pi\hbar}{\omega_{x}} \left(\frac{e}{m}\right)^{2} \frac{\left| \vec{e} \cdot \vec{M}_{vc} \right|^{2} \hbar}{a^{*}eF} \int_{B.z.} \frac{d\vec{k}_{0}}{8\pi^{3}} \\ \times \left| \int_{k_{0x}}^{k_{0x} + a^{*}} dk_{x} \exp\left\{\frac{i}{eF} \left[\left(E_{0} - \hbar\omega + \alpha_{z} k_{0z} + \alpha_{y} k_{0y}\right) k_{x} + \frac{\alpha_{x}}{2} k_{x}^{2} \right] \right\} \right|^{2}$$
(8)

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The integral over k_x can be performed approximately by the saddle point method [see Appendix B, Eq.(B1)], which yields:

$$\epsilon_{2}(\omega,\vec{F}) \simeq \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|}{a^{*}} \int_{0}^{a^{*}} dk_{0x} \int_{S} \frac{dk_{0y} dk_{0z}}{8\pi^{2}} \frac{1}{\alpha_{x}}$$
(9)

where S is a surface E $_0\text{-}\hbar\omega+\alpha_y\,k_{\,0y}+\alpha_z\,k_{\,0z}$ = const with

$$-R \leq const \leq R$$
 (10)

By performing the integrals of Eq.(9) we obtain:

$$\epsilon_{2}(\omega,\vec{F}) \simeq \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{2R}{4\pi\alpha_{x}\alpha_{y}\alpha_{z}} (2R - |E_{0} - \hbar\omega|)$$
(11)

which is just the same expression as is obtained without the electric field (see Appendix A, integral (I A1), Eqs (A7) and (A8)).

b) Two linear terms and one quadratic term: If, in a volume $-R \leq \alpha_x k_x$, $\alpha_y k_y$, $\alpha_z k_z \leq R$, the energy expression $E_c - E_v$ contains two linear terms and one quadratic term, it can be written as:

$$\mathbf{E}_{c} - \mathbf{E}_{v} = \mathbf{E}_{0} + \alpha_{x} \mathbf{k}_{x} + \alpha_{v} \mathbf{k}_{v} + \alpha_{z} \mathbf{k}_{z}^{2}$$
(12)

and we have two different cases:

i) if the electric field is in a direction at which expression (12) is linear, we obtain by using the same procedure as above:

$$\epsilon_{2}(\omega,\vec{F}) = \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \left|\frac{\vec{e}\cdot\vec{M}_{vc}}{a^{*}}\right|^{2} \int_{0}^{a^{*}} dk_{0x} \int_{S^{*}} \frac{dk_{0y} dk_{0z}}{8\pi^{2}} \frac{1}{\alpha_{x}}$$
(13)

where S' is now a surface $E_0 - \hbar \omega + \alpha_y k_{0y} + \alpha_z k_{0z}^2$ = const, with the condition (10). Equations (13) give the same result as is obtained without the electric field [see Appendix A, integral (IA2)].

ii) If the electric field has the direction at which expression (12) is quadratic, we have from Eqs (4) and (6):

$$\epsilon_{2}(\omega,\vec{F}) = \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \left|\vec{e}\cdot\vec{M}_{vc}\right|^{2} \frac{eF}{\hbar a^{*}} \int_{B,z.} \frac{d\vec{k}_{0}}{8\pi^{3}} \left|\int_{k_{0z}}^{k_{0z}+a^{*}} dk_{z} \frac{\hbar}{eF} \exp\left\{\frac{i}{eF}\left[\left(E_{0}-\hbar\omega+\alpha_{x}k_{0x}+\alpha_{y}k_{0y}\right)k_{z}+\frac{\alpha_{z}}{3}k_{z}^{3}\right]\right\}\right|^{2}$$
(14)

By assuming the arbitrary value k_{0z} to have the limits $-a^*/2$ and $+a^*/2$, and then changing the integration variable, we obtain from Eq.(14):

$$\epsilon_{2}(\omega, \vec{F}) = \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e} \cdot \vec{M}_{vc}\right|^{2} \hbar}{a^{*}(eF)^{1/3} \alpha_{z}^{2/3}} \int_{B.z.} \frac{d\vec{k}_{0}}{8\pi^{3}}$$

$$\times \left| \int_{-\frac{a^{*}}{2}} \frac{\alpha_{z}^{1/3}}{eF}}{\int_{B.z.} du \exp\left\{i\left[\frac{u^{3}}{3} + \frac{(E_{0} - \hbar\omega + \alpha_{x}k_{0x} + \alpha_{y}k_{0y})u}{\alpha_{z}^{1/3}(e/F)^{2/3}}\right]\right\}\right|^{2}$$
(15)

For small electric field ($|F| \le 10^4 - 10^5 \text{ V/cm}$) we can take the limits $+\infty$ and $-\infty$ and write:

$$\epsilon_{2}(\omega,\vec{F}) = \frac{4\pi\hbar}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|^{2} \hbar}{a^{*}(eF)^{1/3}\alpha_{z}^{2/3}} \int_{B.z.} \frac{d\vec{k}_{0}}{2\pi} \left| \operatorname{Ai} \left[\frac{E_{0}-\hbar\omega+\alpha_{x}k_{0x}+\alpha_{y}k_{0y}}{\alpha_{z}^{1/3}(eF)^{2/3}}\right] \right|^{2}$$
(16)

where:

$$\operatorname{Ai}(\beta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} du \exp\left[i\left(\frac{u^3}{3} + \beta u\right)\right]$$
(17)

In Fig.1 we show the behaviour of this mathematical function (see Ref.[15]). The integral over k_{0z} of equation [16] cancels the factor 1/a*; the integrals over k_{0x} and k_{0y} can be performed by changing the integration variables. We take as new integration variables:

$$s = \frac{\sqrt{2}}{2} (\alpha_{x} k_{0x}^{+} + \alpha_{y} k_{0y}^{-})$$

$$t = \frac{\sqrt{2}}{2} (\alpha_{y} k_{0y}^{-} - \alpha_{x} k_{0x}^{-})$$
(18)

Equation (16) becomes:

$$\epsilon_{2}(\omega,\vec{F}) = \frac{2\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|^{2}}{(eF)^{1/3} \alpha_{z}^{2/3} \alpha_{x} \alpha_{y}} \int_{-R}^{R} dt \int_{-R}^{R} ds \operatorname{Ai}^{2} \left[\frac{E_{0}-\hbar\omega+s}{\alpha_{z}^{1/3}(eF)^{2/3}}\right]$$
(19)

$$= \frac{2\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e} \cdot \vec{M}_{vc}\right|^{2} (eF)^{1/3}}{\alpha_{z}^{1/3} \alpha_{x} \alpha_{y}} 2R \int_{-R/\alpha_{z}^{1/3} (eF)^{2/3}}^{R/\alpha_{z}^{1/3} (eF)^{2/3}} dq \operatorname{Ai}^{2} \left[\frac{E_{0} - \hbar\omega}{\alpha_{z}^{1/3} (eF)^{2/3}} + q\right]$$
(20)

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FIG.1. The function Ai(β) versus β as given by Eq. (17).

The last integral can be performed with the aid of integral (1 B 2) in Appendix B. By using the asymptotic expansions (B6), (B7), and (B8) which are valid for sufficiently large R we obtain:

$$\epsilon_{2}(\omega,\vec{F}) = \frac{2\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \left|\frac{\vec{e}\cdot\vec{M}_{vc}}{\alpha_{x}\alpha_{y}\sqrt{\alpha_{z}}}\right|^{2} \frac{2R}{\pi} \sqrt{R-E_{0}+\hbar\omega}$$
(21)

which is also the same expression as in the absence of the electric field.

c) One linear term and two quadratic terms: If the energy expansion in a volume $-R \leq \alpha_x k_x \leq R$, $0 \leq \alpha_y k_y^2 + \alpha_z k_z^2 \leq R^2$, has two quadratic and one linear term we can write:

$$\mathbf{E}_{c} - \mathbf{E}_{v} = \mathbf{E}_{0} + \alpha_{x} \mathbf{k}_{x} + \alpha_{y} \mathbf{k}_{y}^{2} + \alpha_{z} \mathbf{k}_{z}^{2}$$
(22)

and we have two different cases:

i) if the field is in the x direction it is easy to see, by using the same approach as in cases (a) and (bi), that the electric field does not change $\epsilon_2(\omega)$ [see Appendix A, integral (IA 3)].

ii) If the electric field is in a direction at which the expansion (22) is quadratic, for example in the z direction, by using the same approach as in case (bii), we obtain an equation equivalent to Eq.(16):

$$\epsilon_{2}(\omega,\vec{F}) = \frac{4\pi\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|^{2}}{a^{*}(eF)^{1/3}\alpha_{z}^{2/3}} \int_{B.z.} \frac{d\vec{k}_{0}}{2\pi} \left|Ai\left[\frac{E_{0}-\hbar\omega+\alpha_{x}k_{0x}+\alpha_{y}k_{0y}^{2}}{\alpha_{z}^{1/3}(eF)^{2/3}}\right]\right|^{2}$$
(23)

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By performing the integral over k_{0z} , Eq.(23) becomes:

$$\epsilon_{2}(\omega,\vec{F}) = \frac{2\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|^{2}}{(eF)^{1/3} \alpha_{z}^{2/3}} \int_{-R}^{R} dk_{0x} \int_{-R}^{R} dk_{0y} \left|Ai\left[\frac{E_{0}-\hbar\omega+\alpha_{x}k_{0x}+\alpha_{y}k_{0y}^{2}}{\alpha_{z}^{1/3}(eF)^{2/3}}\right]\right|^{2}$$
(23a)

The integrals over k_{0x} and k_{0y} may be performed by changing the integration variables and by recalling some properties of the Airy functions. (see Appendix B, integrals (IB2) and (IB3), and the asymptotic expansions (B9), and (B10) which are valid in the case of sufficiently large R. For $\epsilon_2(\omega, \vec{F})$ we obtain:

$$\epsilon_{2}(\omega, \vec{F}) = \frac{2\hbar^{2}}{\omega^{2}} \frac{\left|\vec{e} \cdot \vec{M}_{vc}\right|^{2}}{\alpha_{x} \sqrt{\alpha_{y} \alpha_{z}}} [R' - (E_{0} - \hbar\omega)]$$
(24)

which is again the same result as in the absence of an electric field.

