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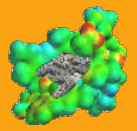


CMS

Modified NRT equations for damage and mixing developed by the OECD NEA primary damage group

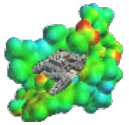
Kai Nordlund 1.10.2012

Department of Physics

University of Helsinki

Finland

OECD
NEA = Nuclear Energy Agency
primary damage group presentation



Kai Nordlund, chair	University of Helsinki
(Andrea Meinander, PhD student)	University of Helsinki
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Bob Averback	University of Illinois
David Bacon	University of Liverpool
Florian Banhart	University of Strasbourg
Maria Caturla	University of Alicante
Sergei Dudarev	CCFE, Oxford
Frank Garner	DSL Extreme, USA
Lorenzo Malerba	SCK-CEN Mol
Taira Okita	University of Tokyo
David Simeone	CEA Saclay
Naoki Soneda	CRIEPI, Japan
Roger Stoller	ORNL
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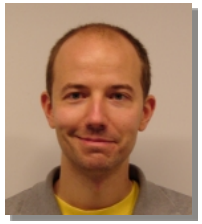
Ion tracks



Dr. Hannu-Pekka Komsa
MoS_2 nanostructures

Dr. Pi-Heng Chen (陈丕恒)
Quasicrystals

M Sc Andrea Meinander
Fusion reactor mat'ls

M Sc Ville Jansson
Fusion reactor mat'ls
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M Sc Jussi Polvi
Organic materials

M Sc Aarne Pohjonen*
Particle physics mat'ls

M Sc Stefan Parviainen*
Particle physics mat'ls

M Sc Marie Backman*
Nanostructures in silica

M Sc Avaz Ruzibaev*
Particle physics mat'ls

M Sc. Mohammad Ullah
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M Sc Laura Bukonte
Fusion reactor mat'ls

M Sc Andrey Ilinov
Nanomechanics

M Sc Kostya Avchachov*
Ion tracks

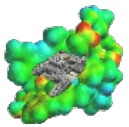
M Sc Aleksi Leino*
Nanostructures in silica

M Sc Wei Ren (任唯)
Carbon nanostructures

MSc Fredric Granberg
Nanowires

MSc Harriet Åhlgren
Graphene

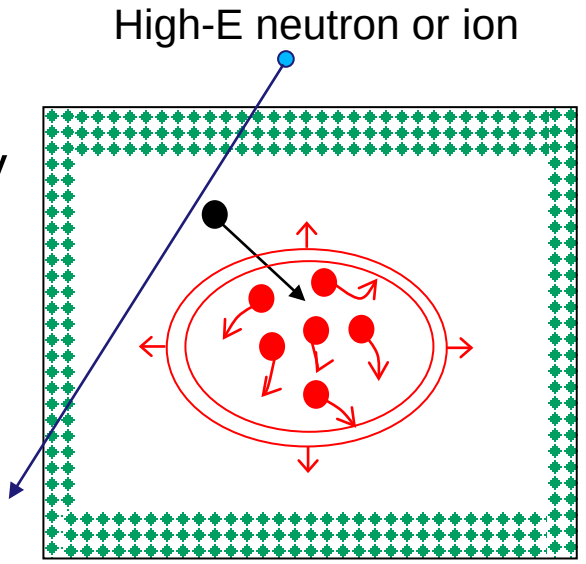
MSc Morten Nagel
Fusion reactor mat'ls

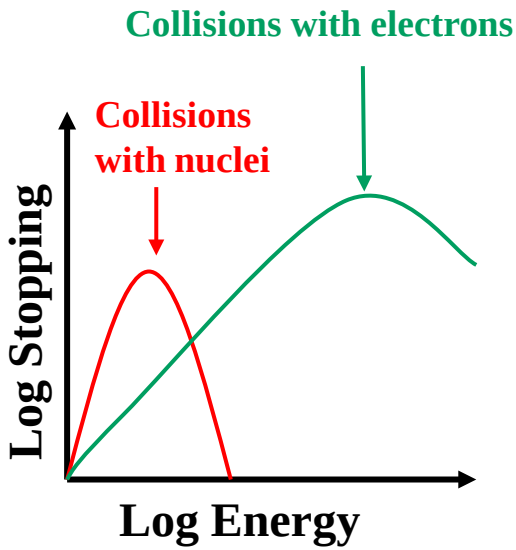


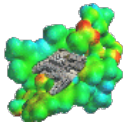
Background

Damage from nuclear energy deposition

- Energetic particles (ions, neutrons, electrons, …) entering a material may with some probability collide with sample ions and give them a recoil energy
- A high-energy ion or recoil moving in a solid will lose energy via electronic stopping (S_e) and collisions with atoms (nuclear stopping S_n)
  - **Electronic stopping does not produce damage except at multi-MeV energies**
  - But always contributes >= 20% to energy loss

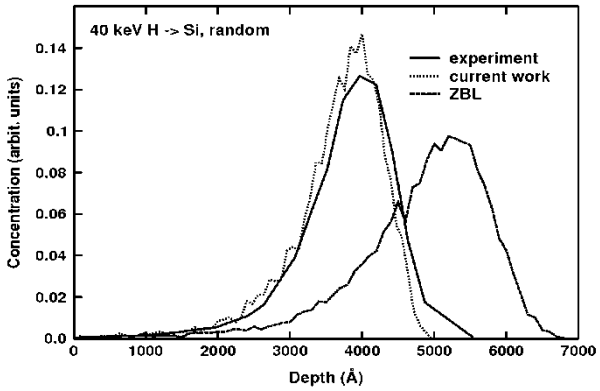


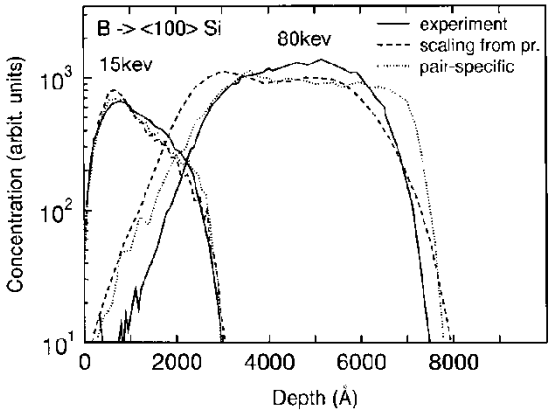




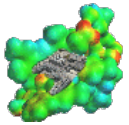
Background
Electronic energy loss

- The energy loss to electronic excitations = electronic stopping can be included as a frictional force in MD
- The nice thing about this is that it **can be compared directly to experiments** via BCA or MD range or ion transmission calculations
- Examples of agreement:





[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 212, 118 (2003)]

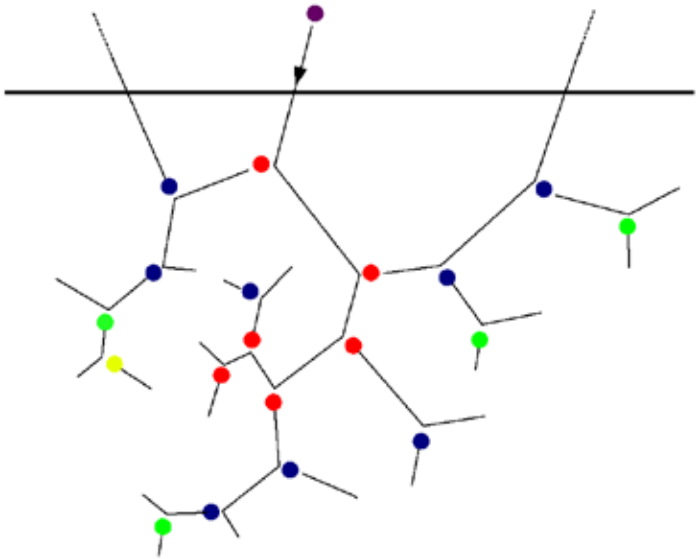


Background

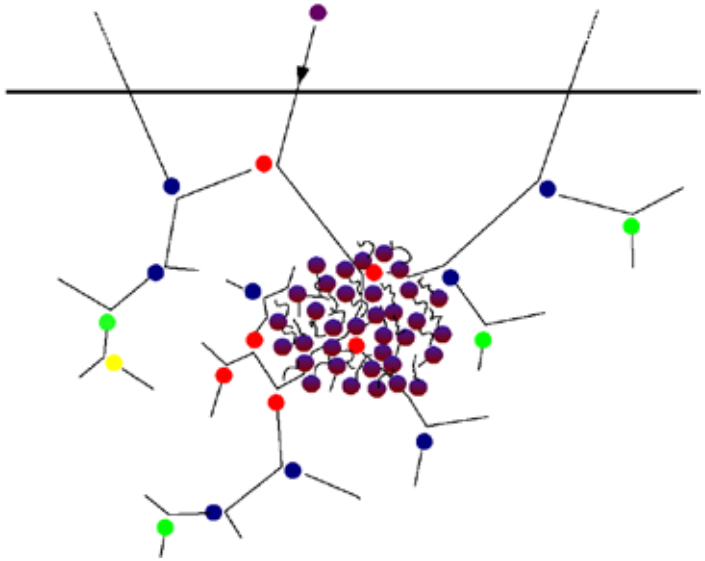
Damage from nuclear energy deposition

- The damage from nuclear energy deposition is produced in linear collision cascades and heat spikes
  - Linear collision cascade = independent binary collisions
  - Heat spike = dense hot region of overlapping damage
    - A.k.a. displacement spike = thermal spike = Brinkman spike

