HELSINGIN YLIOPISTO
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UNIVERSITY OF HELSINKI

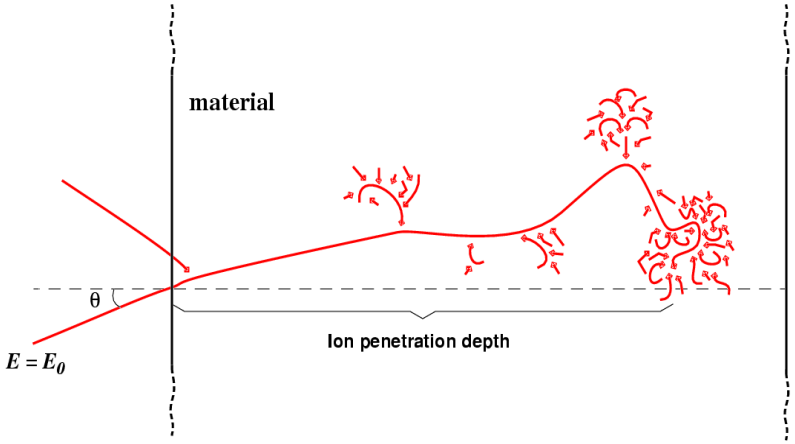
Radiation Damage in Materials

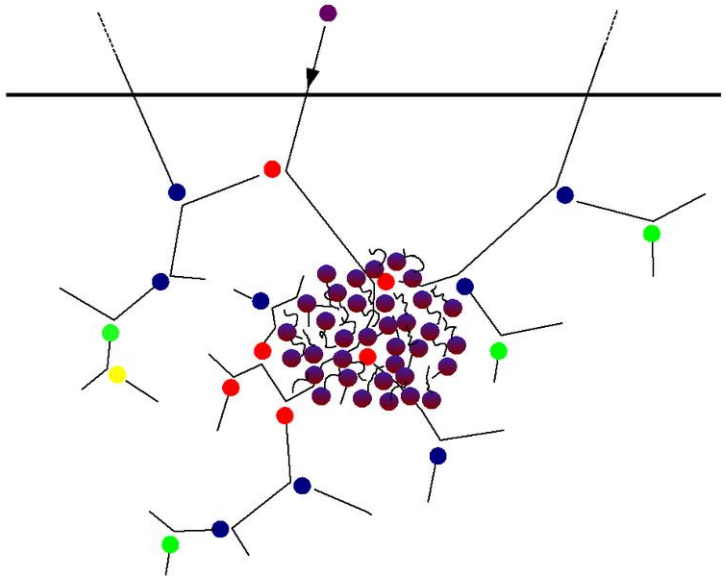
5. Primary damage production from many-body nuclear collisions

Nota bene: **if you read these notes on your own, you cannot see the many animations. However, all of them are available in the web in http://www.acclab.helsinki.fi/~knordlun/rad_dam_course/anims/**

5.1. Many-body collisions

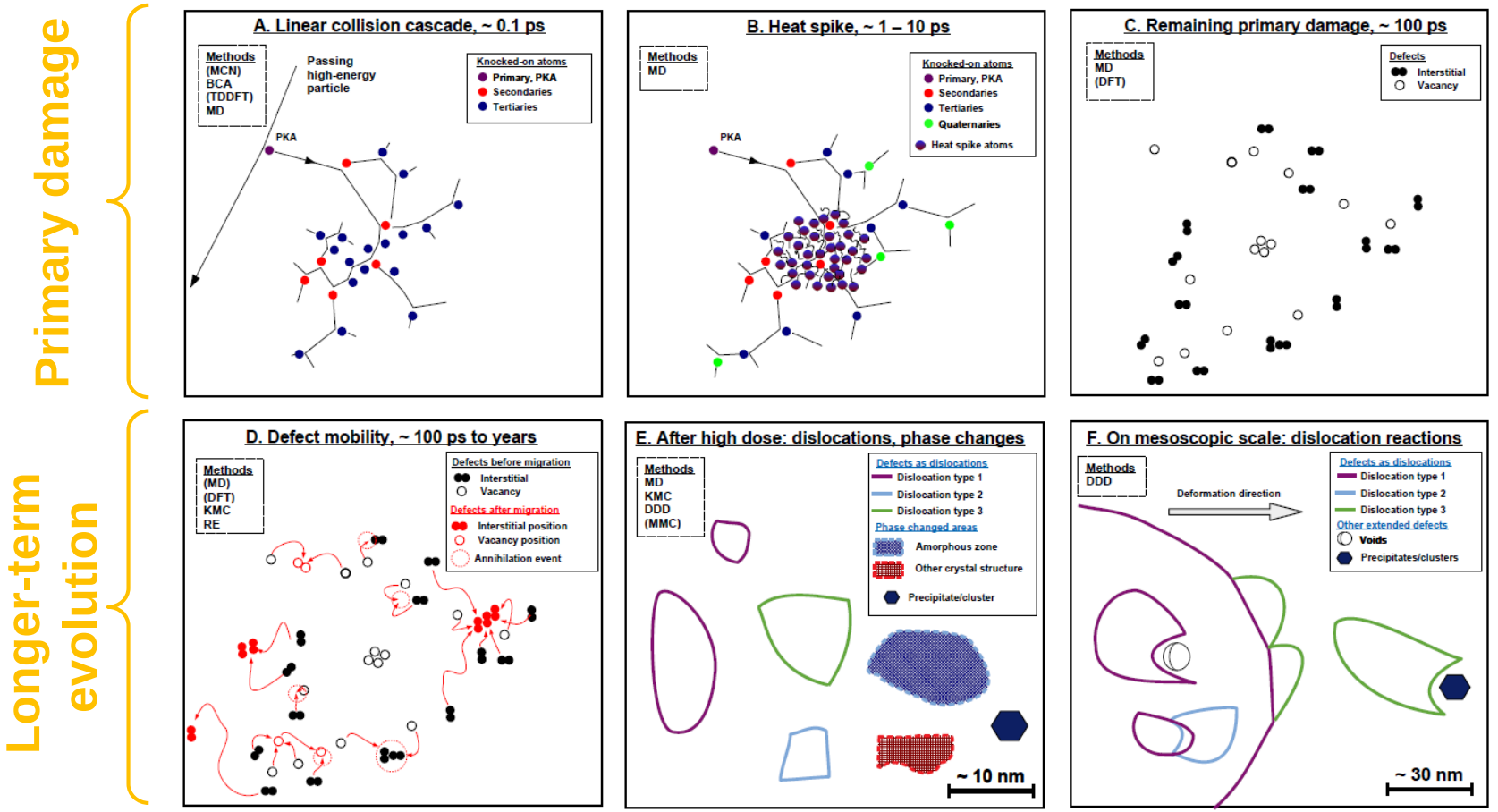
- The final stage of irradiation almost always includes many-body collisions between atoms
- Due to both nuclear and electronic stopping, the high-energy ions and recoils slow down and eventually reach thermal velocities (< 1 eV)
- At this stage they collide with several atoms at the same time = many-body collisions