We can conclude from the previous analysis that an external electric field does not change the optical properties of a semiconductor due to interband transitions in the neighbourhood of a point \vec{k}_c about which the expansion in power terms of \vec{k} of the energy difference $E_c - E_v$ contains one or more dominant linear terms.

4. ELECTRIC FIELD EFFECT AT A CRITICAL POINT

Let us then consider transitions near a critical point, at which $\nabla_k (E_c - E_v)_{\vec{k} = \vec{k}_o} = 0$. We can write:

$$E_{c} - E_{v} = E_{0} + \alpha_{1} k_{1}^{2} + \alpha_{2} k_{2}^{2} + \alpha_{3} k_{3}^{2}$$
(25)

To evaluate the time integrals of Eq.(6) it is convenient to write down expression (25) in a new coordinate system so that the new \vec{k}_z axis is in the direction of the external field:

$$E_{c} - E_{v} = E_{0} + \alpha_{u} k_{z}^{2} + 2 b k_{z} + c$$
 (25a)

where:

$$\alpha_{11} = \alpha_1 \ell^2 + \alpha_2 m^2 + \alpha_3 n^2$$
 (26)

 ℓ , m, n, being the direction cosines of the electric field with respect to the principal axes of the critical point, and the quantities b and c are functions of α_1 , α_2 , α_3 and of the coordinates perpendicular to k_z . By making use of expression (25a) and recalling expressions (4) and (5) we AYMERICH

can perform the time integrals of Eq.(6). By using the same approach as was used to obtain Eq.(16) we obtain:

$$\epsilon_{2}(\omega,\vec{F}) = \frac{2\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|^{2}}{\alpha_{u}^{2/3}(eF)^{1/3}} \int dk_{0x} dk_{0y} \left|Ai\left[\frac{E_{0}-\hbar\omega+1/\alpha_{H}(Ak_{0x}^{2}+Bk_{0y}^{2})}{\alpha_{H}^{1/3}(eF)^{2/3}}\right]\right|^{2}$$
(27)

where A and B are constants which satisfy the relation:

$$AB = \alpha_1 \alpha_2 \alpha_3 \alpha_{"} \tag{28}$$

To perform the integrals in Eq. (27) we must consider separately the different types of critical points. We give here only the results arising in different possible cases. The calculation of the integrals over k_{0x} and k_{0y} are given in Reference [9]. We obtain:

a) For a point M_0 :

$$\epsilon_{2}(\omega,\vec{F}) = \frac{2\pi\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|^{2}}{\sqrt{\alpha_{1}\alpha_{2}\alpha_{3}}} (\alpha_{t})^{1/6} (eF)^{1/3} \int dt \left|Ai(t)\right|^{2}$$

$$(E_{0}-\hbar\omega+(E_{0}-\hbar\omega+R^{2})/\alpha_{t}^{1/3}(eF)^{2/3}$$
(29)

b) For a point M_1 , with $\alpha_{\mu} < 0$:

$$\epsilon_{2}(\omega,\vec{F}) = \frac{2\pi\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e}\cdot\vec{M}_{vc}\right|^{2}}{\sqrt{|\alpha_{1}\alpha_{2}\alpha_{3}|}} \left|\alpha_{\mathfrak{n}}\right|^{1/6} \frac{(E_{0}-\hbar\omega+R^{2})/|\alpha_{\mathfrak{n}}|^{1/3}(eF)^{2/3}}{(eF)} dt \left|\operatorname{Ai}(-t)\right|^{2}$$
(30)

c) For a point M_1 , with $\alpha_n > 0$:

$$\epsilon_{2}(\omega, \vec{F}) = \frac{2\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{\left|\vec{e} \cdot \vec{M}_{vc}\right|^{2}}{\sqrt{\left|\alpha_{1}\alpha_{2}\alpha_{3}\right|}} \alpha_{u}^{1/3} (eF)^{2/3} \\ \times \int dt \arccos h \left\{\frac{R^{2}}{\left|t \alpha_{u}^{1/3} (eF)^{2/3} + E_{0} - \hbar\omega\right|}\right\} \left|Ai(t)\right|^{2} (31)$$

$$(E_{0} - \hbar\omega - R^{2})/\alpha_{u}^{1/3} (eF)^{2/3}$$

where R^2 is related to the dimension of the area in which expansion (25) is taken to be valid and does not correspond to the same condition on k_{0x} and k_{0y} for cases (b) and (c).

The results for a critical point of type M_2 with $\alpha_{\parallel} > 0$ and $\alpha_{\parallel} < 0$ are obtained from Eqs (30) and (31), respectively, by reversing the sign of $E_0 - \hbar \omega$. The result for a critical point of type M_3 is obtained from Eq.(29). From Eqs (30) and (31) we see that when $\alpha_{\parallel} = 0$ there is no effect of an electric field on $\epsilon_2(\omega)$ because the limit $\alpha_{\parallel} \to 0$ must give the same result as the limit $F \to 0$. It is more convenient to put our results in another form by considering the expressions $\Delta \epsilon_2(\omega, \vec{F}) = \epsilon_2(\omega, \vec{F}) - \lim_{F \to 0} \epsilon_2(\omega, \vec{F})$.

We can write:

$$\Delta \epsilon_2(\omega, \vec{F}) = \frac{2\hbar^2}{\omega^2} \left(\frac{e}{m}\right)^2 \frac{\left|\vec{e} \cdot \vec{M}_{vc}\right|^2}{\sqrt{|\alpha_1 \alpha_2 \alpha_3|}} \left|\alpha_u\right|^{1/6} (eF)^{1/3} F(\xi, R')$$
(32)

where:

$$\xi = \frac{E_0 - \hbar \omega}{\alpha_{\mu}^{1/3} (eF)^{2/3}}$$
(33)

$$R^{12} = R^2 / \alpha_{\mu}^{1/3} (eF)^{2/3}$$
 (34)

and $F(\xi, R')$ is given by:

a') For a point M_0 :

$$\mathbf{F}(\boldsymbol{\xi},\mathbf{R}') = \boldsymbol{\pi} \int_{\boldsymbol{\xi}}^{\mathbf{R}'^2 + \boldsymbol{\xi}} dt \left| \operatorname{Ai}(t) \right|^2 - \eta(-\boldsymbol{\xi}) \sqrt{-\boldsymbol{\xi}}$$
(35)

where $\eta(x)$ is the usual step function

$$\eta(\mathbf{x}) = \begin{cases} 1, \ \mathbf{x} > 0 \\ 0, \ \mathbf{x} < 0 \end{cases}$$

b') For a point M_1 , with $\alpha_n < 0$:

$$\mathbf{F}(\boldsymbol{\xi},\mathbf{R}^{\dagger}) = \pi \int_{\boldsymbol{\xi}}^{\mathbf{R}^{\dagger}2+\boldsymbol{\xi}} dt \left| \operatorname{Ai}(-t) \right|^{2} - \left[\sqrt{\mathbf{R}^{\dagger}2+\boldsymbol{\xi}} - \eta \left(\boldsymbol{\xi}\right) \sqrt{\boldsymbol{\xi}} \right]$$
(36)

c') For a point M_1 , with $\alpha_{\parallel} > 0$

$$F(\xi, \mathbf{R}') = \int_{-\mathbf{R}'^2 + \xi} dt \operatorname{ar} \cosh\left(\frac{\mathbf{R}'^2}{\left|t + \xi\right|}\right) \left|\operatorname{Ai}(t)\right|^2 - \left[\left(\frac{2 + \lg 2}{\pi} \mathbf{R}' + \frac{2 - \lg 2}{\pi} \frac{\xi}{2\mathbf{R}'}\right) - \eta(\xi) \sqrt{\xi}\right]$$
(37)

We can perform the integrals of Eqs (35) and (36) by using Eqs (B3) and (B4) of Appendix B and we can see, by using the asymptotic expansions (B6), (B7), and (B8) of Appendix B, that the quantity $\epsilon_2(\omega, \vec{F})$ does not depend on R when R is sufficiently large. We are then justified to take R as going to infinity in Eqs (35) and (36) which gives the results of Aspnes [7] in this limit. We obtain:

 a^{11}) For a point M_0

$$F(\xi) = \lim_{R \to \infty} F(\xi, R') = \pi \left[\operatorname{Ai}^{2}(\xi) - \xi \operatorname{Ai}^{2}(\xi) \right] - \eta(-\xi) \sqrt{-\xi}$$
(35a)