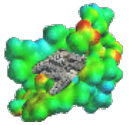
Linear collision cascade



Linear cascade+heat spike in center

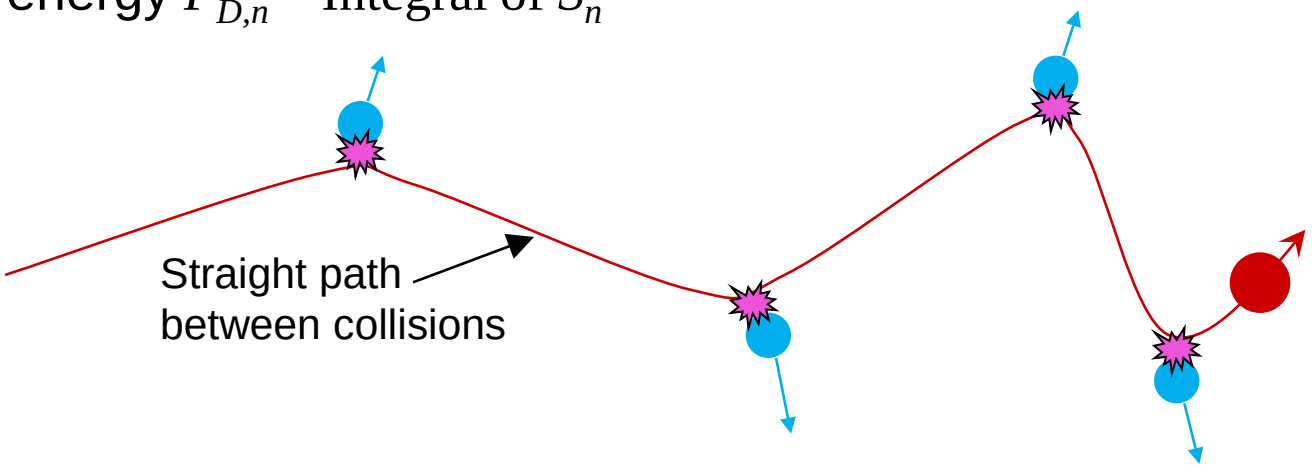


[Pictures: wikipedia by me]

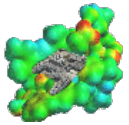


Background
Linear cascade damage

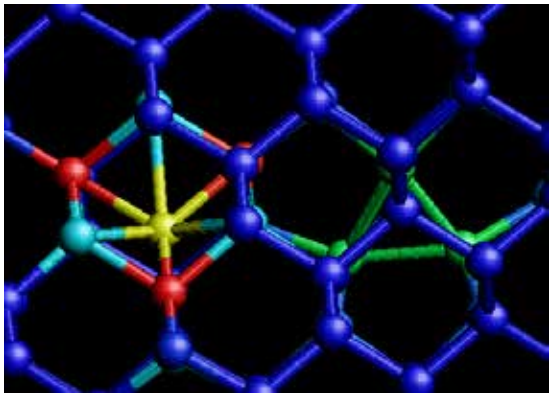
- The damage from linear cascades can be well treated with the **binary collision approximation, BCA.**
- In it one assumes that the ions collide far away from each other that the collision can be considered independent of each = binary
- Leads naturally to prediction damage ∝ nuclear deposited energy $F_{D,n}$ = Integral of S_n



Background
Threshold displacement energy



- The threshold displacement energy is the smallest amount of kinetic energy needed to permanently displace an atom from its lattice site to an interstitial position
  - A vacancy is left behind so a Frenkel pair is produced

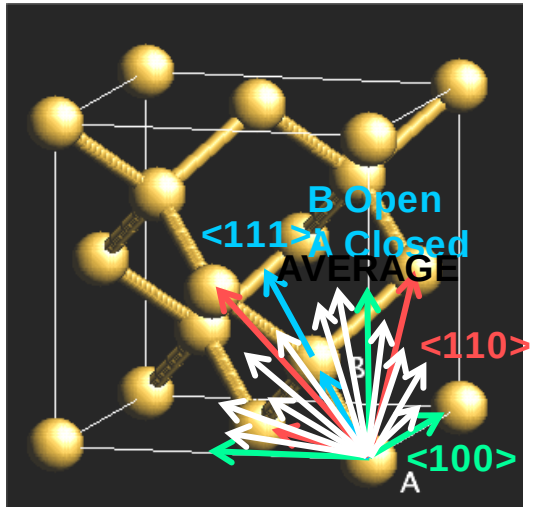


- The full concept is a 3D function:

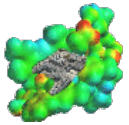
$$p(T,\alpha,\varphi) = 0, \quad T < T_d(\alpha,\varphi)$$
$$= 1, \quad T \geq T_d(\alpha,\varphi)$$

$$T_{d,\text{ave}} = \text{ave}\left(T_d(a,j)\right)$$

$$T_{d,\text{min}} = \min\left(T_d(a,j)\right)$$



I. Introduction

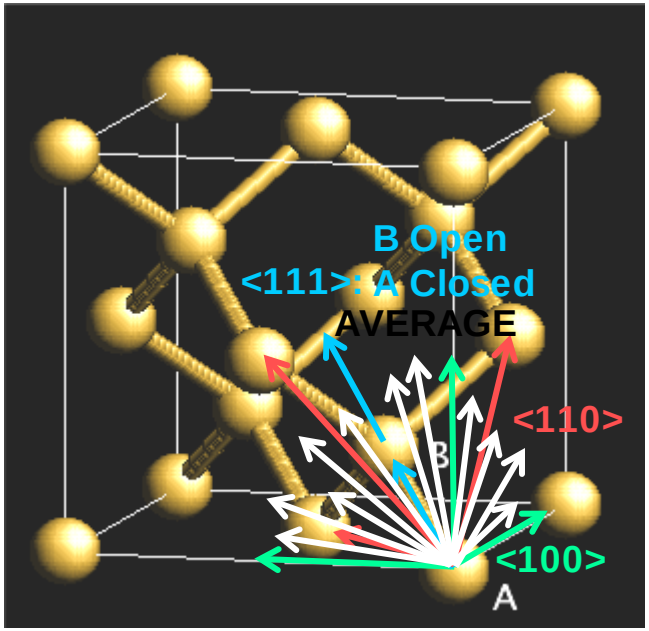


- Minimum vs. average threshold displacement energy:
  - Direction-specific thresholds: $T_{d,100}$, $T_{d,110}$, …
  - Average threshold displacement energy:

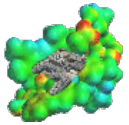
$$T_{d,\mathrm{ave}} = \mathrm{ave}\left(T_d(a,j)\right)$$

  - Minimum threshold displacement energy:

$$T_{d,\mathrm{min}} = \min\left(T_d(a,j)\right)$$



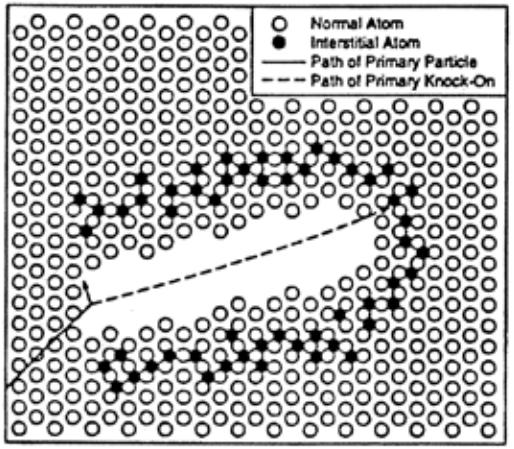
    - Usually in one of principal directions



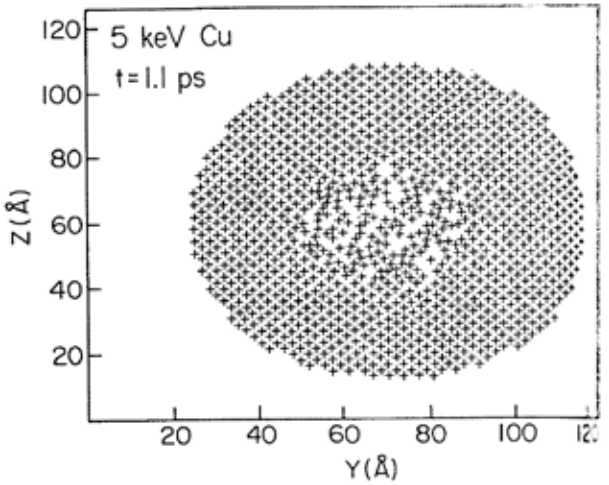
Background
Very brief history of heat spikes

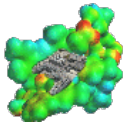
- The exact nature of heat spikes and even whether they exist at all remained unclear for a long time
- In 1987 Diaz de la Rubia, Averback, Benedek and King showed using MD that heat spikes in metals behave much like the prediction in 1954 by Brinkman