From initial recoil to final damage

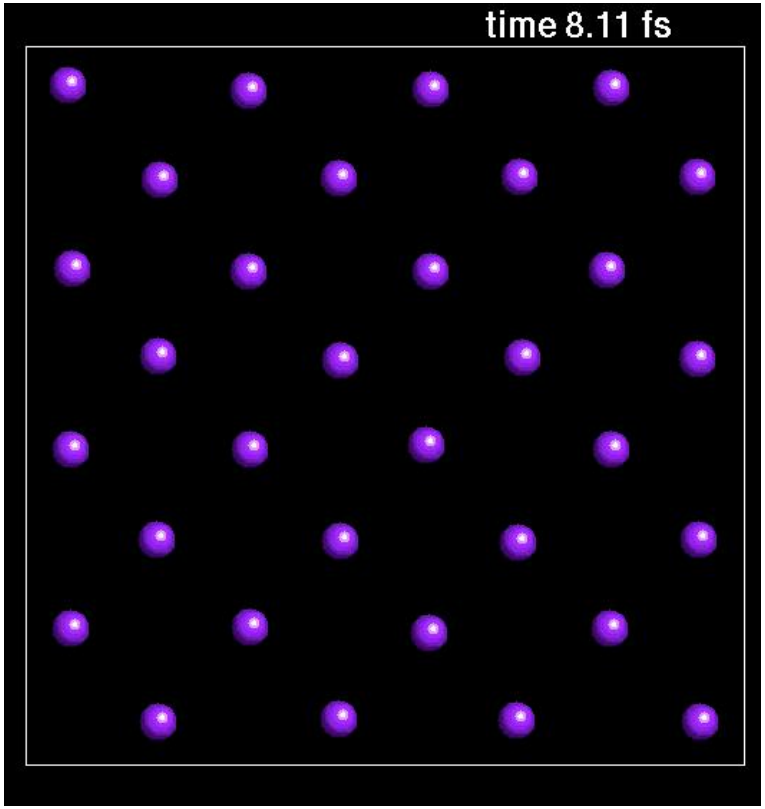
- Schematic overview of progress of damage production with time and dose:



[Figure adapted from: K. Nordlund, http://www.acclab.helsinki.fi/~knordlun/pub/Nor18b.pdf J. Nucl. Mater. 520, 273 (2019)]

5.2. How to simulate the many-body collisions: The molecular dynamics method

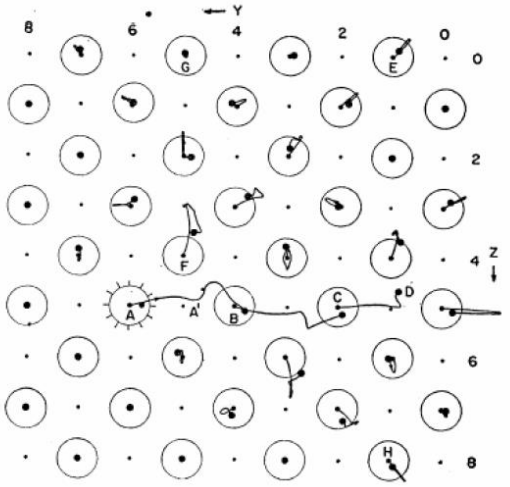
- The molecular dynamics (**molekyldynamik / molekyylidynamiikka**) (MD) simulation method is ideally suited for simulating many-body collisions
- The MD method is normally a standard tool in materials physics, chemistry and biochemistry for simulating atom motion
- Very basic example: motion of atoms in Cu at 600 K



[Animation: cutemp.mpg]