The function $F(\xi)$ given in Eq.(35a) is equal to the function $F(\eta)$ defined by Eq.(E1e) of Ref.[7]. The function $F(\eta)$ drawn in Fig.1 of Ref.[7] is reported in Fig.2.

b") For a point M_1 , with $\alpha_n < 0$

$$F(\xi) = \lim_{R \to \infty} F(\xi, R') = -\pi [A'i^2(-\xi) + \xi A'i(-\xi)] - \eta(\xi) \sqrt{\xi}$$
(36a)

The function $F(\xi)$ given by Equation (36a) is equal to $-F(-\eta)$ as given in Table 1 of Ref.[7]. The function $F(\xi)$ is drawn in Fig.3. The integral of Eq.(37) may be calculated numerically with different values of R, and we can see that also in this case the quantity $\Delta \epsilon_2(\omega, \vec{F})$ does not depend on R when R is sufficiently large. By letting R go to infinity we can show that lim $F(\xi, R)$ in case (c) is equal to the function $G(\xi)$ defined by Eq.(E1f) of Ref.[7].

c'') For a point M_1 , with $\alpha_n > 0$

$$F(\xi) = \lim_{R \to \infty} F(\xi, R') = \pi \left[\operatorname{Ai}(\xi) \operatorname{Bi}(\xi) - \xi \operatorname{Ai}(\xi) \operatorname{Bi}(\xi) \right] - \eta(\xi) \sqrt{\xi} \quad (37a)$$

where [15]:

$$\operatorname{Bi}(\beta) = \frac{1}{\pi} \int_{0}^{\infty} \operatorname{du}\left[\exp\left(-\frac{u^{3}}{3} + \beta u\right) + \sin\left(\frac{u^{3}}{3} + \beta u\right)\right]$$
(38)



FIG.2. The function $F(\eta)$ versus η given by Eq. (35a), describing the effect of an electric field at a point M₀. From Ref. [7], Fig.1.



FIG.3. The function $F(\xi)$ versus ξ given by Eq. (36a) describing the effect of an electric field at a point M_1 , with $\alpha_{11} < 0$.

In Fig. 4 the function $G(\xi)$ given in Fig.2 of Ref.[7] is shown. We can conclude that an external electric field has an effect on $\epsilon_2(\omega)$ only in a small region near a critical point. This effect depends on the type of critical point, on the magnitude of the electric field, and on the value of the reduced effective mass in the direction of the electric field.



FIG.4. The function $F(\xi)$ versus ξ given by Eq. (37a) describing the effect of an electric field at a point M_1 , with $\alpha_{\mu} < 0$. From Ref. [7], Fig.2.

For a critical point of type M_0 the external field produces an exponential tail on $\epsilon_2(\omega)$ at energies below the energy gap E_0 (Franz-Keldysh effect), and gives oscillations of $\epsilon_2(\omega, \vec{F})$ about the zero-field value at energies above E_0 . The amount of the exponential shift and the period of the oscillations is proportional to $F^{2/3}$ through the quantity $\alpha^{1/3}$. A number of experimental measurements with different magnitude and direction of F can give a good estimate of the α [16]. For a critical point of type M_1 the field produces oscillations of $\epsilon_2(\omega, \vec{F})$ about $\epsilon_2(\omega, 0)$ above or below E_0 depending on whether that α_n is positive or negative. Also for a point M_1 the period of oscillations is proportional to $(eF)^{2/3} |\alpha_n|^{1/3}$; we can obtain an estimate of the α by a number of measurements with different magnitude and direction of the electric field [17].

5. CRITICAL POINT AT $\vec{k}_c \neq 0$. EFFECT OF THE DIRECTION OF THE ELECTRIC FIELD AND OF THE POLARIZATION OF LIGHT

The results we have obtained up to now are valid in the case of allowed transitions at a single critical point \vec{k}_c in the Brillouin Zone. If $\vec{k}_c \neq 0$ we have to consider the effect arising from all equivalent critical points (which are obtained from one of them by applying the symmetry operations of the crystal) to evaluate the resulting $\epsilon_2(\omega, \vec{F})$. Equation (32) must be modified in the following way:

$$\Delta \epsilon_{2}(\omega, \vec{F}) = \frac{2\hbar^{2}}{\omega^{2}} \left(\frac{e}{m}\right)^{2} \frac{(eF)^{1/3}}{\sqrt{|\alpha_{1}\alpha_{2}\alpha_{3}|}} \sum_{c} \left|\vec{e} \cdot \vec{M}_{vc}\right|^{2} \left|\alpha_{v,c}\right|^{1/6} F(\xi_{c})$$
(32)

where ξ_c is given by:

$$\xi_{c} = \frac{E_{0} - \hbar\omega}{\left|\alpha_{r_{e}c}\right|^{1/3} (eF)^{2/3}}$$
(33)

The matrix element $|\vec{e} \cdot \vec{M}_{yc}|_c^2$ in Eq. (32a) may be different for every critical point of the star \vec{k}_c depending on the selection rule of the transition, on the direction of \vec{k}_c , and on the direction of the polarization of light with respect to the crystallographic axes. The quantity $\alpha_{,c}$ and consequently ξ_c and $F(\xi_c)$ may be different for every critical point depending on the values of the effective masses on the direction of \vec{k}_c , and on the direction of \vec{k}_c , and on the direction of the external electric field with respect to the crystallographic axes.

As an example illustrating how to take into account all these elements, we consider a critical point of type M_1 in the Λ direction corresponding to a transition between a Λ_3 state and a Λ_1 state, as is the case for many cubic semiconductors (see the lectures given by Antončík [18]).

In the Brillouin zone there are eight equivalent critical points in the directions [111], $[1\overline{11}]$, $[1\overline{11}]$, $[\overline{11}1]$, $[\overline{11}\overline{11}]$, $[\overline{11}\overline{11}]$, $[\overline{11}\overline{11}]$, $[\overline{11}\overline{11}]$, $[\overline{11}\overline{11}]$. For each of them, we can write, for reasons of symmetry

$$\alpha_{\mathbf{n},\mathbf{c}} = \alpha_{\mathbf{t}} \sin^2 \varphi_{\mathbf{c}} - \left| \alpha_{\ell} \right| \cos^2 \varphi_{\mathbf{c}}$$
(39)

where

$$\cos^2 \varphi_c = \frac{\left|\vec{k}_c \cdot \vec{F}\right|^2}{\left|k_c\right|^2 \left|\vec{F}\right|^2}$$
(40)

and, because the transitions $\Lambda_3-\Lambda_1$ are allowed only for light polarized perpendicular to the Λ direction:

$$\left| \vec{\mathbf{e}} \cdot \vec{\mathbf{M}}_{\mathbf{vc}} \right|^2 \simeq C^2 \cos^2 \theta_c \tag{41}$$

where

$$\cos^2 \theta_{\rm c} = 1 - \frac{\left|\vec{\mathbf{e}} \cdot \vec{\mathbf{k}}_{\rm c}\right|^2}{\left|\mathbf{e}\right|^2 \cdot \left|\vec{\mathbf{k}}_{\rm c}\right|^2} \tag{42}$$

From Eq. (39) we can see that for a given value of $\alpha_t / |\alpha_t|$, $\alpha_{n,c}$ may be positive for some critical points of the star of \vec{k}_c or negative for others of them, depending on the direction of the electric field with respect to the crystallographic axes. In Table 1 we give as an example the expression of $\alpha_{n,c}$ for each point of the star Λ , when the electric field is in the direction [110] and in the direction [100].

When F is parallel to [100] all critical points contribute to $\Delta \epsilon_2(\omega, \vec{F})$ with the same value of α_{\star} which is positive if $\alpha_t/|\alpha_t| > 1/2$, or negative if $\alpha_t/|\alpha_t| < 1/2$. The effect of the electric field is purely transverse

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TABLE I. WEIGHT FACTOR APPROPRIATE TO ALL EQUIVALENT CRITICAL POINTS AT Λ FOR DIFFERENT DIRECTIONS OF ELECTRIC FIELD AND POLARIZATION OF LIGHT

Critical points	F [100]	\vec{F} It [110] in the plane (111)		
	α _# ,c	^α ", _c .	cos ² θ , c	cos ² θ _⊥ , c
(111) (111)	$\frac{1}{3}(2\alpha_t - \alpha_\ell)$	$\frac{1}{3}(\alpha_t - 2 \alpha_\ell)$	$\frac{1}{3}$	<u>7</u> 9
(111) (111)	$\frac{1}{3}(2\alpha_t - \alpha_\ell)$	$\frac{1}{3}(\alpha_t - 2 \alpha_\ell)$	· 1/3	<u>7</u> 9
(111) (111)	$\frac{1}{3}(2\alpha_t - \alpha_\ell)$	α _t	1	<u>1</u> 9
(ī11) (1īī)	$\frac{1}{3}(2\alpha_t - \alpha_{\ell})$	α _t	1	1

Note: The light is polarized in the same plane as the electric field \vec{F} , perpendicular and parallel to the field. The angle φ_c is defined by the directions of \vec{F} and of the principal axes of the critical point. The angles $\theta_{\parallel,c}$ and $\theta_{\perp,c}$ are defined by the direction of polarization of light and by the normal to the principal axis of the critical point.

 $(\alpha_n > 0)$, oscillations at energies higher than E_0 , or purely longitudinal $(\alpha_n < 0)$, oscillations at energies lower than E_0 .