Brinkman, 1954

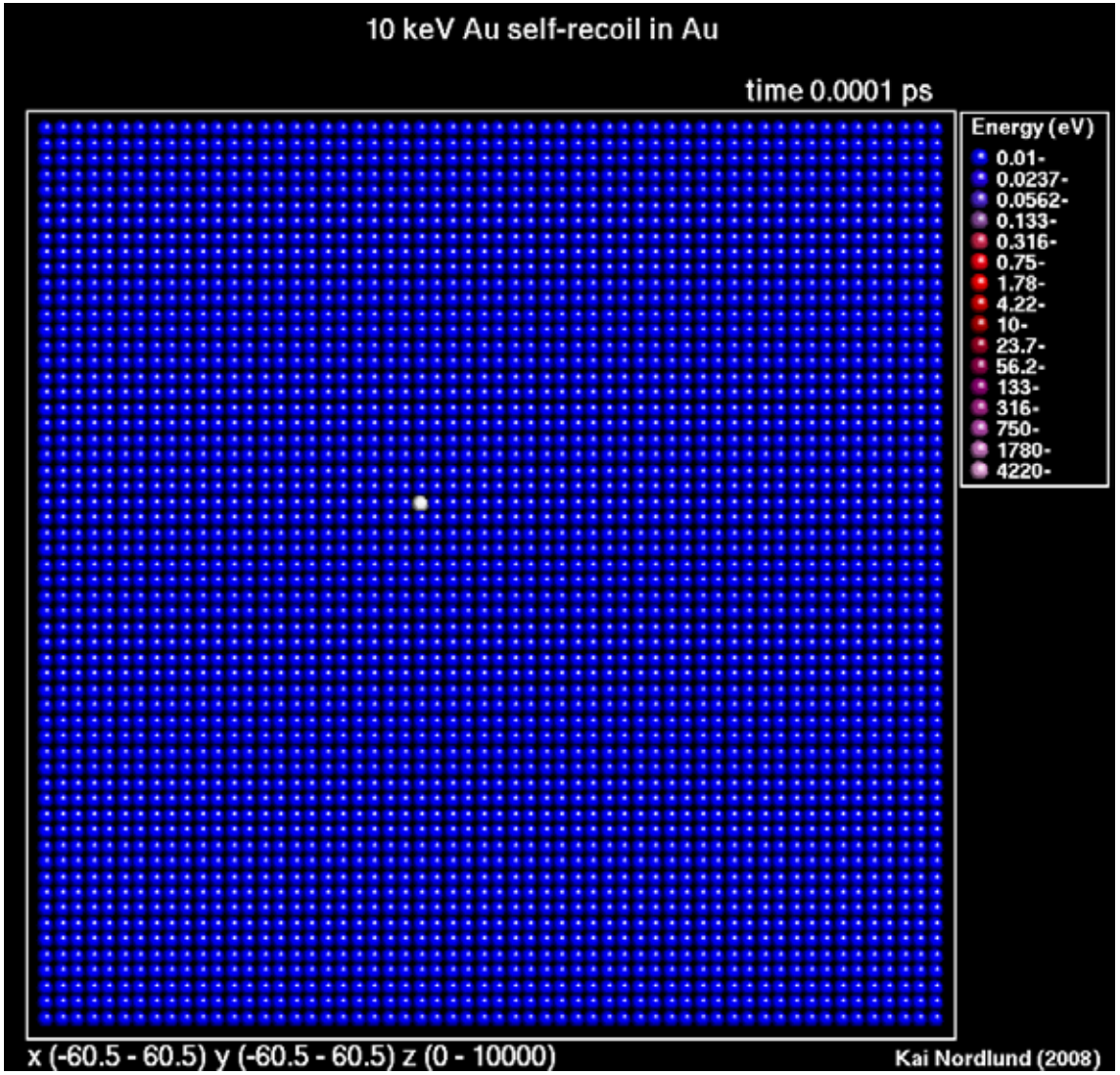


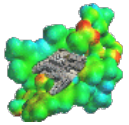
Diaz de la Rubia *et al.* , PRL 1987





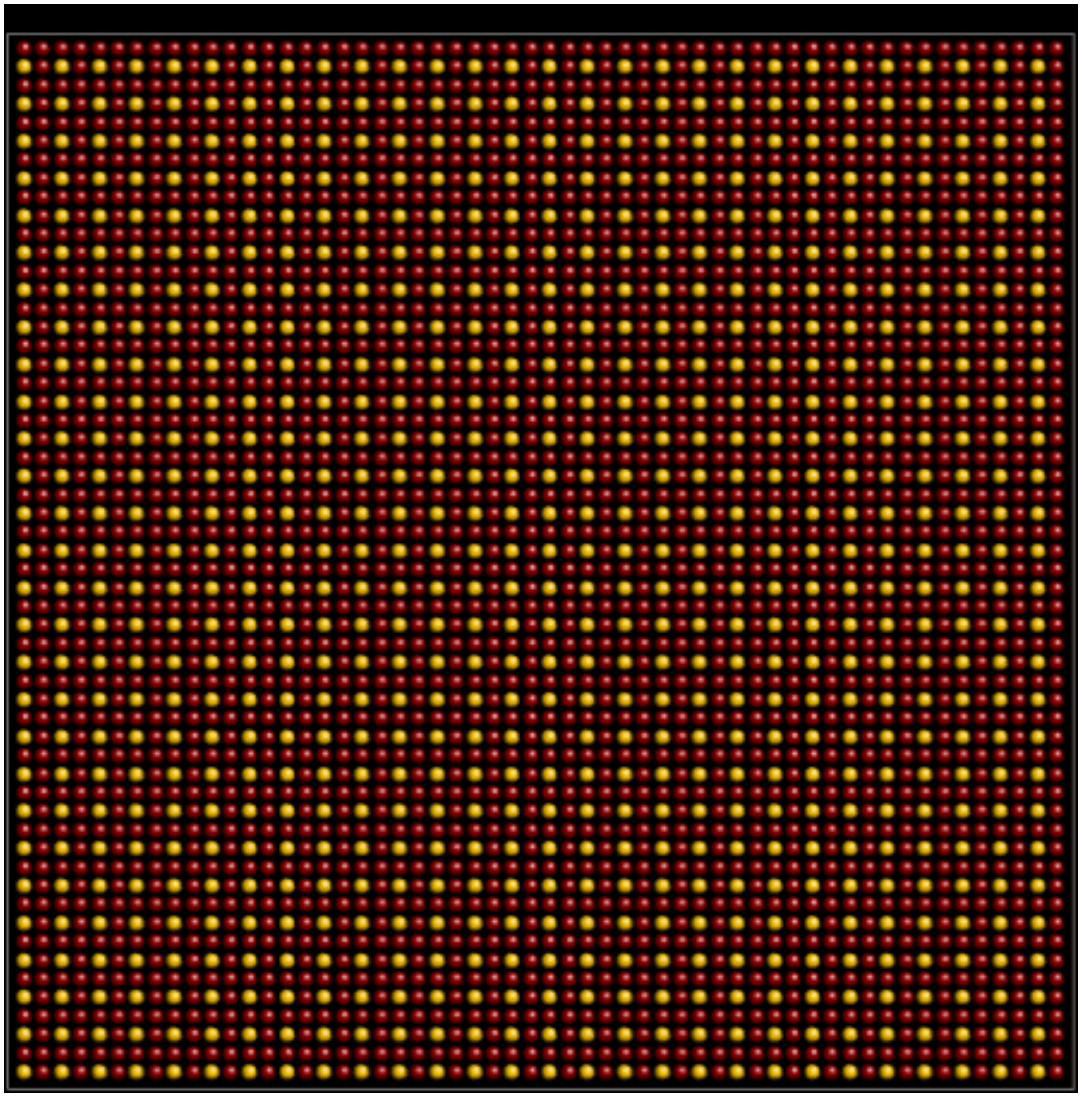
Background
Modern animation: 10 keV cascade in Au

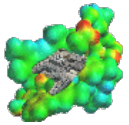




Background

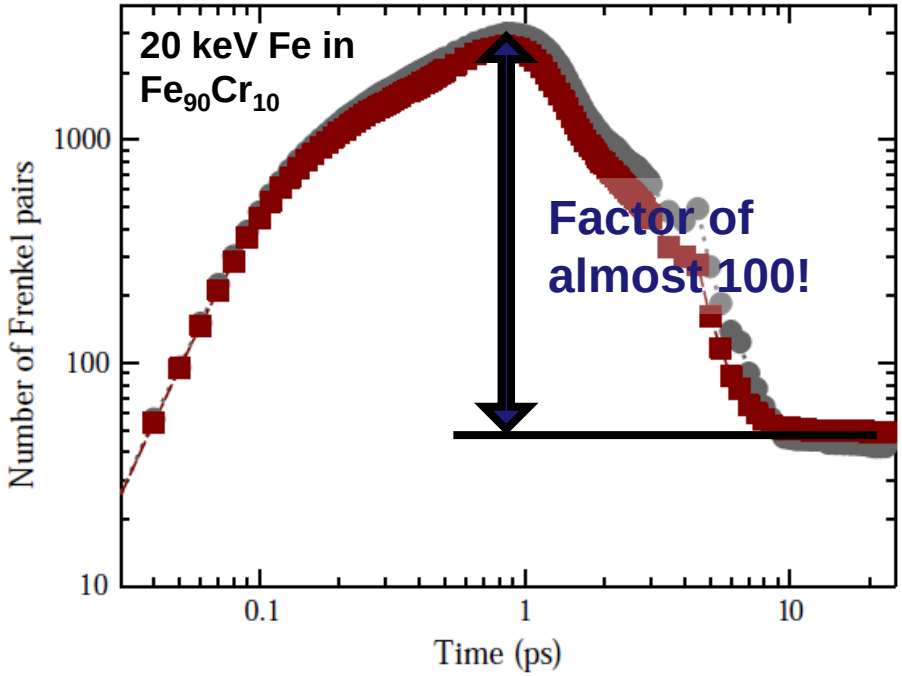
Modern animation: 10 keV cascade in Cu_3Au





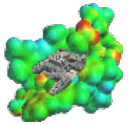
Background
Damage recombination in metals

- As evident from the animations, many many more atoms are displaced than remaining as final damage
  - Reason can be called “athermal in-cascade annealing”
- This has been quantitatively analysed in MD many times