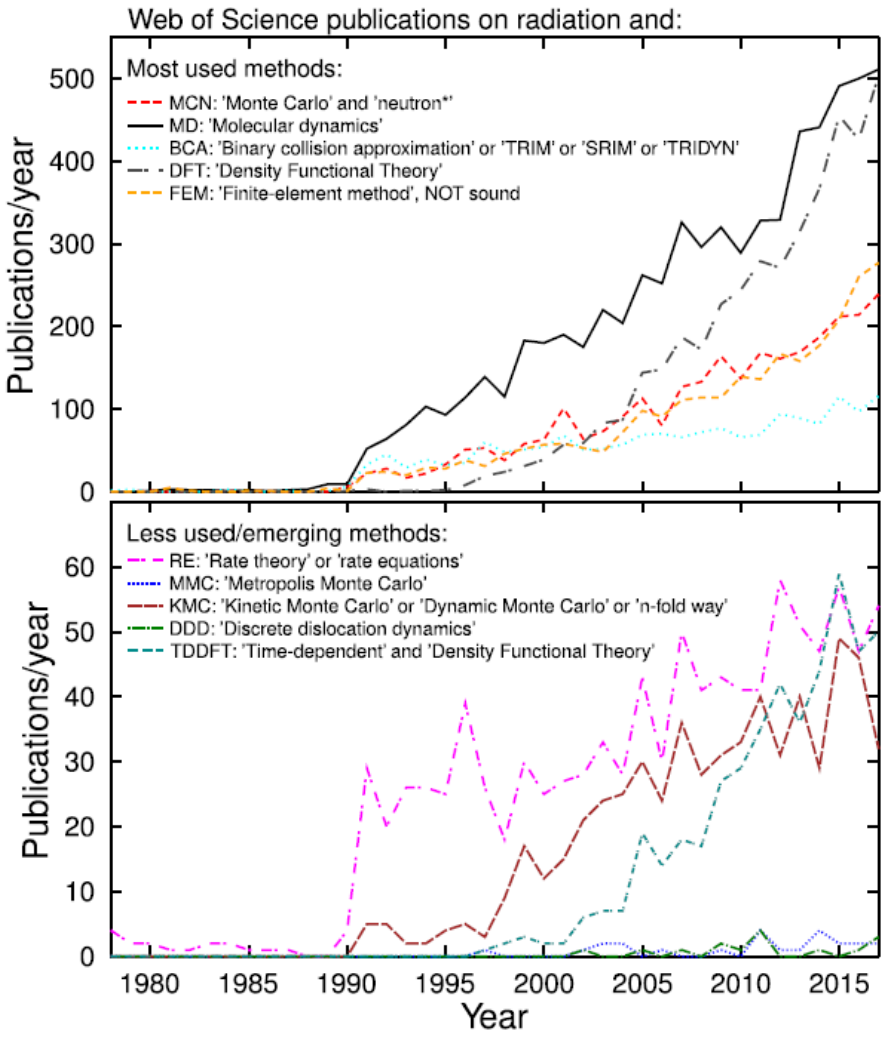
History of molecular dynamics

- MD is solving the Newton's (or Lagrange or Hamilton) equations of motion to find the motion of a group of atoms
- Originally developed by Alder and Wainwright in 1957 to simulate atom vibrations in molecules
  - Hence the name "molecular"
  - Name unfortunate, as much of MD done nowadays does not include molecules at all
- Already in 1960 used by Gibson to simulate radiation effects in solids [Phys. Rev. 120 (1960) 1229)]
  - A few hundred atoms, very primitive pair potentials
  - But found replacement collision sequences!



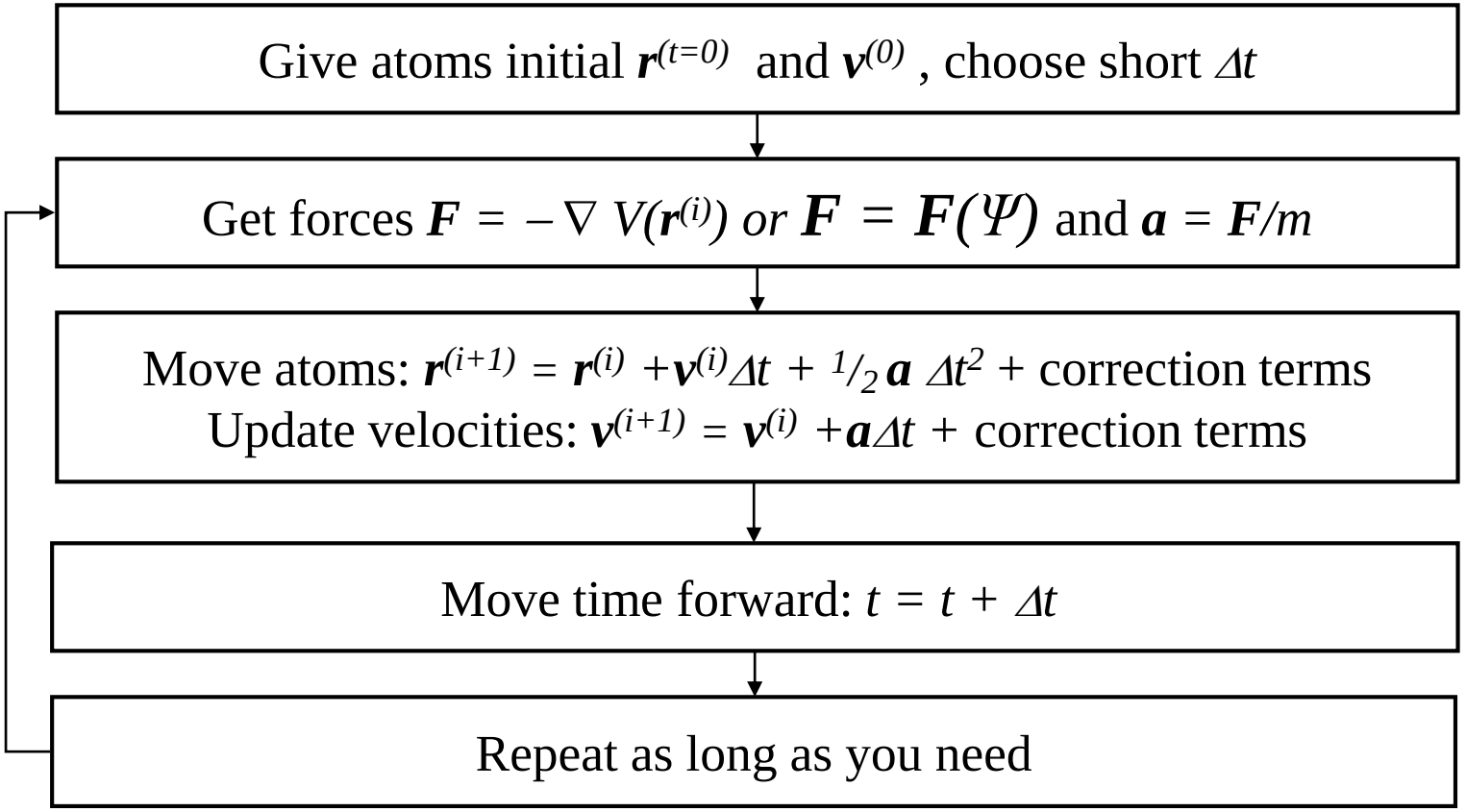
Review of simulation methods for radiation damage