When the electric field is in the [110] direction the critical points [111], [111], [111], and [111] contribute to $\Delta \epsilon_2$ with $\alpha_n > 0$ (transverse effect, oscillation at high energy side), while the critical points [111], [111], [111], and [111] contribute to $\Delta \epsilon_2$ with $\alpha_n > 0$ or $\alpha_n < 0$ depending on the fact that $\alpha_t/|\alpha_\ell| > 2$ or $\alpha_t/|\alpha_\ell| < 2$, respectively.

The same kind of analysis may be performed when the electric field is in other directions. By a sufficient number of experimental measurements at different orientations of the electric field with respect to the crystallographic axes, the direction of the critical point responsible for the effect and the ratio $\alpha_t/|\alpha_t|$ may be determined in a rather good approximation. We recall here that the optical coefficients measured experimentally are functions of the real and imaginary parts of the dielectric constant, and to compare theory and experiments, we must take account of ϵ_1 as well as of ϵ_2 . (this kind of analysis is done in Ref.[19]).

When the electric field introduces an anisotropy between the equivalent points of the star of \vec{k}_c through $\alpha_{n,c}$ the quantity $\Delta \epsilon_2(\omega, \vec{F})$ given by Eq.(32a) strongly depends on the polarization of light.

This is the case in our example when the electric field is in the [110] direction. In Table 1 the values of $\cos^2 \theta_c$ when the light is polarized parallel and perpendicular to the electric field are given. We can see that the weight factor (42) arising from the critical points $[111], [\overline{111}], [11\overline{1}], and [\overline{111}]$ is 12/9 when the light is polarized parallel to the electric field and 28/9 when the light is polarized perpendicularly to the electric field, while the weight factor arising from the critical points $[1\overline{1}1]$, $[\overline{1}1\overline{1}]$, $[\overline{1}11]$, and $[1\overline{1}\overline{1}]$ is 36/9 when the light is polarized parallel to the electric field and 20/9 when the light is polarized perpendicularly to the electric field. Consequently, the contribution of the first four critical points to $\Delta \epsilon_2$ is greater when $\vec{e}_1 \vec{F}$ than when $\vec{e} \| \vec{F}$, the opposite being true for the contribution due to the last four critical points. If $\alpha_t/|\alpha_\ell| < 2$, from the previous discussion we expect oscillations on both sides of the critical point energy, E_0 , and the oscillations above E_0 are enhanced compared to the oscillations below E_0 when $\vec{e} \parallel \vec{F}$; the opposite situation occurs when $\vec{e_1}\vec{F}$. This result seems to explain the dichroism recently found by Rehn and Kyser [20] on GaAs. (A detailed discussion on the effect of the direction of the electric field and of the polarization of light is given in Ref. [21]).

APPENDIX A

Integrals which occur in calculating $\epsilon_2(\omega)$

We have the following integral:

$$IA1 = \int_{-R}^{R} dx \int_{-R}^{R} dy \int_{-R}^{R} dz \ \delta (E_0^{-}\hbar\omega + x + y + z) =$$
(A1)

$$= \int_{-R}^{R} dx \int_{-R}^{R} dy \quad \text{on surfaces given by:}$$

$$\hbar\omega - E_0 - (x+y) = c \tag{A2}$$

where:

$$-R \le c \le R \tag{A3}$$

By changing the integration variables:

$$s = \frac{\sqrt{2}}{2} (x+y)$$

$$t = \frac{\sqrt{2}}{2} (y-x)$$
(A4)

where:

$$-R \leq s \leq R$$
 (A5)

-
$$R \leq t \leq R$$

with the supplementary condition:

$$R+\hbar\omega - E_0 \ge s \ge -R+\hbar\omega - E_0$$
(A6)

we obtain, if $E_0 - \hbar \omega > 0$:

$$IA1 = 2R \int_{-R}^{R+\hbar\omega - E_0} ds = 2R [2R - (E_0 - \hbar\omega)]$$
(A7)

and if $E_0 - \hbar \omega < 0$:

IA1 = 2R
$$\int_{-R+\hbar\omega-E_0}^{R} ds = 2R[2R-(\hbar\omega-E_0)]$$
 (A8)

$$IA2 = \int_{-R}^{R} dx \int_{-R}^{R} dy \int_{-R}^{R} dz \ \delta(E_0 - \hbar\omega + x + y + z^2)$$
$$= \frac{1}{2} \int_{-R}^{R} dx \int_{-R}^{R} dy \ \frac{1}{\sqrt{\hbar\omega - E_0 - (x + y)}}$$
(A9)

with the condition:

.

$$0 \leq \hbar \omega - E_0 - (x+y) \leq R^2$$
(A10)

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By using the integration variables defined by Eq.(A4) with condition (A5), and recalling expression (A10), we obtain:

IA2 = R
$$\int_{-R}^{\hbar\omega - E_0} ds \frac{1}{\sqrt{\hbar\omega - E_0 - s}} = 2 R \sqrt{R - (E_0 - \hbar\omega)}$$
 (A11)

$$IA3 = \frac{1}{2} \int_{-R}^{R} dx \int_{0}^{2\pi} d\theta \int_{0}^{R^2} \delta (E_0 - \hbar\omega + x + r^2) =$$
(A12)

$$= \pi \int_{-R}^{R} dx \quad \text{on lines}$$

$$-R \quad \hbar \omega - E_0 - x = c \quad (A13)$$

With the condition:

$$0 \le c \le R^2 \tag{A14}$$

we obtain

$$IA3 = \pi [R - (E_0 - \hbar \omega)]$$
(A15)

APPENDIX B

Integrals which occur in calculating $\epsilon_2(\omega, \vec{F})$

We have:

IB1 =
$$\int_{a}^{b} g(x) e^{ikf(x)} dx \simeq g(x_0) \frac{\pi^{1/2} e^{ikf(x_0)}}{|k f''(x)|_{x=x_0}^{1/2}}$$
 (B1)

if k is large and $f'(x_0) = 0$ for $a \le x_0 \le b$.

and:

IB2 =
$$\int_{0}^{\infty} \frac{dt}{\sqrt{t}} A_{i}^{2}(x+t) = \frac{1}{2} A_{i_{1}}(2^{2/3} x)$$
 (B2)

where:

$$\operatorname{Ai}_{1}(\mathbf{x}) = \int_{\mathbf{x}}^{\infty} \operatorname{Ai}(t) dt$$
(B3)

[see Aspnes [7], Eq.(B27)]

Furthermore,

$$I B3 = \int_{x_{1}}^{x_{2}} dt Ai_{1}(x+t)$$

= $\int_{0}^{\infty} du Ai_{1}(x+x_{1}+u) - \int_{0}^{\infty} dq Ai_{1}(x+x_{2}+q)$
= $[Ai'(q)+q Ai_{1}(q)]_{x+x_{2}} - [Ai'(u)+u Ai_{1}(u)]_{x+x_{1}}$ (B4)

[see Aspnes [7], Eq.(B14)].

and

I B4 =
$$\int_{x_1}^{x_2} dt Ai^2(t) = [Ai^2(t) - t Ai^2(t)]_{x_2}^{x_1}$$
 (B5)

[see Aspnes [7], Eq.(B21)].

Asymptotic expansions of the Airy function and related functions for $x \rightarrow \infty$.

$$x \operatorname{Ai}^{2}(x) \sim \frac{1}{4\pi} x^{1/2} e^{(-4/3 x^{3/2})} \sim \operatorname{Ai}^{2}(x)$$
 (B6)

[see Aspnes [7], Eq.(C8a)].

x Ai²(-x)
$$\sim \frac{1}{\pi} (-x)^{1/2} \sin^2 \left[\frac{2}{3} (-x)^{3/2} + \frac{\pi}{4} \right]$$
 (B7)

[see Aspnes [7], Eq.(C8b)].

$$\operatorname{Ai}^{j_2}(-\mathbf{x}) \sim \frac{1}{\pi} (-\mathbf{x})^{1/2} \cos^2 \left[\frac{2}{3} (-\mathbf{x})^{3/2} + \frac{\pi}{4} \right]$$
 (B8)

[see Aspnes [7], Eq.(C8c)].

$$x \operatorname{Ai}_{1}(x) \sim \frac{1}{2\sqrt{\pi}} x^{1/4} e^{\left(-\frac{2}{3}x^{3/2}\right)} \sim \operatorname{Ai}'(x)$$
 (B9)

x Ai₁(-x) ~ x -
$$\frac{1}{\sqrt{\pi}}$$
 x^{1/4} cos $\left(\frac{2}{3}$ x^{3/2} + $\frac{\pi}{4}\right)$ ~ x + Ai(-x) (B10)

The last two equations are obtained from Ref. [15].

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SOME PROBLEMS IN STUDYING THE BAND STRUCTURE OF DISORDERED SYSTEMS

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Abstract

1. Introduction: specific features of the systems in question. 2. Density of states and the local density of states. 3. Electrical conductivity. 4. Bands and effective levels.

1. INTRODUCTION: SPECIFIC FEATURES OF THE SYSTEMS IN QUESTION

The electronic properties of disordered systems including liquids, amorphous or heavily doped semiconductors, etc., has become of considerable interest in the last few years.