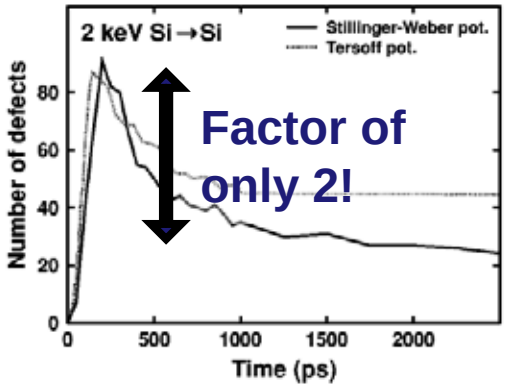


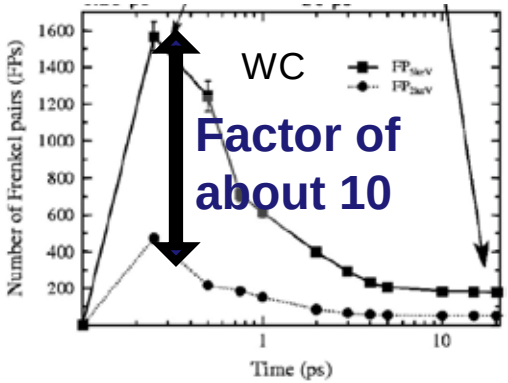
[Vörtler et al, J. Nucl. Mater. 382 (2008) 24–30]

Background
Damage recombination in non-metals



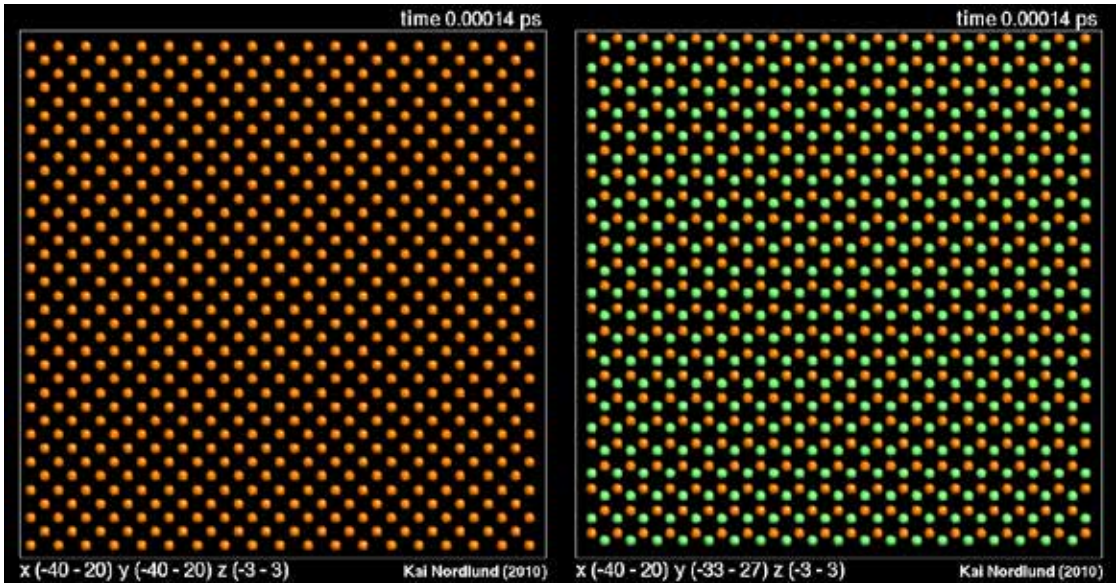
- It is important to realize that non-metals are very different in this respect!
  - In most of them recombination exists but is much weaker

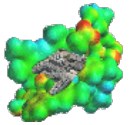




W 5 keV

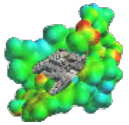
WC 5 keV





Background
Primary damage

- Within the OECD NEA dpa group we consider specifically ***primary damage***
- True primary damage can be defined as the damage produced by an energetic particle in a solid *in the absence of any* ***thermally activated*** *annealing*
- Naturally an experimentally measured damage may be affected by many processes occurring after the production of primary damage:
  - Close-range Frenkel pair recombination
  - Long-range defect migration
  - Extended defect shape reordering
  - Electronic excitations from other ions recombining damage
  - TEM electron beam recombination of damage
  - Damage recombination at a nearby surface (image interaction)
  - ….



Background
Primary damage and the dpa concept

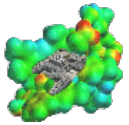
- The Binary collision / linear cascade model leads naturally to a model which says primary damage increases linearly with nuclear deposited energy E_d.
- The basic displacement per atom (dpa) concept is the Kinchin-Pease equation, in the NRT form:

$$N_d(T_d) = \begin{bmatrix} 0 & T_d < E_d \\ 1 & E_d \le T_d < 2\,E_d/\beta \\ \dfrac{\beta T_d}{2E_d} & 2E_d/\beta \le T_d < \infty \end{bmatrix}$$

$b = 0.8$ from old BCA simulations

Designation: E 693 – 01 (Reapproved 2007)

Standard Practice for Characterizing Neutron Exposures in Iron and Low Alloy Steels in Terms of Displacements Per Atom (DPA), E 706(ID)[1]



Background

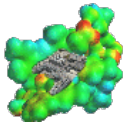
Dpa in metals does not correspond to anything!

- The final damage is ~ 2 - 10 times smaller than the dpa number
- The real number of displaced atoms that have moved from their lattice sites can be ~ 10-100 times higher
  - Ion beam mixing experiments show this!
- Example: Self-recoils in Cu:

Recoil energy (keV)	# Frenkel pairs*	# dpa from NRT (E_d = 25 eV)	# Displaced atoms*
0.4	1.8	6	28
2	6.4	26	370
10	15	126	3000

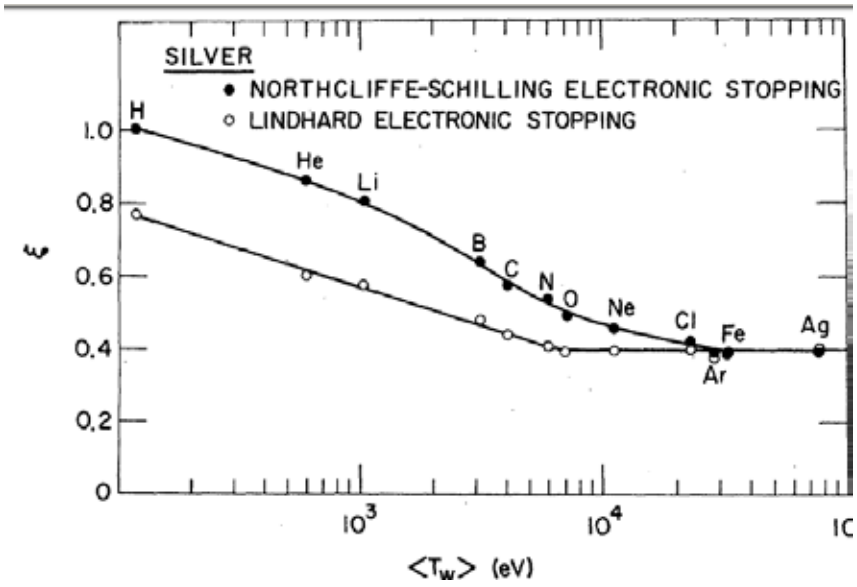
*[MD data from: Nordlund et al, PRB 57 (1998) 7556]

Background
Damage efficiency



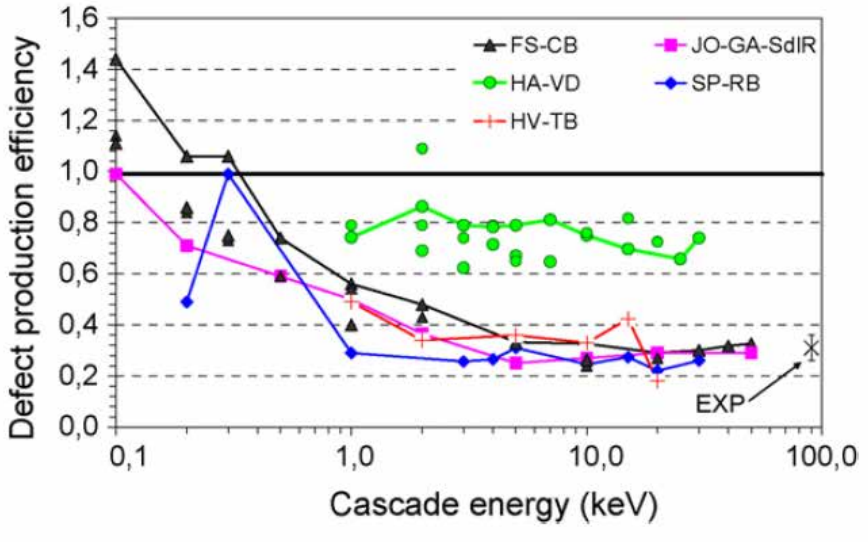
- Damage efficiency ξ : True primary damage N_{FP} = ξ x NRT
- ξ is well known to deviate strongly from 1.0 !

Experiment

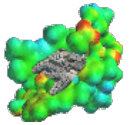


[Averback et al, PRB 18 (1978) 4156]

Simulations



[L. Malerba, J. Nucl. Mater. 351 (2006) 28]



Background
Corrected dpa's?

In view of the fact that the dpa is widely known to be misleading, in the June 2011 meeting we decided to ***attempt*** to device a "corrected dpa", a new function for the factor ξ(E).

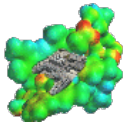
… while acknowledging that original dpa concept is good for relative comparison and as an exposure parameter!