- In a recent review, Nordlund analyzed the historical development of the usage of different computer simulation techniques for simulating radiation damage
  - Publication statistics showed that initially BCA and rate equations dominated, since about 1990 molecular dynamics



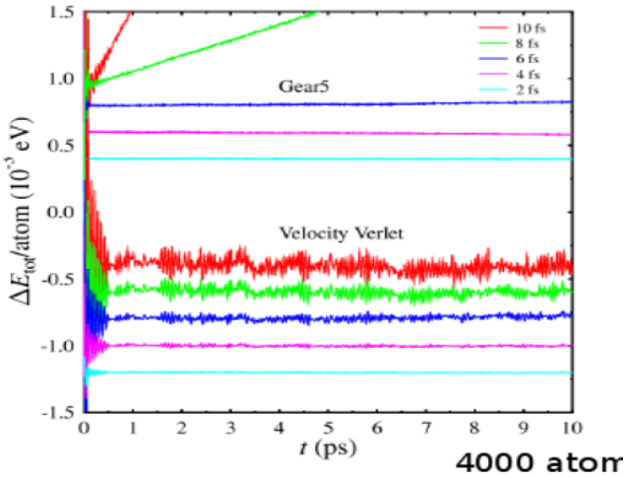
[K. Nordlund, http://www.acclab.helsinki.fi/~knordlun/pub/Nor18b.pdf *Historical review of computer simulation of radiation effects in materials*, J. Nucl. Mater. **520**, 273 (2019)]

MD algorithm



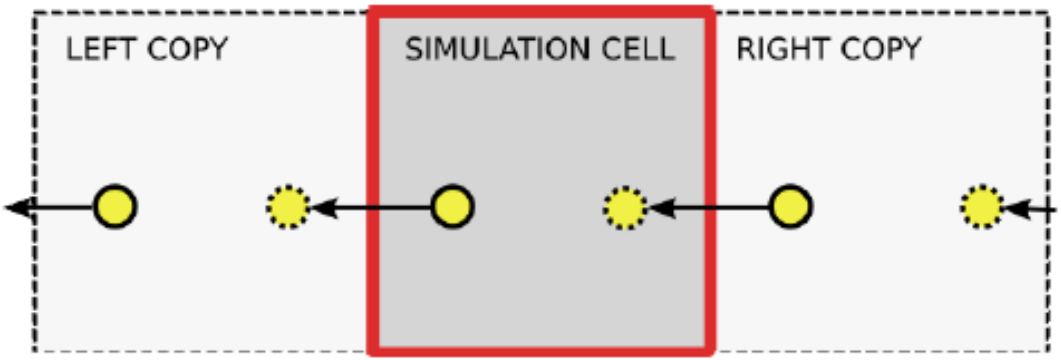
MD – the time step limit

- Time step selection is a crucial part of MD
  - Choice of algorithm for solving equations of motion and time step are related
- Way too long time step: system completely unstable, “explodes”
- Too long time step: total energy in system not conserved
- Too short time step: waste of computer time
  - Pretty good rule of thumb: the fastest-moving atom in a system should not be able to move more than 1/20 of the smallest interatomic distance per time step – about 0.1 Å typically
- This leads to time steps of the order of fs in equilibrium simulations, and for high-energy recoils even down to as (attoseconds)!
- This severely limits the time scale MD can handle