The theoretical papers on the subject are mostly based on the standard band theory concepts. The same concepts are usually used to interpret the experimental results. However, the conventional band theory came out as a result of studying the one-electron problem in a spatially periodic field of the perfect lattice. Therefore the problem of how to apply it to disordered systems is somewhat unclear. We shall attempt here to give an answer to this question.

A system will be called disordered if it does not posses any longrange order though a short-range one may exist. Certainly, this definition is very broad since it covers everything except perfect crystals. Nevertheless, all the systems in question do possess some features in common.

The first of these features is that, in contrast to the perfect crystal, the components of the crystal momentum are no longer good quantum numbers. The reason is obvious: no translational invariance of the Hamiltonian exists. In other words, the states with prescribed crystal momentum are non-stationary. Thus, the concept of a dispersion relation giving energy in terms of the crystal momentum, strictly speaking, does not make sense in this case. In particular, no notion of a Fermi surface exists in the case of degenerate systems. This result is well-known in the theory of heavily doped semiconductors (see Ref.[1]). Note that the concept of a dispersion relation is one of the building stones of conventional band theory.

The second specific feature of the systems in question is the random nature of the force field in which the charge carriers move. The reasons for this are as various as they are obvious, including, say, the random distribution of the chains in glass over their dimensions, or the random distribution of impurities in a semiconductor sample, or just the heat motion of atoms in a liquid. The net result, however, is the same in all cases: the force field is randomly different in different samples and even in different parts of the same sample. On the other hand, most of the macroscopic experiments deal, as a rule, with the sample as a whole. This means that in a macroscopic experiment an automatic averaging is made over all the possible values of the random field. This has to be reflected in the theory. Note that the averaging procedure is alien to the conventional band theory. Moreover, it makes the very concept of the wave function a not very convenient one, persuading us to work preferably with some other quantities, which would allow the averaging process to be performed in a natural way. Such quantities are the Green's functions (or the spectral functions and reduced density matrices derived from them).

The third feature is the increased role of some many-body effects in degenerate systems as compared to the case of a perfect crystal. There are generally three types of the many-body effects: screening, energy renormalization, and damping of the elementary excitations due to particle-particle scattering. In a perfect crystal, the third effect is known to be very small near the Fermi surface. The reason is that the exclusion principle combined with the energy and momentum conservation laws greatly restricts the volume of the phase space available for the process in question. For a disordered material the last factor drops out. Therefore, the conventional quasi-particle picture may become invalid if applied to such materials. Note that it was just this concept that made it possible to justify the standard band scheme when applied to many-electron systems.

The features just described may or may not be important quantitatively, depending upon the particular properties of the substance in question. It is not impossible that some models might be invented that would for some reasons allow description in conventional terms. However, in such cases we never know which result reflects the nature of the things and which the nature of the model. Therefore, an attempt seems desirable to study the problem from a somewhat more general point of view. The first question that arises in this respect is the following: are there any band theory concepts that could be preserved in the general case of a disordered system? In particular; what (if any) is the exact meaning of the very concept of a band? Evidently, to answer this question we have to find out what are the exact quantities that could effectively describe a many-body system of the general type.

2. DENSITY OF STATES AND THE LOCAL DENSITY OF STATES

The quantities in question are well known from the general manybody theory (see, e.g. Ref.[1]). One of the most important of these quantities is the generalized density of states, $\rho(E)$ (to be called just the density of states in what follows). In the Fermi system it is defined by the relation

$$\rho(E) = \frac{2}{V} \operatorname{Tr} \operatorname{Im} G_{r}(E)$$
 (2.1)

Here E is the energy variable, V the volume of the system¹, $G_r(E)$ the

¹ The right-hand side of Eq.(2, 1) may be shown to be asymptotically volume-independent, if $V \rightarrow \infty$, the average particle concentration n being finite.

Fourier-transform (with respect to time) of the one-particle retarded anticommutator Green's function. The latter is defined with the sign convention used in Ref. [2]:

$$G_{r}(\lambda,\lambda^{\dagger};t) = i\theta(t) \langle [a(\lambda,x_{0}), \bar{a}(\lambda^{\dagger}, x_{0}^{\dagger})] \rangle$$

$$(2.2)$$

Here t = $x_0 - x'_0$, x_0 and x'_0 are the time variables, λ , λ' the arguments specifying the chosen representation, a, \bar{a} the annihilation and creation operators, respectively; the symbol $\langle \dots \rangle$ means taking the usual expectation value over the Gibbs ensemble and averaging over the random field. The particular choice of the variables is of course irrelevant when $\rho(E)$ is calculated.

Using the spectral representation of the Green's function (2) we see immediately that the argument E means the increase (or decrease) of the energy of the whole system when one of the particles is added to it (or removed). If there is a dispersion relation it is convenient to put $\lambda = \lambda' = \vec{p}$, where \vec{p} is the crystal momentum. Then

$$\operatorname{Im} G_{r}(\vec{p}, E) \sim \delta(E - W_{p})$$
(2.3)

where W_p is the single-particle energy expressed in terms of the crystal momentum and the definition (2.1) reduces exactly to the standard expression used in the statistics of the perfect gas (band theory included); the argument E designates the single particle (or quasiparticle) energy, in this case.

In the general case, relation (2.3) does not hold. However, definition (2.1) always has an exact meaning, irrespective of the nature of the interactions governing the behaviour of the system. Moreover, it is easily seen that the density of states, (2.1) contains all the information needed to establish the thermodynamic properties of the system. The average particle concentration n is, indeed, given by (see Refs [1-3]):

$$n = \int_{-\infty}^{+\infty} \left[e^{\beta (E - \mu)} + 1 \right]^{-1} \rho(E) dE \qquad (2.4)$$

where μ is the chemical potential, and β an inverse temperature (in energy units). Thus, if the function $\rho(E)$ is known it is, in principle, possible to obtain an explicit relation between n and μ from which all thermodynamic quantities can be calculated by the well known formal methods. In this way it was possible (see Refs [3,4]) to study some low-temperature thermodynamic properties of the Fermi system without making use of a dispersion-relation concept.

Moreover, according to the meaning of the argument E in Eq. (2.1), there must still be a correlation between the density of states and the kinetic properties of the system – such as conductivity, light absorption (or emission) coefficient, the I-V curve of the tunnelling system, etc. Such a correlation was indeed shown to exist (see Refs [3,5-7]) without any assumptions concerning the validity of the dispersion relation concept. However, up to now only the so-called macroscopically homogeneous

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systems were considered. By this we mean the systems in which the averaged electron concentration is either constant all over the sample (up to small surface terms) or is piece-wise constant (the tunnelling case). On the other hand, systems possessing not only a random spatial variation of the electron concentration but also a systematic one, may be of some interest. The last one is by definition preserved after averaging over the random field. In such cases the quantity (2.1), while still preserving an exact meaning, gives too incomplete a description of the system: it determines just a spatial average value of the electron concentration, (2.4), but not the local one. In fact, using co-ordinate representation, Eq.(2.1) may be rewritten in the form

$$\rho(E) = \frac{2}{\overline{V}} \int d\vec{x} \operatorname{Im} G_{r}(\vec{x}, \vec{x}; E)$$
(2.5)

where x means the three coordinates (and the spin quantum number if needed) and the integral is taken over the volume V. On the other hand, the local concentration is (see Ref. [2]):

$$n(\vec{x}) = \int_{-\infty}^{+\infty} 2 \operatorname{Im} G_{r}(\vec{x}, \vec{x}; E) \left[e^{\beta(E-\mu)} + 1 \right]^{-1} dE$$
(2.6)

It seems natural therefore to define a local density of states

$$\rho(\vec{x}, E) = 2 \operatorname{Im} G_r(\vec{x}, \vec{x}; E)$$
 (2.7)

of which ρ (E) is the spatially averaged value²:

$$\rho(\mathbf{E}) = \frac{1}{V} \int d\vec{\mathbf{x}} \ \rho(\vec{\mathbf{x}}, \mathbf{E})$$
(2.8)

Both quantities, $\rho(E)$ and $\rho(\vec{x}, E)$, are non-negative. Note, however, that $\rho(E)$ is obviously unitarily invariant while $\rho(\vec{x}, E)$ is by definition in terms of the co-ordinate representation only.

To establish the connection between the local density of states and the kinetic coefficients, it is convenient to use the mixed (Wigner) representation putting ($\hbar = 1$)

$$G_{r}(\vec{x},\vec{x}';E) = G_{r}^{t}\left(\vec{x}-\vec{x}', \frac{\vec{x}+\vec{x}'}{2}; E\right) = \int d\vec{p} e^{i\vec{p}\cdot(\vec{x}-\vec{x}')} G_{r}^{t}\left(\vec{p}, \frac{\vec{x}+\vec{x}'}{2}; E\right)$$
(2.9)

Then

$$\rho(\vec{x}, E) = 2 \int d\vec{p} \, Im \, G_r^{\dagger}(\vec{p}, \vec{x}; E)$$
 (2.7)

² The two quantities obviously coincide in the macroscopically homogeneous case, when $G_r(\vec{x},\vec{x}^*; E) = G_{\downarrow}(\vec{x}-\vec{x}^*; E)$.

In a homogeneous system G! does not depend upon the second argument, $G_1'(\vec{p}, E)$ becomes just a usual Fourier transform of the Green's function and the right-hand side of Eq.(2.7') reduces to a standard expression for the function $\rho(E)$. Note, however, that the function $\operatorname{Im} G_1'(\vec{p}, \vec{x}; E)$ is not generally positive-definite. This property is characteristic only of its integral over \vec{x} .