In the September 2011 meeting, we decided to make 2 corrections:

- one for damage
- other one (on initiative by Steve Zinkle) for atom mixing

We also decided to name these:

- athermal recombination-corrected dpa **= arc-dpa**
- athermal mixing-corrected dpa = **amc-dpa**

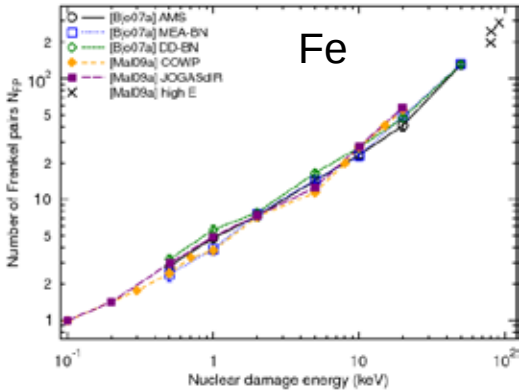


Athermal-recombination corrected dpa
Functional form?

- Lots of groups have found independently that the damage production data can be well fit by a function of the form

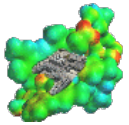
$$N_{FP} = E^{x}$$

with x ~ 0.8



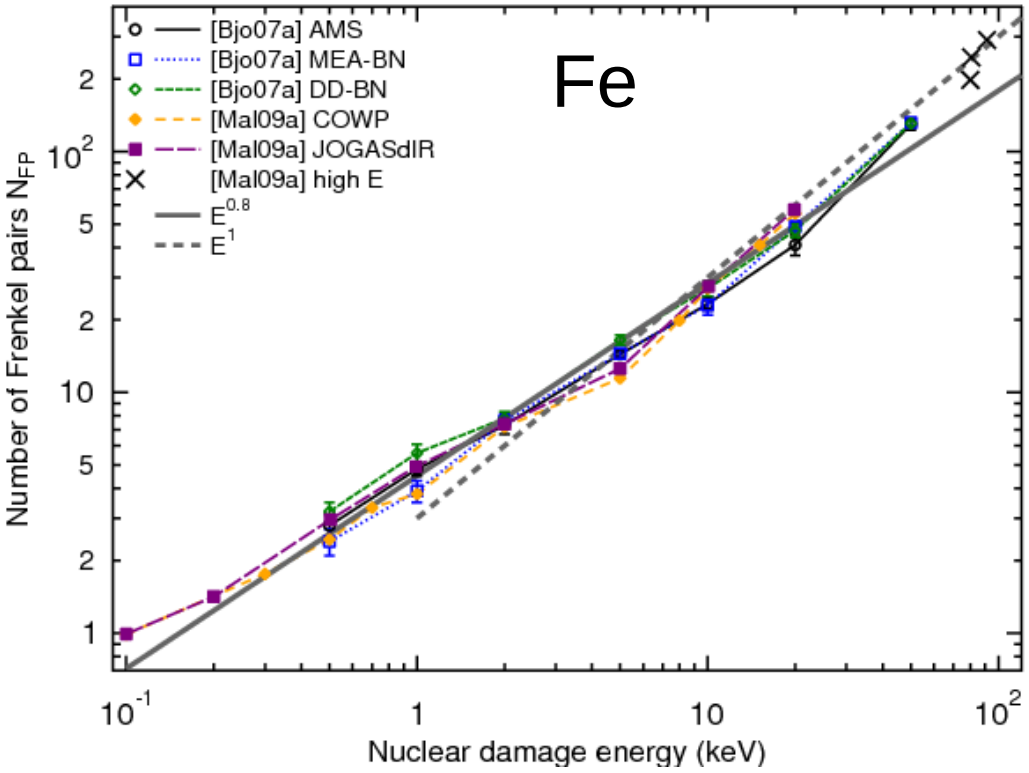
- However, this cannot be the whole truth: for some recoil energy, cascades are fully split into subcascades and the increase must become linear

$$N_{FP} = E^{1}$$



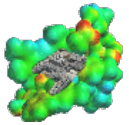
Athermal-recombination corrected dpa
Nonlinear and linear parts

- This transition starts to be visible in data simulated up to >~ 20 keV:



Nota bene: The data sets selected here are not important *per se*, just something used in my testing. I expect a more careful selection for the final fits

[Data sets and notation selected from:
Bjo07a: Björkas and Nordlund, NIM B 259 (2007) 853
Mal09a: Malerba review, JNM 406 (2010) 19]



Athermal-recombination corrected dpa
Compound power law fit

- The function $N_{FP}(E)$ to be fit has thus to fulfill at least the limit $N_{FP}(E) \rightarrow aE^1$ when $E \rightarrow \infty$ but cannot be just linear based on the previous results of $E^{0.8}$ at low E
- A simple function that obviously fulfills this criterion:

$$N_{FP} = a' E^{b+1} + c' E^1$$

where a, b and c are fitting constants

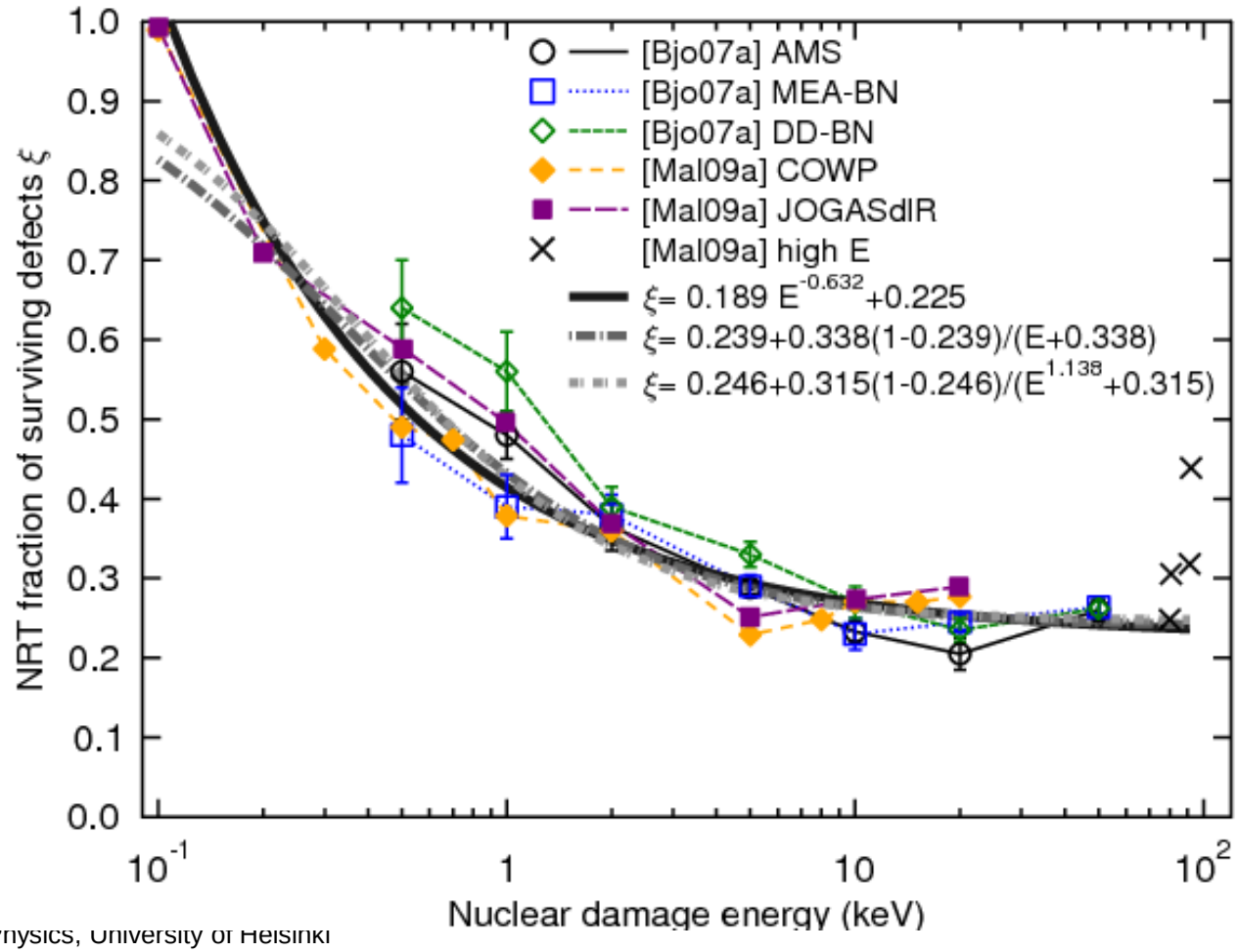
- The corresponding damage efficiency function (above $2E_d$):

$$\chi(E) = \frac{N_{FP}}{N_{NRT}} = \frac{a' E^{b+1} + c' E^1}{0.8E/(2E_d)} = \frac{a' E^b + c'}{0.8/(2E_d)} = aE^b + c$$

- From this form one sees that the constant c' corresponds to the saturation level at high E, and hence c' ≈ 0.3