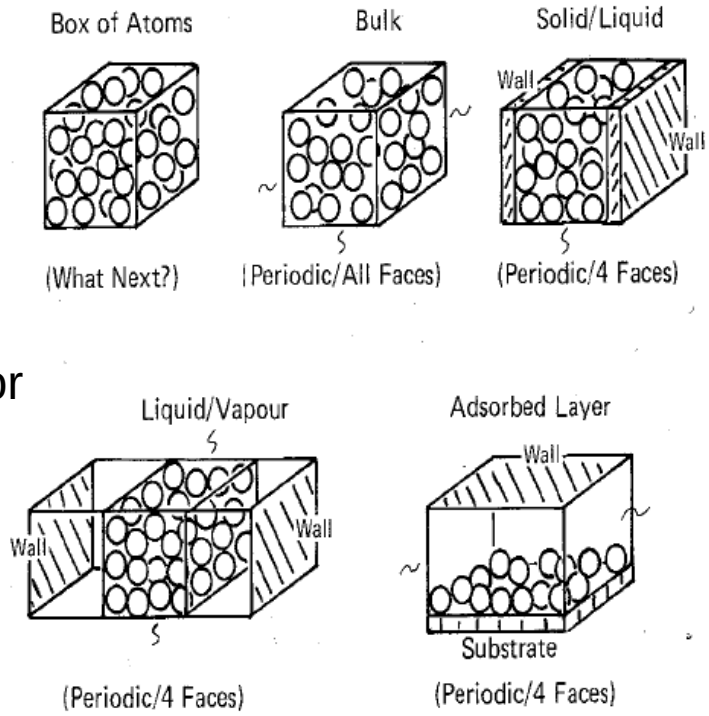
MD – Periodic boundary conditions

- A real lattice can be extremely big
  - E.g. 1 cm^3 of Cu: 2.1e22 atoms => too much even for present-day computers
  - Hence desirable to have MD cell as segment of bigger real system
- Standard solution**: periodic boundary conditions**
  - This approach involves “copying” the simulation cell to each of the periodic directions (1–3) so that the initial system “sees” another system, exactly like itself, in each direction around it. So, one can create a “virtual infinite” crystal.



MD – Boundary conditions

- There are alternatives, though:
- **Open boundaries** = no boundary condition, atoms can flee freely to vacuum
  - Obviously for surfaces
- **Fixed boundaries**: atoms fixed at boundary
  - Unphysical, but sometimes needed for preventing a cell from moving or making sure pressure waves are not reflected over a periodic boundary
- **Reflective boundaries:** atoms reflected off boundary, “wall”
- Combinations of these for different purposes



MD – Temperature and pressure control

- Controlling temperature and pressure is often a crucial part of MD
- “Plain MD” without any T or P control is same as simulating NVE thermodynamic ensemble
  - **In irradiation simulations NVE only correct approach to deal with the collisional phase !!**
- NVT ensemble simulation: temperature is controlled
- NPT ensemble simulation: both temperature and pressure is controlled

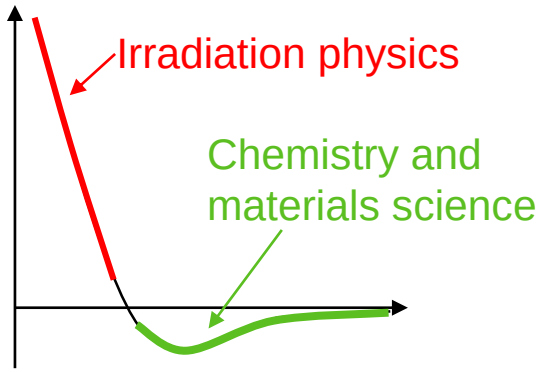
Nonequilibrium extensions to MD

- The standard MD algorithms **are not** suitable for high-energy interactions, and does not describe electronic stopping at all
- But over the last ~25 years augmentations of MD to be able to handle this have been developed
  - We will here discuss the most central ones

What is needed to model irradiation effects?

keV and MeV-energy collisions between nuclei

- To handle the high-E collisions, one needs to know the high-energy repulsive part of the interatomic potential
  - We have developed DFT methods to obtain it to within ~1% accuracy for all energies above 10 eV
  - The so Universal ZBL potential described in chapter 4 accurate to ~5% and very easy to implement
- Simulating this gives the ***nuclear stopping*** explicitly from MD!

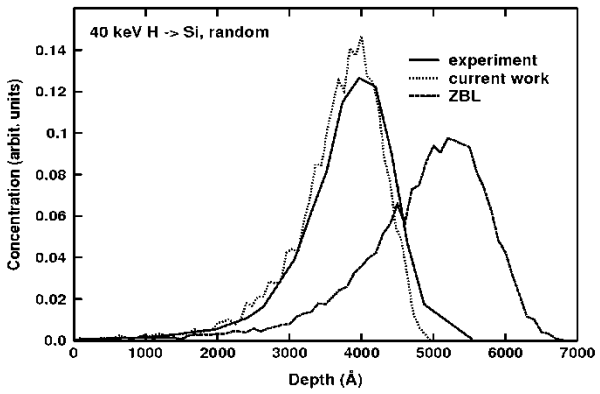


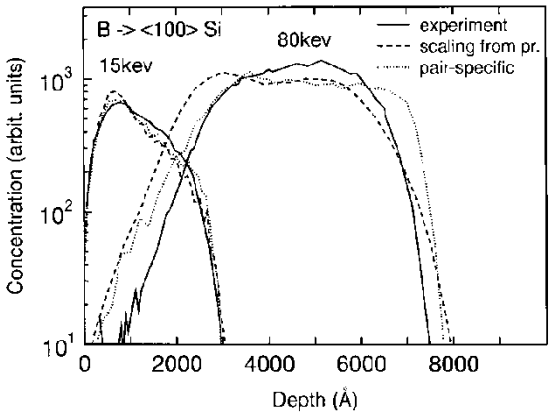
[K. Nordlund, N. Runeberg, and D. Sundholm, Nucl. Instr. Meth. Phys. Res. B 132, 45 (1997)].

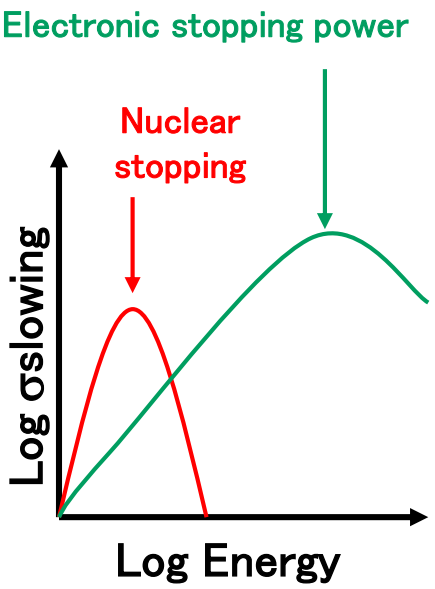
What is needed to model irradiation effects?