The essence of the representation (2.9) lies in the fact that there is a certain class of macroscopically inhomogeneous systems that seems to be of a special interest. These are the systems where the systematic spatial variation of the electron concentration (and of other quantities of interest) is smooth enough: the function $n(\vec{x})$, averaged over the random field, remains practically constant on the microscopic scale defined, say, by the length $n^{-1/3}$ or the mean free path (if it has any meaning). Such systems (to be called quasi-homogeneous and the only ones to be dealt with in what follows) possess, at least, two very different spatial scales. The Green's function of such a system, G'($\vec{p}, \vec{x}; E$), depends only weakly upon the second argument while it may depend upon the first one in an arbitrary fashion. It is just this fact that makes the representation (2.9) especially convenient: the two types of the co-ordinate dependence are explicitly separated.

3. ELECTRICAL CONDUCTIVITY

Representation (2.9) is also convenient in the problem of electrical conductivity. We shall confine ourselves to the case of an electric field varying slowly in space (in a sense described above). Then the real part of the complex conductivity tensor at frequency ω is (see Ref.[2]):

$$\sigma_{ij}(\vec{x},\omega) = \operatorname{Re}\left\{(-i)\frac{\partial}{\partial\kappa_{j}}\int d\vec{y} e^{-i(\vec{\kappa},\vec{x}-\vec{y})}\lambda_{i}^{0}(\vec{x},\vec{y};\omega)\right\}_{\vec{\kappa}=0}$$
(3.1)

Here κ is the wave vector of the electromagnetic wave, $\lambda_i^0(\vec{x}, \vec{y}; \omega)$ is the Fourier transform with respect to time $t = x_0 - y_0$ of the quantity

$$\lambda_{i}^{0}(\mathbf{x}, \mathbf{y}) = \frac{e^{2}}{2m_{0}} \lim_{\substack{\mathbf{x}' \to \mathbf{x} \\ \mathbf{x}_{0}^{i} > \mathbf{x}_{0}}} \left(\frac{\partial}{\partial \mathbf{x}_{i}} - \frac{\partial}{\partial \mathbf{x}_{i}^{i}} \right) \\ \times \operatorname{Tr} \int d\mathbf{y}^{i} d\mathbf{y}^{i} \left\{ G_{c}(\mathbf{x}, \mathbf{y}^{i}) \Gamma^{0}(\mathbf{y}^{i}, \mathbf{y}^{i}; \mathbf{y}) G_{c}(\mathbf{y}^{i}, \mathbf{x}^{i}) \right\}$$
(3.2)

Here m_0 is the true electron mass, x, y, y', y'' are the four-dimensional quantities (x = { \vec{x}, x_0 }, etc.), the trace (in contrast to Eq.(2.1)) is taken over the spin variables only, Γ^0 is the full scalar vertex part, G_c is the causal Green's function defined as an average over the Gibbs ensemble only, the curly brackets mean averaging over the random field³. The well-known "plasma" term is omitted on the right-hand side of Eq.(3.2) since it contributes only to the imaginary part of the conductivity.

³ Note that it is just the product $G_C \Gamma^0 G_C$ as a whole that is to be averaged in this case, and not the various multipliers separately. This is a particular case of the general rule: the averaging procedure is applied to the observable quantity in question.

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It is convenient to write the vertex part in a form analogous to expression (2.9):

$$\Gamma^{0}(y^{1}, y^{''}; y) = \Gamma^{10}\left(y^{1} - y, y^{''} - y; \frac{y^{1} + y^{''}}{2}\right)$$
$$= \frac{1}{(2\pi)^{8}} \int d\kappa^{1} d\kappa^{''} \Gamma^{10}\left(\kappa^{1}, \kappa^{''}; \frac{y^{1} + y^{''}}{2}\right) e^{-i(\kappa^{'}, y^{'} - y) + i(\kappa^{''}, y^{''} - y)}$$
(3.3)

where κ^{\dagger} , $\kappa^{\prime\prime}$ are the four-dimensional variables.

Note that the third argument of the integrand contains only the spatial coordinates, $(\vec{y'} + \vec{y''})/2$: we consider the thermodynamic system which is homogeneous with respect to time.

The function G_c is also written in a form analogous to expression (2.9), the only difference being that, no averaging over the random field being implied, the dependence upon the second argument must not necessarily be smooth. However, after the integrand of the integral in Eq.(3.2) is averaged in this sense only the smooth part of the dependence on y' + y'', x + y' and y'' + x survives. On the other hand, the relevant values of the wave vectors κ' , κ'' , p are not generally small. Thus, we may neglect the derivatives of Γ^{10} and G'_c with respect to these spatial variables as compared to the products of the type $\kappa_i \Gamma^{10}$ and $p_i G'_c$. In this way one obtains:

$$\sigma_{ij}(\vec{x},\omega) = \frac{e^2}{m_0} (2\pi)^4 \operatorname{Re} \lim_{t \to +0} \operatorname{Tr} \frac{\partial}{\partial \kappa_j}$$

$$\int d\vec{p} \int_{-\infty}^{+\infty} dp_0 e^{ip_0 t} p_i \left\{ \Gamma^{\dagger 0} \left(\vec{p} + \frac{\vec{\kappa}}{2}, p_0^{\star}, \vec{p} - \frac{\vec{\kappa}}{2}, p_0^{\star}; \vec{x} \right)$$

$$G_c^{\dagger} \left(\vec{p} + \frac{\vec{\kappa}}{2}, p_0^{\star}; \vec{x} \right) G_c^{\dagger} \left(\vec{p} - \frac{\vec{\kappa}}{2}, p_0^{\star}; \vec{x} \right) \right\}_{\vec{\kappa} = 0}$$
(3.4)

Here $p_0^{\pm} = p_0 \pm \omega/2$.

In the case of the homogeneous system this equation reduces to the well-known result (see Ref.[2], section 15). Note that the same spatial argument \vec{x} enters both the left and right-hand sides of Eq.(3.4). This means that the quantity σ_{ij} is a local function of the local charge carrier concentration. This standard and very trivial result is a consequence of the quasi-homogeneous approximation. In the general case, it is, of course, incorrect, and the conductivity is non-locally expressed in terms of $n(\vec{x})$.

It is a simple matter to write down the Ward identity for an inhomogeneous system. Proceeding in the standard way we obtain

$$(\kappa_{0}^{i} - \kappa_{0}^{''}) \Gamma^{10}\left(\kappa^{i}, \kappa^{''}; \frac{\vec{y}^{i} + \vec{y}^{''}}{2}\right) - (\kappa_{1}^{i} - \kappa_{1}^{i'}) \Gamma^{i}\left(\kappa^{i}, \kappa^{''}; \frac{\vec{y}^{i} + \vec{y}^{''}}{2}\right)$$

$$= (2\pi)^{4} \left[G_{c}^{i-1}\left(\kappa^{''}, \frac{\vec{y}^{i} + \vec{y}^{''}}{2}\right) - G_{c}^{i-1}\left(\kappa^{i}, \frac{\vec{y}^{i} + \vec{y}^{''}}{2}\right) \right]$$

$$(3.5)$$

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The argument $(\vec{y}^{\dagger} + \vec{y}^{"})/2$ enters this equation as a parameter. This makes it possible to transform Eq.(3.5) in the same way as it was done in the case of a homogeneous system (see Ref.[3]), expressing Γ^{10} in terms of $G_c^{\dagger}(\vec{p},\vec{x})$ and of its derivatives with respect to \vec{p} and p_0 . Thus, the theorem on the correlation between the conductivity and the density of states proven previously for the macroscopically homogeneous systems is generalized to the quasi-homogeneous case, the local density of states $\rho(\vec{x}, E)$ replacing the function $\rho(E)$. In particular, the following statements are valid:

(1) At zero temperature the static conductivity is non-zero if and only if the chemical potential lies in the region of the energy space where the local density of states is non-zero and continuous.

(2) Let the local density of states be effectively equal to zero at $E \leq E_0$ (possibly $E_0 = E_0(\vec{x})$) and $\mu < E_0$, $\beta(E_0 - \mu) \gg 1$. Then the static conductivity contains an exponential factor

Its origin is obvious: according to expressions (2.6) and (2.7) under conditions stated above we have $n(\vec{x}) \sim \exp\{-\beta(E_0 - \mu)\}$.

(3) The frequencies of eventual optical transitions ω must satisfy the condition $\hbar \omega \approx E_1 - E_2$, where E_1 and E_2 (both possibly functions of \vec{x}) are some energy values at which the local density of states is non-zero.

These statements would be completely trivial in the frame of the conventional band theory. The point is, however, that they turn out to be true also in the far more general case of any quasi-homogeneous disordered system irrespective, for instance, of whether there is or there is no dispersion relation. Thus, the local density of states correlates with practically all the kinetic properties of the system. Qualitatively, it may be used to predict them much in the same way as if we had to deal with a one-electron theory of the perfect crystal.

4. BANDS AND EFFECTIVE LEVELS

The correlation between the kinetic coefficients and the local density of states as well as the thermodynamic importance of the latter quantity enables us to give a precise definition of the concepts of allowed and forbidden bands⁴. An allowed band is the energy range where the local density of states is non-zero and continuous, a forbidden band is the range where it is identically equal to zero. Note, however, that the last definition is conditional to some extent: strictly speaking, the random nature of the force field makes the function $\rho(\vec{x}, E)$ unequal to zero at any finite E. In other words, the "edges" of an allowed band are always somewhat smeared off, thereby forming the so-called tails. However, a rather large

⁴ In case of the macroscopically homogeneous systems it has already been given in Ref. [1].

energy range may exist where the local density of states is negligibly small which justifies our definition 5 .