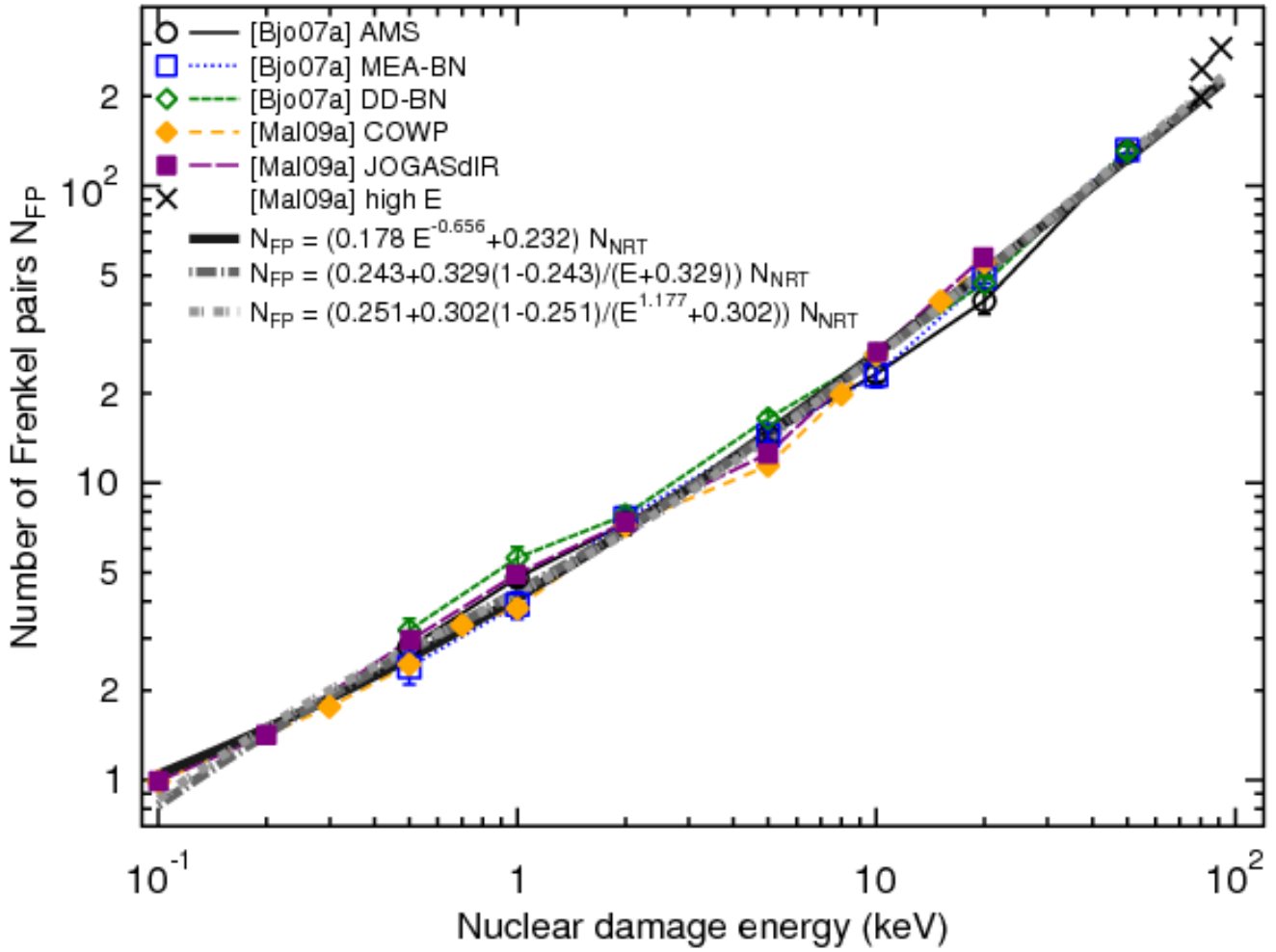
Athermal-recombination corrected dpa
Results of test fits

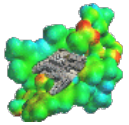
- Test fit results of selected data to the 3 forms for $\xi(E)$:



Athermal-recombination corrected dpa
Results of test fits

- Test fit results of selected data to the 3 forms for $N_{FP}(E)$





Athermal-recombination corrected dpa
Modified form with fixed minimum

- At the September meeting, **Roger Webb suggested to adjust the function such that it starts from exactly 1.0** at the threshold
- I have now done such a revised form, but found it works better if it starts from $2E_d/b$ instead of E_d
- This is easily achievable by solving

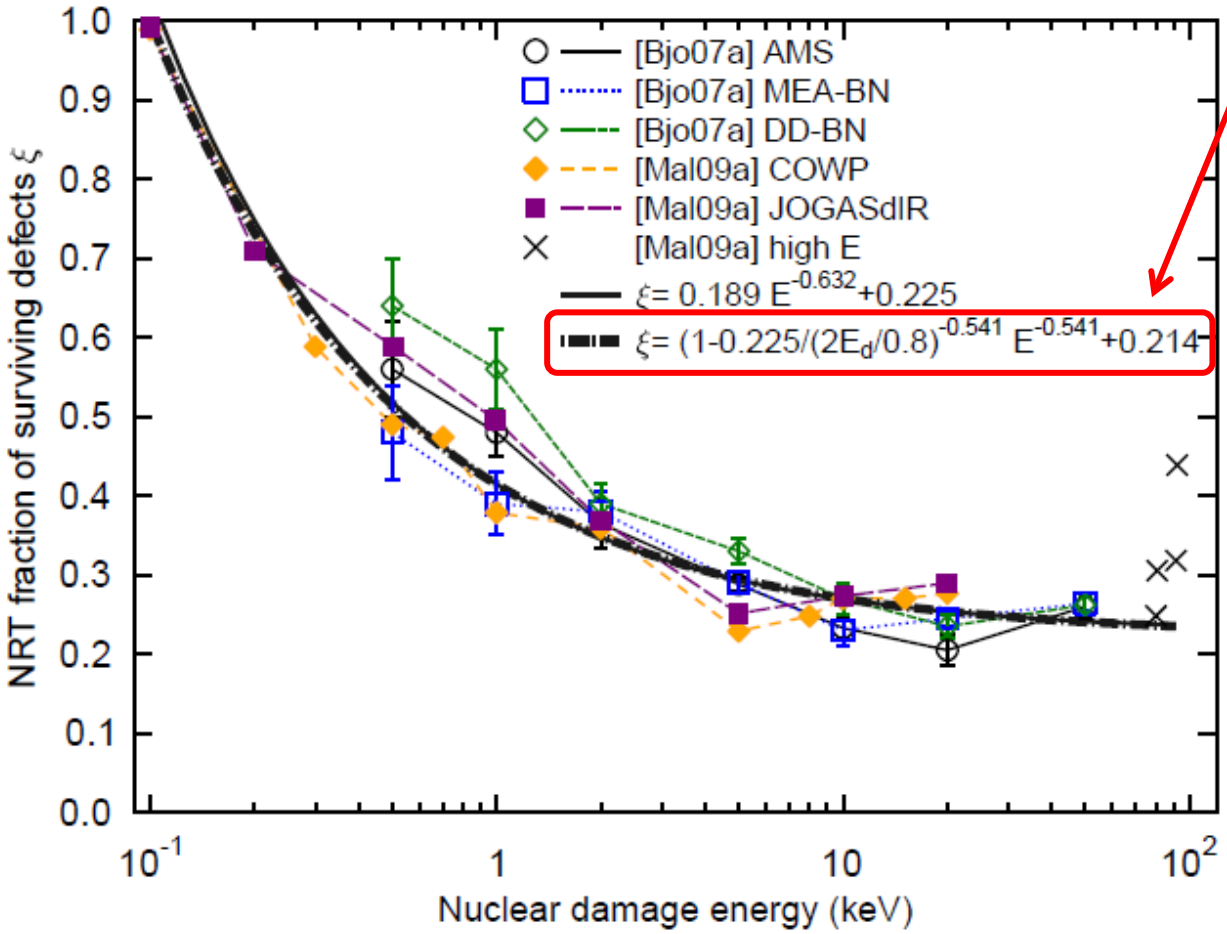
$$\xi(2E_d/0.8) = a(2E_d/0.8)^b + c = 1$$

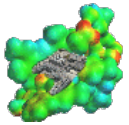
for the constant a, which then fixes it and gives the form

$$\xi(E) = \frac{1 - c}{(2E_d/0.8)^b} E^b + c$$

Athermal-recombination corrected dpa
Modified form with fixed minimum

- I redid the fit to the Fe data with this data, and obtained:



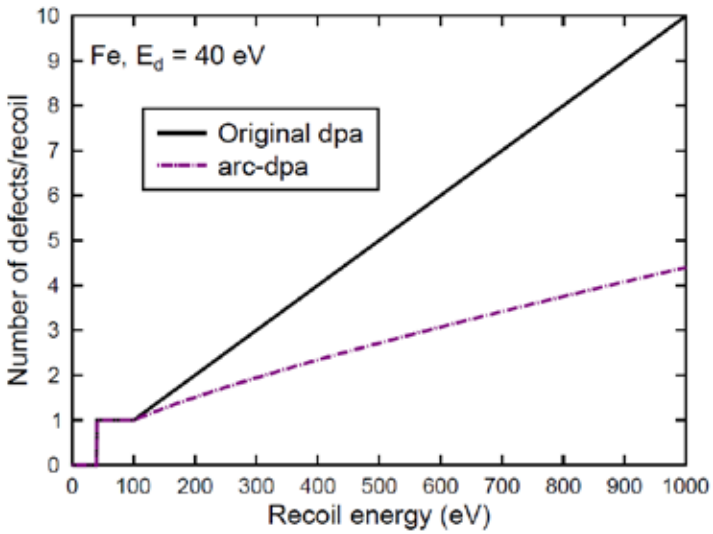


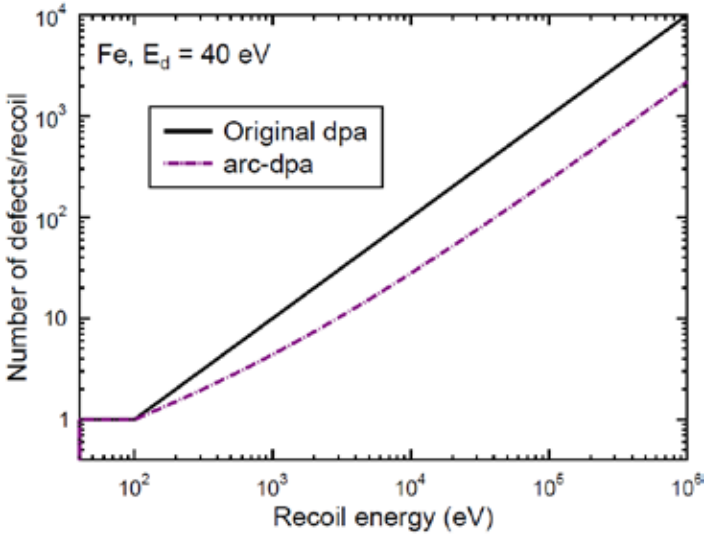
Athermal-recombination corrected dpa
Modified form