Energy loss to electronic excitations

- The 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:







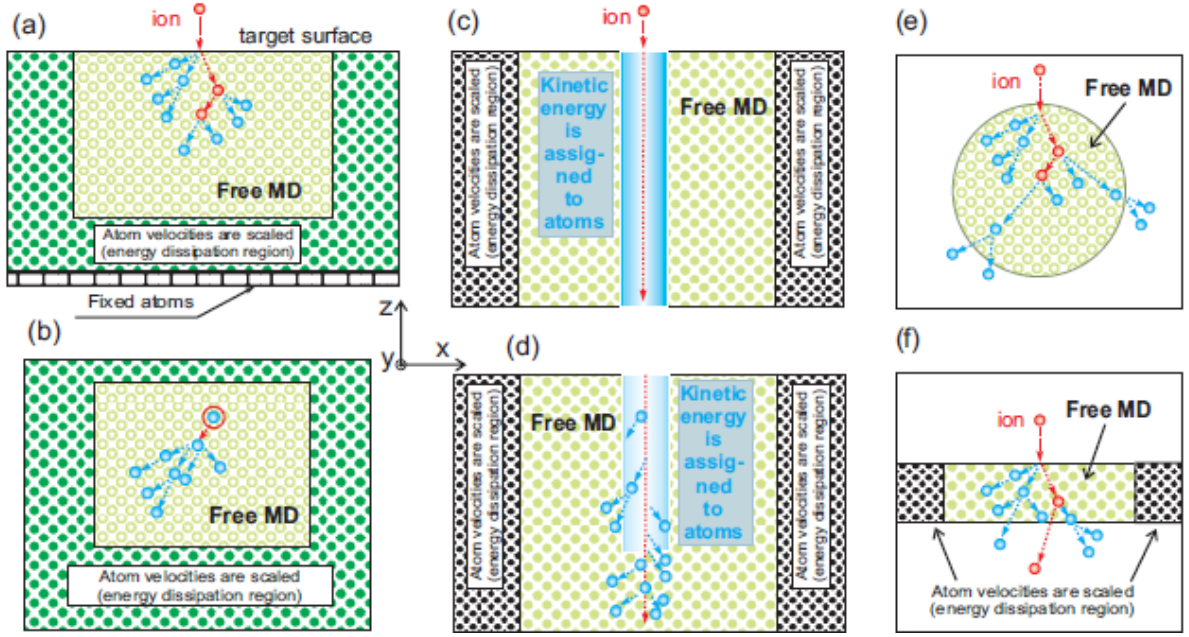
[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen,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

What is needed to model irradiation effects?

MD irradiation temperature control

- For irradiation simulations the central part where the high-E collisions occur has to be in NVE ensemble, but on the other hand extra energy/pressure wave introduced by the ion or recoil needs to be dissipated somehow
- Exact approach to take depends on physical question:

a) surface, b) bulk recoil, c-d) swift heavy ion, e) nanocluster, f) nanowire

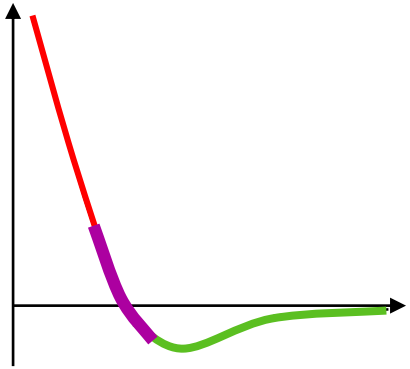


 [A. V. Krasheninnikov and **K. Nordlund**, J. Appl. Phys. (Applied Physics Reviews) **107**, 071301 (2010).

What is needed to model irradiation effects?

Realistic equilibrium interaction models

- Finally one also needs the **normal equilibrium part** of the interaction model, and a **smooth joining** of the high-energy and equilibrium part



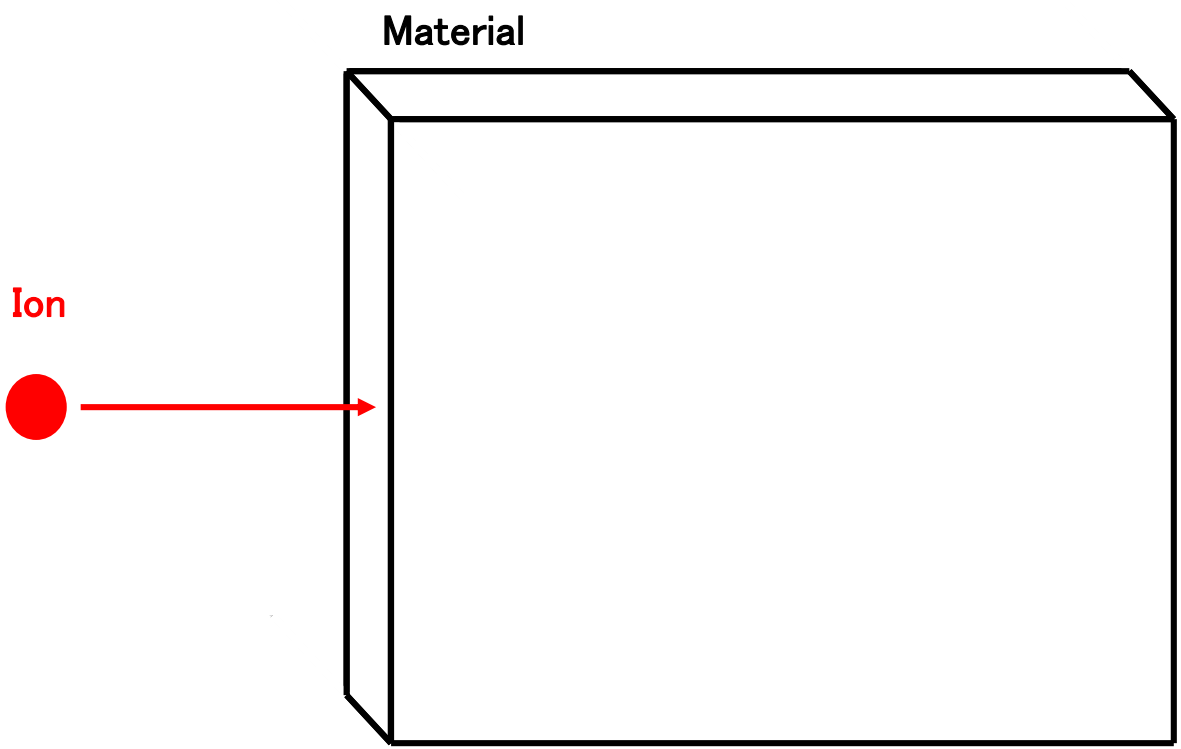
- Since we start out with the extremely non-equilibrium collisional part, all chemical bonds in system can break and reform and atoms switch places => one needs so called ‘reactive’ interatomic potentials