Note that this definition takes natural account of the systematic bending of the bands in some external fields.

There may be several regions of the energy space where the local density of states is non-zero, separated by the forbidden bands. Thus, we may speak of different allowed bands (possibly with different mobilities). Correspondingly, a concept of the density of states in a certain band becomes meaningful in the general theory; it is especially useful in view of statement (2) of the preceding section.

In idealized systems the density of states may have discontinuities: δ -like peaks of the local density of states may arise in the forbidden band. It is natural to call the relevant E values "the local levels". The random nature of the field leads to an unavoidable smearing-off of the peaks; so, strictly speaking, we should call them bands, too – in the sense of the definition given above. However, the width of the peak Δ (to be defined precisely in what follows) may be small compared to other relevant energies (in particular, compared to $T \equiv \beta^{-1}$ and to the distance from the other peak or the effective edge of a band). This usually corresponds to the low d.c. mobility, and if this is really the case then it makes sense to preserve the concept of an "almost discrete" level. From a thermodynamic point of view, the peak in question behaves as if it were a single "effective level" possessing an energy E, defined by the relation

$$N_t n_F(E_t^*) = \int \rho(\vec{x}, E) n_F(E) dE \qquad (4.1)$$

Here $n_F(E) = [exp\beta(E - \mu) + 1]^{-1}$ is the Fermi function, N_t is the concentration of the peaks. The integral on the right-hand side of Eq.(4.1) is, strictly speaking, taken about the centre of the peak, E_t . However, under the conditions described above the function $\rho(\vec{x}, E)$ drops off quickly with the distance. $|E - E_t|$, and we may effectively integrate within the infinite limits. The quantity E_t^* is then easily expressed in terms of E_t , and the moments of the local density of states; these may be regarded just as some phenomenological quantities. Put

$$\Delta = \int d\mathbf{E} \left| \mathbf{E} - \mathbf{E}_{t} \right| \mathbf{N}_{t}^{-1} \rho(\vec{\mathbf{x}}, \mathbf{E})$$
(4.2)

$$m_{\ell} = \Delta^{-1} \int dE \left(E - E_{t} \right)^{\ell} N_{t}^{-1} \rho \left(\vec{x}, E \right), \quad \ell = 1, 2, \dots \dots \qquad (4.3)$$

Neglecting quantities of the order of $(\Delta/T)^2$ we obtain

$$E_{t}^{*} = E_{t} + \Delta \left\{ m_{1} + \frac{\Delta}{2T} (m_{1}^{2} - m_{2}) + h \frac{E - \mu}{2T} \right\}$$
 (4.4)

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⁵ The definition adopted may seem to be somewhat incomplete since no assumptions are made concerning the mobility. Its values may be very different in different parts of the continuous spectrum. However, very low mobilities correspond most often to the narrow bands; in such cases, the concept of an effective level is introduced (see below).

These are just the quantities E_t^* that enter all the statistical equations. This is, in particular, valid for bent bands. Indeed, the electrostatic potential φ may be uniquely separated into a systematic (φ_s) and a random (φ_r) part:

$$\varphi = \varphi_{s} + \varphi_{r}; \quad \{\varphi\} = \varphi_{s}, \quad \{\varphi\} = 0 \tag{4.5}$$

The Poisson equation averaged over the random field takes the form

$$\nabla^2 \varphi_{s} = -\frac{4\pi e}{\epsilon} \{ p(\vec{x}) - n(\vec{x}) \}$$
(4.6)

where e is the electron charge, ϵ the dielectric function of the material (assumed constant), $p(\vec{x})$ the concentration of holes (both free and trapped, if any). To obtain n and p as some functionals of ϕ_s we note that the effective (in the sense of Ref.[2]) Schroedinger equation determinating the E values contains the potential in the form

$$-e\varphi - E = -e\varphi_{s} - e\varphi_{r} - E \qquad (4.7)$$

The random part, $-e\varphi_r$, contributes to the eigenvalues (providing, in fact, their random character). On the other hand, the systematic part, being smooth enough, may be taken account of by the standard method of the bent bands. Then the quantity $\mu + e\varphi_s$ will enter Eqs (2.4), (4.1), etc., instead of μ , or, equivalently, effective energy levels will always enter in the combination $E_t^* - e\varphi_s$. Thus, when determining the shape of the bands, we have to deal with the averaged potential only, the latter being obtained in the standard self-consistent way from Eq.(5.6) containing just the effective levels.

Evidently, the activation energy determining the temperature dependence of the conductivity of an amorphous semiconductor is also given in terms of effective levels. Thus, it is seen that the smearing-off of the levels due to the fluctuations of the random field leads to a specific temperature dependence of the activation energy, given explicitly by Eq. $(4.4)^6$. Note that this result is not due to any assumptions of the modellike nature and is therefore applicable to the levels of any nature, once they are narrow enough.

Thus, quite a number of conventional band theory concepts turn out to make sense under much broader conditions than those under which they were originally derived. Essentially all the phenomenological energy picture of the band theory is preserved in the general case (with the smeared-off band edges). Of course, this does not at all imply general validity of the calculational methods of the band theory. The only thing that was proven was that it is possible to obtain some band parameters in an empirical way since they were found to have an exact meaning.

⁶ The quantity E_t may still contain the well-known term which is linear in temperature and due to the degeneracy of the level in question. However, this term does not depend upon the position of the peak relative to the Fermi level.

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This is, in fact, a justification of many attempts undertaken to apply band theory to disordered systems, but it is a justification of a rather special kind: it retains just the many-electron contents of the theory leaving out everything that was essentially based on the one-electron or periodic-field approximations. Thus, there is generally no justification for anything connected with the crystal momentum conservation and with the concept of a dispersion relation. There is for example, no reason for introducing a single dynamical effective mass tensor: one can speak only of the "masses" entering various observed quantities (such as the optical mass, density-of-states mass, etc.)⁷. Furthermore, no Van Hove singularities of the density of states are to be expected.

It is seen that one of the first theoretical problems of the disordered systems is that of calculating the generalized density of states. Numerous papers have been published on the subject; however, the extreme difficulty of the problem made it necessary to resort to rather drastic approximations or to confine the calculations to some specially adopted models. Therefore it might be of interest to invent some ways of determining the density of states directly from experimental data. This is a difficult matter since the kinetic coefficients being correlated with the density of states in the way described above may not generally be expressed explicitly in terms of it. There are two reasons for this, both of which are as obvious as they are of a principal nature: firstly, the trace of the Green's function contains less information than the function G_r itself; secondly, the kinetics is determined as well by the relevant transition probabilities. Therefore, some special situations have to be looked for to extract some reliable information on the density of states from experiment. It seems that such situations might, in fact, be realized in some cases, at least (see Ref. [6]), but the problem as a whole deserves further study.

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⁷ This situation is well known in the theory of heavily doped semiconductors.

THE THEORY OF SURFACE STATES IN SEMICONDUCTORS

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Abstract

Introduction. 1.1. Analytic properties of Bloch states. 1.2. Symmetry of surface states.
 The wave function of the surface state. 3. Numerical results.

1. INTRODUCTION

The states of an electron in a perfect crystal of infinite extension in three dimensions are Bloch functions of the form

$$\psi_{\vec{nk}}(\vec{r}) = e^{\vec{ik} \cdot \vec{r}} u_{\vec{nk}}(\vec{r})$$
(1)

where the function $u_{n\vec{k}}(\vec{r})$ is periodic, with the same translational symmetry of the whole crystal lattice. Besides, the function $\psi_{n\vec{k}}(\vec{r})$ transforms, under the symmetry operations contained in the group of the wave vector $\vec{k} - i.e.$ that subgroup G_k of the lattice space group G which leaves \vec{k} invariant – as one row of some definite irreducible representation of G_k (see Ref.[1]).

The permissible values of the components of \vec{k} in an infinite crystal are real, since otherwise the norm of $\psi_{n\vec{k}}(\vec{r})$ would diverge at infinity.

Let us now consider an ideal case of a crystal with a plane boundary. In this case it is possible to consider complex values of the component of \vec{k} perpendicular to the boundary plane, as long as its sign is the appropriate one to form an exponentially damped wave function $\psi_{n\vec{k}}$ within the crystal.

We shall assume, in our ideal model (Fig. 5), that the potential in the vacuum half-space is just a constant, positive if we take the top of the valence band as the origin of the energy scale, so that the wave function outside will be some linear combination of products of plane waves and possibly damped exponentials, depending on the energy eigenvalue of ψ_{nk} .

We shall now look for electronic states with real energy E within the band gap, with a wave function damped toward both sides of the boundary plane in the direction perpendicular to it. These we shall call "surface states" [2]. Tamm [3] was the first to consider the existence of surface states in a one-dimensional model. Maue [4] has discussed surface states in one dimension and also established the basic formalism for their calculation in three dimensions which we shall apply in what follows. A similar discussion was undertaken by Goodwin [5], with applications to some simple models, and, to a more realistic case, by Autončik [6].
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The two main points to be kept in mind in any calculation of surface states are: (a) the analytic properties of the Bloch functions $\psi_{\vec{nk}}$ (\vec{r}) and of their eigenvalues $E_n(\vec{k})$ and (b) the symmetry of the surface states.