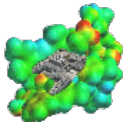
- The new fit is clearly of comparable quality, and has the advantage that there is only 2 adjustable parameters left
- ***The OECD group will proceed with this form:***

$$x(E) = \frac{1 - c}{(2E_d / 0.8)^b} E^b + c$$

- Illustration of functional form on lin-lin and log-log plots:



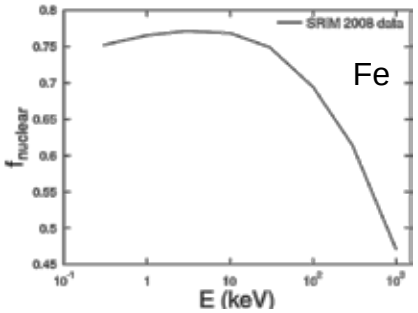




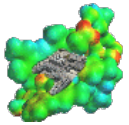
Athermal-recombination corrected dpa
Important thing to remember

- An important detail to remember is that the E used in these fits to MD data is the damage energy for recoils ***not*** affected by electronic stopping
  - … because people simulating cascades in Fe have historically neglected electronic stopping (contrary to many other materials where it was included)
    - E.g. if E_{MD} = 10 keV and 70% of real PKA energy goes to nuclear stopping, $\mathrm{E_{MD}}$ corresponds to E_{PKA}=10/0.7 = 14.3 keV
- Hence for correspondence to experiments, one has to correct

$$\mathrm{E}_{\text{real PKA}} = \frac{E_{MD}}{f_{nuclear}(\mathrm{E}_{\text{real PKA}})}$$



where $f_{nuclear}$ is the fraction of E given to nuclear stopping



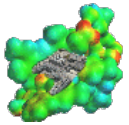
Athermal-recombination corrected dpa
Sketch of final form

- The final result **for arc-dpa** from the OECD group is:

$$N_d(E) = \begin{cases} 0 & E < E_d \\ 1 & E_d < E < 2E_d / 0.8 \\ \dfrac{0.8E}{2E_d}\,\xi(E) & 2E_d / 0.8 < E < \infty \end{cases}$$

where $\xi(E)$ is given by

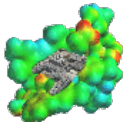
$$\xi(E) = \frac{1 - c}{(2E_d / 0.8)^b} E^b + c$$



Athermal-recombination corrected dpa
Caveats

- There are numerous caveats remaining even if taking into the use of the arc-dpa:
  - **Defect clustering not accounted for!**
    - We recently showed using MD+KMC that large damage clusters may have a major role on long-term evolution

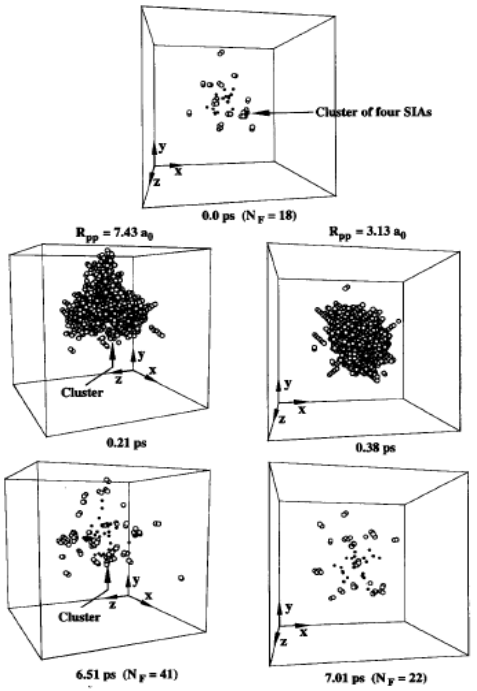
      [C. Björkas, K. Nordlund, and M. J. Caturla Phys. Rev. B 85, 024105 (2012)]
  - Thermal recombination of damage
  - Reduction of damage at high ambient temperatures
- But further developments of the model might be able to address some of these issues – after more data is available
- In any case we consider the “arc-dpa” to be a step forward!

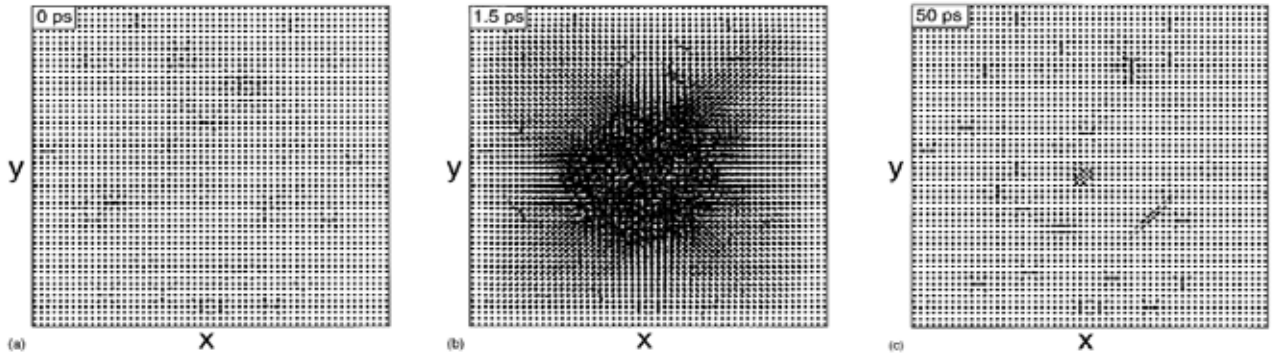


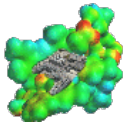
Athermal-recombination corrected dpa

Longer term effects: damage saturates

- In 1996 Gao and Bacon showed that one cascade overlapping the damage of a previous one recombines some of the damage
- In 1997 Nordlund and Averback showed that pre-existing interstitials are recombined if their concentration exceeds ~ 1%
- This is beyond any simple dpa equation





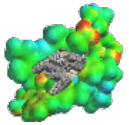


Athermal-mixing corrected dpa, amc-dpa
Background on mixing

- Steve Zinkle [ORNL] pointed out that also a mixing-corrected dpa could be needed
- Ion beam mixing is a well known effect, and important e.g. for bilayer mixing, precipitate dissolution by irradiation, radiation-enhanced diffusion etc.
- It can be experimentally measured with marker layer experiments, and this has been done in many materials
- For a review see e.g.:

  [Paine and Averback, NIM B 7/8 (1985) 666]

Athermal-mixing corrected dpa
Background

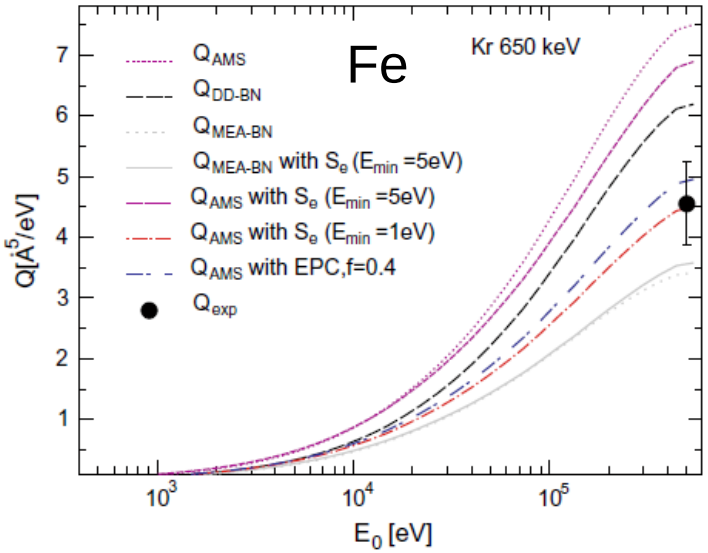


- Experimental ion beam mixing results can be well reproduced by MD simulations
  - At least if interatomic potential has good melting point and electronic stopping treated suitably…

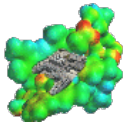
TABLE I. Simulated (sim.) and measured (exp.) values for the mixing efficiency Q.