Importance of potentials in MD

- The reliability of the interatomic potential is a **major issue** in MD, and non-equilibrium effects are espcially demanding
  - For common pure elements many good potentials exist, but even these are not always good enough for irradiation simulations
  - For some common compounds potentials exist – but not nearly all
  - To assess reliability needs an expert in the field
- When a potential is used, the MD is called **classical** MD
  - With parallel computers, classical MD can be done with hundreds of millions of atoms
- Nowadays it is also possible to obtain the forces from quantum mechanical calculations, typically the approximate so called Density Functional Theory (DFT) approach
  - But then system size limited to <~ 1000 atoms
- **For more on MD, we have a course for it at our department**

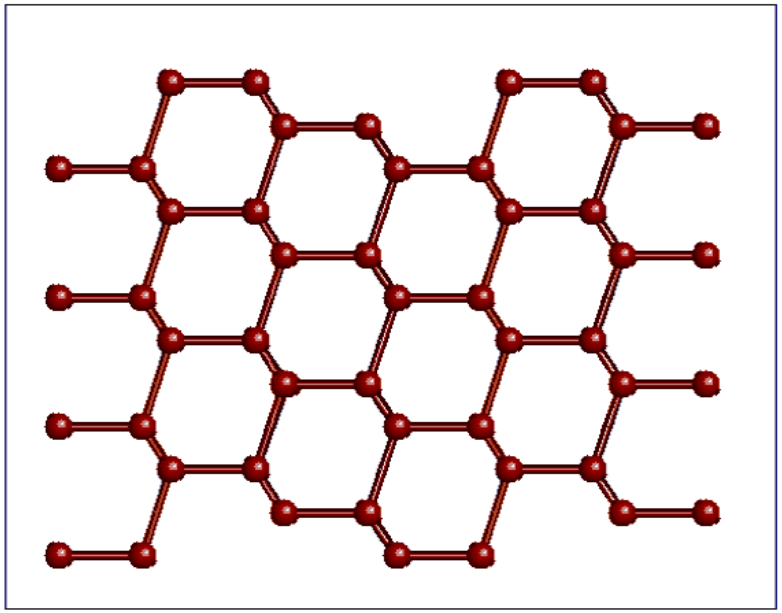
Cross-sectional views of MD simulation results

- For illustrating MD simulations if is very common to use a 2D cross sections of a true 3D view
  - Typically 2-4 atom layers thick



5.3. Damage from MD near the threshold E

- If the ion energy is just barely above the threshold, the damage production is easy to understand: the atom which receives a kick from a passing particle (e.g. electron, gamma, low-mass ion) or a nuclear decay process can enter an interstitial site and leave behind a vacancy
- Shown here: Atom given 16 eV recoil energy in Si just above the threshold energy in 111 crystal direction
  - Final state: single vacancy + single interstitial => simple



[Animation: 111_16eV.avi]