1.1. Analytic properties of Bloch States

The periodic part of the Bloch function, $u_{nk}(\vec{r})$, satisfies the equation

$$[p^{2} + 2\vec{k} \cdot \vec{p} + k^{2} + V(\vec{r})] u_{n\vec{k}}(\vec{r}) = E_{n}(\vec{k}) u_{n\vec{k}}(\vec{r})$$
(2a)

$$H(\vec{k}) u_{\vec{n}\vec{k}}(\vec{r}) = E_n(\vec{k}) u_{\vec{n}\vec{k}}(\vec{r})$$
(2b)

which is written in convenient atomic units.

It can be shown [7] that the function $E_n(\vec{k})$ satisfies the condition:

$$E_{n}(\vec{k}^{*}) = [E_{m}(\vec{k} + \vec{K}_{p})]^{*}$$
(3)

where $m \neq n$ only in case of degeneracy of the n and m bands, but otherwise m = n. The asterisk denotes complex conjugation, and \vec{K}_{ℓ} is some reciprocal lattice vector, which, in particular, can be $\vec{K}_{\ell} = 0$.

We shall consider $\vec{k} = \vec{k}_{\parallel} + \vec{k}_{\perp}$, where """ means parallel and "" perpendicular to the boundary plane. In what follows, we assume that \vec{k}_{\parallel} has any definite value, and we shall forget about it. It is, however, important to realize that \vec{k}_{\parallel} is the index of an irreducible representation of the twodimensional translational symmetry which is not destroyed by the existence of the boundary and, therefore, must also label the wave function in the vacuum half-space and the surface-state wave function.

Let us write $k_1 = k_1 + iq$, where k_r and q are real. Heine [8] shows that in the (k_r, q) complex plane there are curves defined by the equations

$$Im \{ E_{n}(k_{r}, q) \} = 0$$
 (4)

Besides, he shows that they must be normal to the k_r axis at a point where $E_n(k_r)$ has an extremum. These curves are called "real energy lines". A real energy line can: (a) leave the k_r axis and go to infinity (Fig. 1a); (b) leave the k_r axis at a point k_1 , go around one or more branch points in the (k_r, q) complex plane and return to the k_r axis at a point k_2 (Fig. 1b), thus joining a minimum/maximum to a maximum/minimum of the $E(k_r)$ curves; (c) it can leave the k_r axis, reach a branch point and go back along the same path in the (k_r, q) plane, as would be the case if $k_r = 0$ and $\vec{k}_{11} = 0$ (Fig. 1c). Real energy lines such as (b) and (c) are called "loops".

Let us assume that we have obtained, through some band calculation, the function $E_n(k_r)$ and its analytic continuation in the complex k_\perp plane, including branch points and real energy lines. We have now come to the question of symmetry.

1.2. Symmetry of surface states

Let us just remark that a crystal with a boundary is less symmetric than an infinite one: its symmetry group \overline{G} , contained in the space group

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FIG.1. Possible real energy lines, $k_1 = k_r + iq$.

of the crystal, cannot contain mirror or glide planes, nor axes, which are not perpendicular to the boundary. It cannot contain any translation not parallel to it either. This fact eliminates all screw axes.

Let us call G_k and $\overline{G_k}$ the groups of the \overline{k} vector in the unlimited and the bounded crystal, respectively. In general, unless they coincide, $\overline{G_k} \subset G_k$. Thus, a given irreducible representation D^{α} of G_k will be in general reducible into a sum of several irreducible representations \overline{D}^i of G_k . Namely,

$$D^{\alpha} = \sum_{i} C_{i}^{\alpha} \overline{D}^{i}$$
(5)

where the C_i^{α} are integers.

It could happen that two or more different representations D^{α} and D^{β} both contain a given $\overline{D}{}^{\,i}.$

2. THE WAVE FUNCTION OF THE SURFACE STATE

This implies that we can make a linear combination of all those states with the same \vec{k}_{μ} and the same real energy E contained within the gap which, although belonging to different energy lines (e.g., having, in general, different space symmetry), all belong to the same surface symmetry type. This linear combination is an acceptable wave function for a surface state, inside the crystal. For $\vec{k}_{\mu} = 0$ we can express it as

$$\psi^{\text{in}}(\vec{\mathbf{r}}, \mathbf{E}) = \sum_{j=1}^{N} \gamma_{j} \psi_{j}(\vec{\mathbf{r}}) = \sum_{j=1}^{N} \gamma_{j} e^{i(k_{T}^{j} + iq^{j})\zeta} \sum_{m=1}^{L} \alpha_{jm} \Gamma_{m}(\xi, \eta, \zeta)$$
(6)

Here, j labels the N different degenerate analytically continued Bloch functions with real energy (e.g., j labels the real energy line) which we consider. γ_j are arbitrary coefficients to be determined by the boundary conditions. The values of k_j^j and q^j are determined by the equations

Im { E (
$$k_r^j$$
, q^j) } = 0, j = 1, ..., N
Re E (k_r^1 , q^1) = Re E (k_r^2 , q^2) = = Re E (k_r^N , q^N) = E

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The functions $\Gamma_{\rm m}(\vec{r})$ are the solutions of Eq.(2) for $\vec{k} = 0$. We express $\psi_{j, k_1^j + i q j}(\vec{r})$ in terms of these, and the expansion coefficients α_{jm} can be determined, for example, with the " $\vec{k} \cdot \vec{p}$ " method [9]. The coordinates (ξ, η, ζ) express \vec{r} in an orthogonal system where ζ is

normal to the boundary plane.

The wave function outside can be written

$$\psi_{\text{out}}(\vec{r}, E) = \sum_{h, \ell} C_{h\ell} e^{-2\pi i (h\xi + \ell\eta)} e^{-q'_{h, \ell} |\xi|}$$
(7)

It is convenient to use a set of M linearly independent, two-dimensional symmetrized plane waves ϕ_{λ} (ξ , η). In terms of these, we have

$$\Gamma_{\rm m}(\vec{\mathbf{r}}) = \sum_{\lambda=1}^{M} \beta_{\rm m\lambda}(\zeta) \phi_{\lambda}(\xi,\eta), \quad {\rm m} = 1, \dots, {\rm L}$$
(8)

Therefore,

$$\psi_{\text{out}} = \sum_{\lambda=1}^{M} \mu_{\lambda} e^{q'_{\lambda} |\xi|} \phi_{\lambda}(\xi, \eta)$$
(9)

We substitute also expression (8) into Eq. (6), and impose the boundary conditions that at $\zeta = \zeta_0$, which is the co-ordinate of the boundary plane,

$$\psi_{\text{in}}\left(\xi,\,\eta,\,\zeta_{0}\right)=\psi_{\text{out}}\left(\xi,\,\eta\,,\,\zeta_{0}\right)$$

and

$$\frac{\partial \psi_{\text{in}}(\xi, \eta, \zeta)}{\partial \zeta} \bigg|_{\zeta = \zeta_0} = \frac{\partial \psi_{\text{out}}(\xi, \eta, \zeta)}{\partial \zeta} \bigg|_{\zeta = \zeta_0}$$
(10)

If N = M, we obtain, by eliminating { μ_{λ} }, the matrix equation

$$\gamma \cdot \mathbf{A} = \mathbf{0} \tag{11}$$

where

$$A_{j\lambda}(E) = \sum_{m=1}^{L} e^{i(k_{r}^{j}+iq^{j})\zeta_{0}} \alpha_{jm}(E) \left\{ \left(ik_{r}^{j}-q^{j}-q_{\lambda}^{i}\right)\beta_{m\lambda}(\zeta_{0}) + \left(\frac{d\beta_{m\lambda}}{d\zeta}\right)_{\zeta_{0}} \right\}$$
(12)

Therefore, solving the compatibility equation

$$\det A(E) = 0 \tag{13}$$

for E we obtain the energy eigenvalue and the wave function, by making use of Eqs (4) to (11).

3. NUMERICAL RESULTS

We have solved the main problem of finding the eigenvectors and eigenvalues of H(k) by using the $\vec{k} \cdot \vec{p}$ method [8] (Eq.(2)). We show the results for $k_r = 0$, $k_{\parallel} = 0$ in the (100) direction in Si (Fig.2). The dotted curves are plots of E (q) using Kane's two-band model. Figure 3 is a plot of α_{jm} (q), i.e., the different components of the eigenvectors in the basis system consisting of the 15 lowest (4 valence and 11 conduction) bands [9, 10].



FIG.2. Real energy lines in Si calculated for $\vec{k_{\perp}} = iq$ (100) with the $\vec{k} \cdot \vec{p}$ method, using a 15-wave basis (see Ref.[10]).



FIG.3. Eigenvector components for the same case as in Fig.2.



FIG.4. Real k bands and surface states in Si (see Ref.[10]).



FIG.5. Sketch of the model potential used in the calculations.

Similar calculations have been made by Jones [11] and Bartos [12]. An approximate preliminary calculation has been made of surface states of Si (see Ref.[10]). The wave functions have been approximated by symmetrized plane waves. In Fig.4 we plot the bands of Si for real k_r and the positions of the surface states found. A more complete calculation is currently being performed. The model of the surface potential is the simplest possible; it is sketched in Fig.5. The parameter W is the photoemission threshold and has been taken from experiment (see Ref.[13]).

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