Material	Beam	Q_{sim} (Å^5/eV)	Q_{exp} (Å^5/eV)
Ni	600 keV Kr	5.1±0.4	4.8±0.5[a]
Ni	650 keV Kr	5.2±0.4	5.0±0.7[b]
Pd	600 keV Kr	9.8±0.8	8.4±0.8[a]
Pd	400 keV Kr	9.5±0.8	9±1[c]
Pt	1 MeV Kr	14±1	14±2[b]

[K. Nordlund, L. Wei, Y. Zhong, and R. S. Averback, Phys. Rev. B (Rapid Comm.) 57, 13965 (1998)]

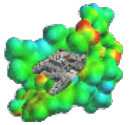


[C. Björkas and K. Nordlund, Nucl. Instr. Meth. Phys. Res. B 267, 1830 (2009)]



Athermal-mixing corrected dpa
Reanalysis of old data

- The data we simulated for Ni, Pd and Pt is still available, and for the current purpose I now reanalyzed it
- Due to heat spike effects, the number of displaced atoms for mixing is very large
- The "real" number of displaced atoms for mixing can be written as $N_{mix} = \xi_{\mathrm{mix}}(\mathrm{E})\ \mathrm{x}\ \mathrm{NRT}$ where $\xi_{\mathrm{mix}}(\mathrm{E})$ is obviously different from the previous $\xi(\mathrm{E}) = \xi_{\mathrm{damage}}(\mathrm{E})$
- Since $\xi_{\mathrm{mix}}(\mathrm{E}) > 1$, the same functional form as before cannot be used
- However, already in the 1998 PRB paper we had devised another form for the square of atom displacement distances, and I now found that it seems to work well also for the number of displaced atoms



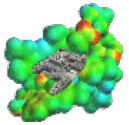
Athermal-mixing corrected dpa
Functional form for fitting mixing data

- The basic form is

$$x_{mix}(E) = a\frac{E^c}{b^c + E^c}$$

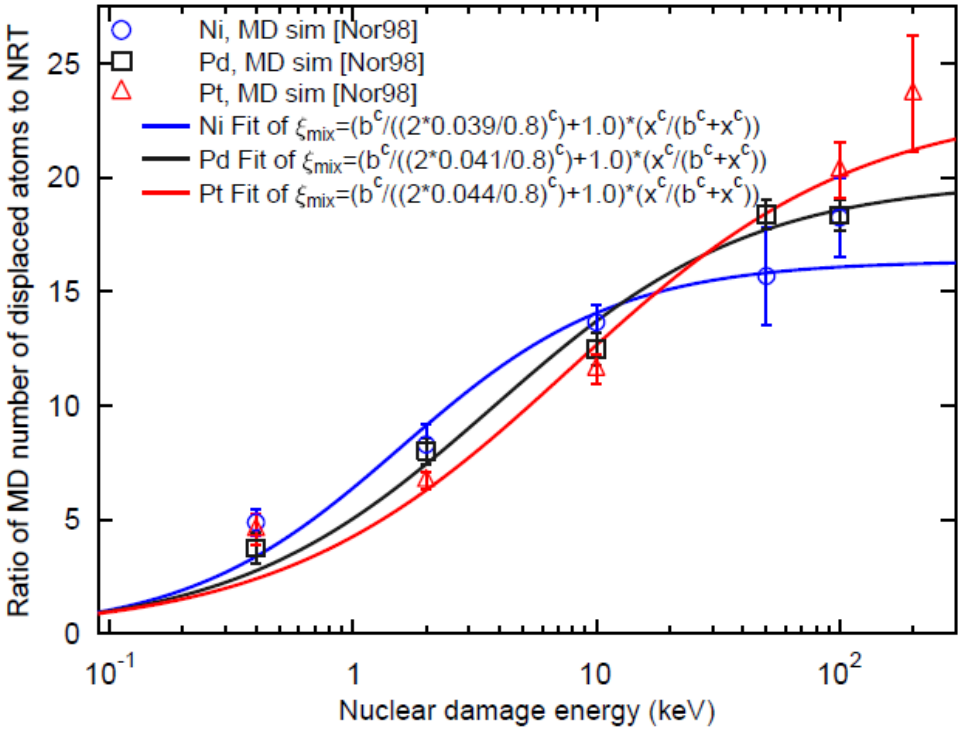
- This has the correct limit of becoming constant for large E
- Again we can set the criterion $x_{\mathrm{mix}}(2E_d/b) = 1$ which allows to fix a
- Thus one arrives at

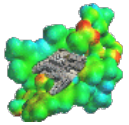
$$x_{\mathrm{mix}}(E) = \left(\frac{b^c}{(2E_d/0.8)^c} + 1\right)\frac{E^c}{b^c + E^c}$$



Athermal-mixing corrected dpa
First fits to mixing data

- This I fitted to the available data for number of displaced atoms(E) for Ni, Pd, Pt / NRT
  - Unfortunately the data was scarce and not fully converged in the high E limit, but good fits were obtained in all cases!

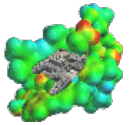


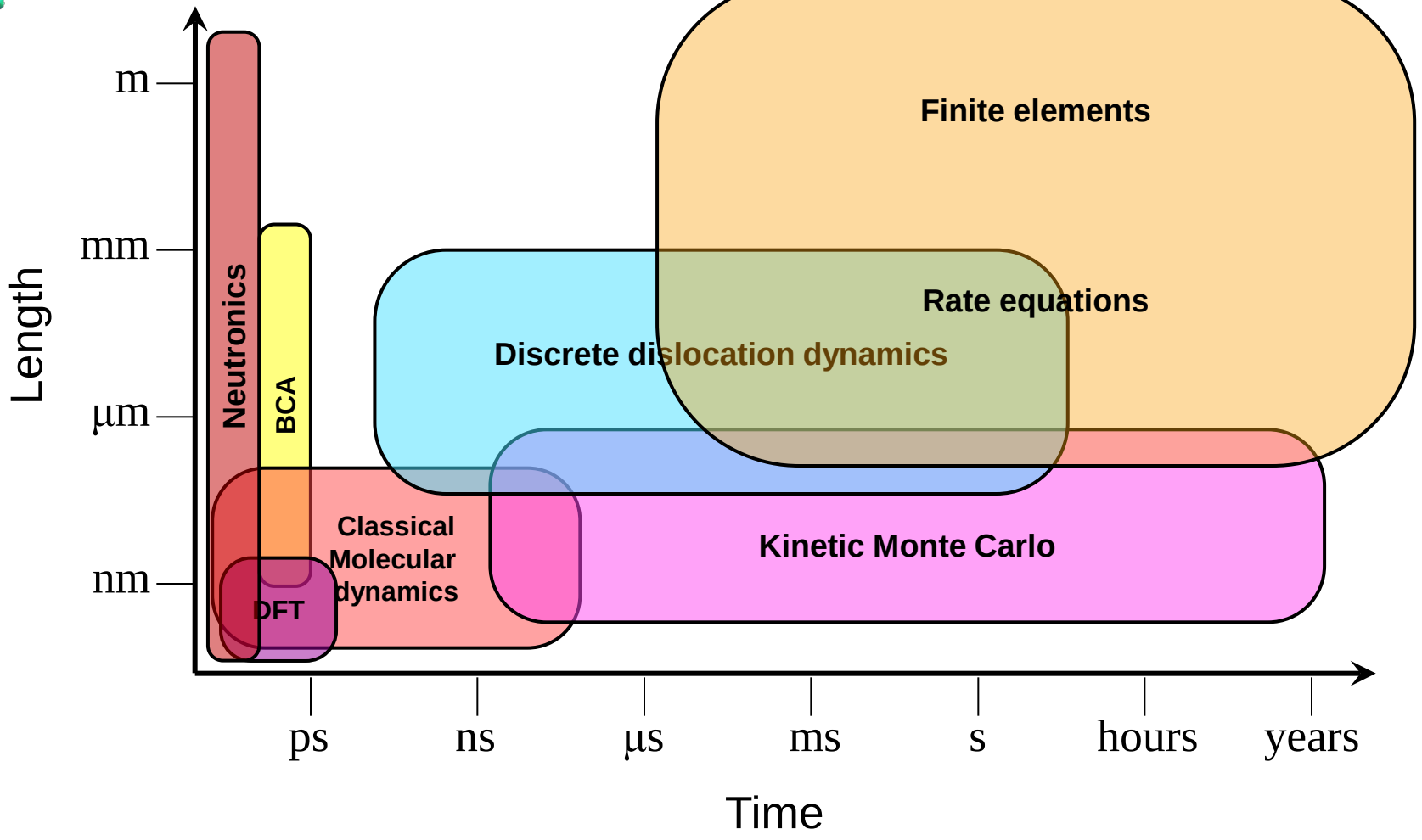


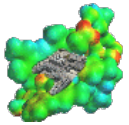
Athermal-mixing corrected dpa
Comments on mixing fit

- Values of the threshold energy were taken from literature (Landolt-Börnstein tables), $E_{d,\mathrm{Ni}}$ = 39 eV, $E_{d,\mathrm{Pd}}$ = 41 eV, $E_{d,\mathrm{Pt}}$ = 44 eV,
- The functional form for mixing also has the advantage that the b fitting parameter has a physical interpretation:
  - It gives the point where the transition from an power law behaviour E^c starts to transform into a linear behaviour corresponding to cascades being split to subcascades
  - I.e. it is a measure of the subcascade threshold energy
- We need more data to do a more reliable fit, but are now in the process of collecting it (more energies, up to 200 keV, more statistics)
  - Same data will also give damage values for $\xi_{\mathrm{damage}}(\mathrm{E})$ fit

Instead of any dpa, better would be:
Full multiscale modelling!?







Future; Relation to this IAEA activity?

- **Report in writing, about ½ finished**
  - Delayed mainly due to chairman (me) being busy
  - Also additional data collected
  - Will also deal with all other inorganic materials: ionics, semiconductors, carbon-based materials, …
- **My best idea is that the OECD NEA group** needs to finish its work by making a first version of the arc-dpa and amc-dpa concepts and write it up as an OECD NEA report and/or publication
- **Us, the IAEA future CRP, can then proceed from this:**
  - Critical evaluation of new forms
  - Data collection for new improved fits
  - Formulating ways of incorporation into neutronics software!
  - Including full multiscale modelling: Neutronics -> MD -> KMC