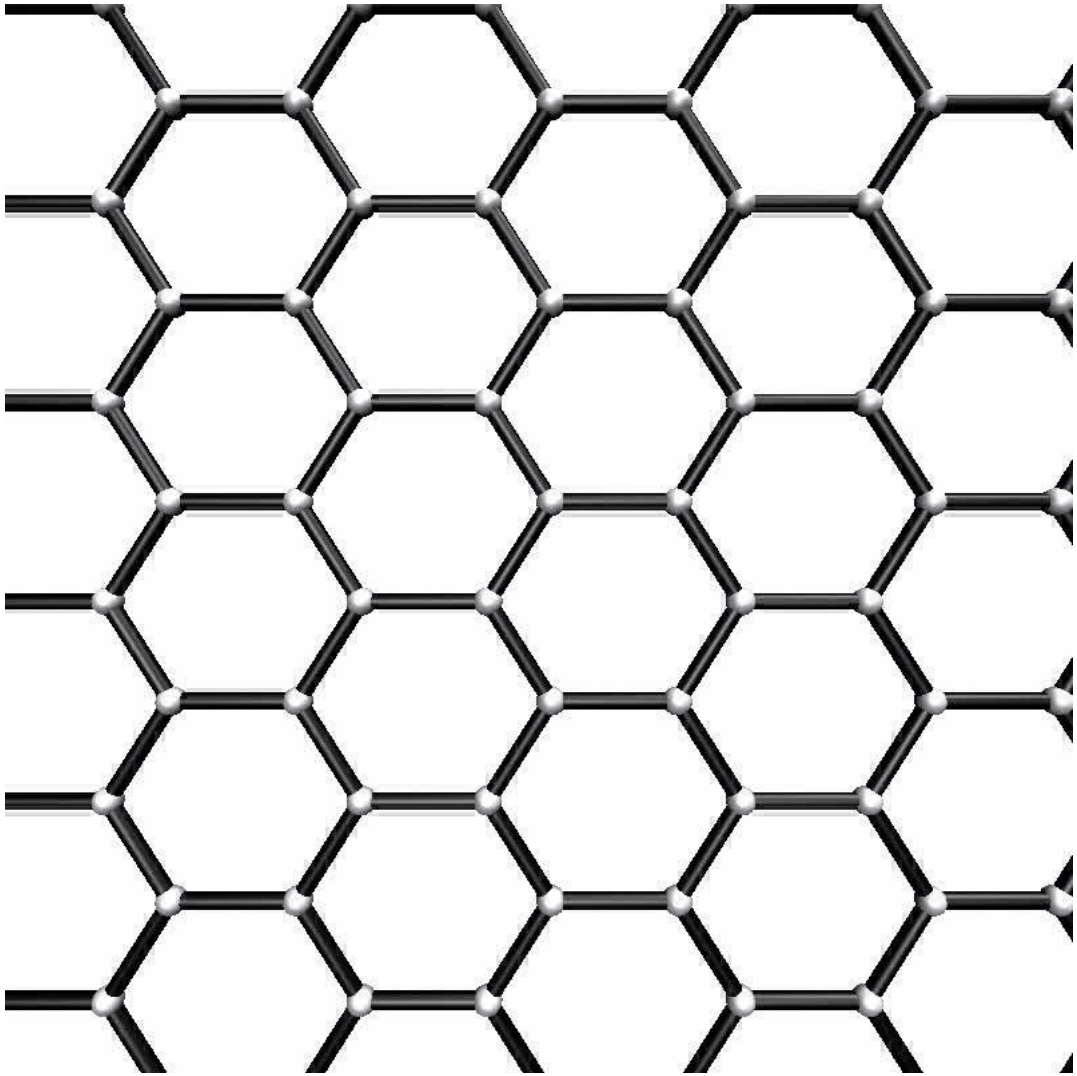
[E. Holmström, A. Kuronen, and **K. Nordlund**, Phys. Rev. B **78**, 045202 (2008)]

Concept of primary damage

- What this animation, and all other MD simulations, show is the production of **primary damage** (*primära skador / primäärit säteilyvauriot*)
- This is the damage produced initially in a cascade on sub-nanosecond timescales, not counting any possible damage recombination by thermally activated processes
- In many cases the thermally activated recombination is actually very important, especially when diffusion occurs
  - This will be dealt with later during the course
- Physically the mechanisms of the two varieties are quite different and fairly well separated in time, so it makes sense anyway to describe them independently.

Damage from MD near threshold in graphene

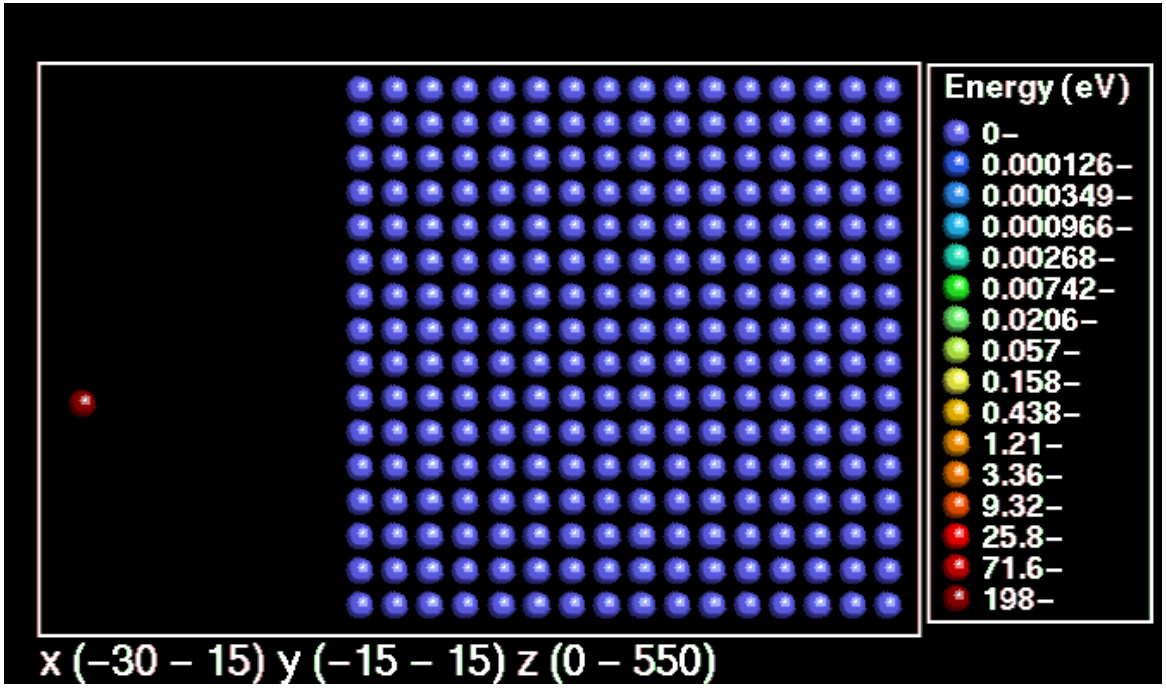
- Low-energy recoil in a single sheet of graphene
  - (Defect created is a topological defect known as the Stone-Wales one)



[J. Kotakoski et al]

[Animation: sw-direct.wmv]

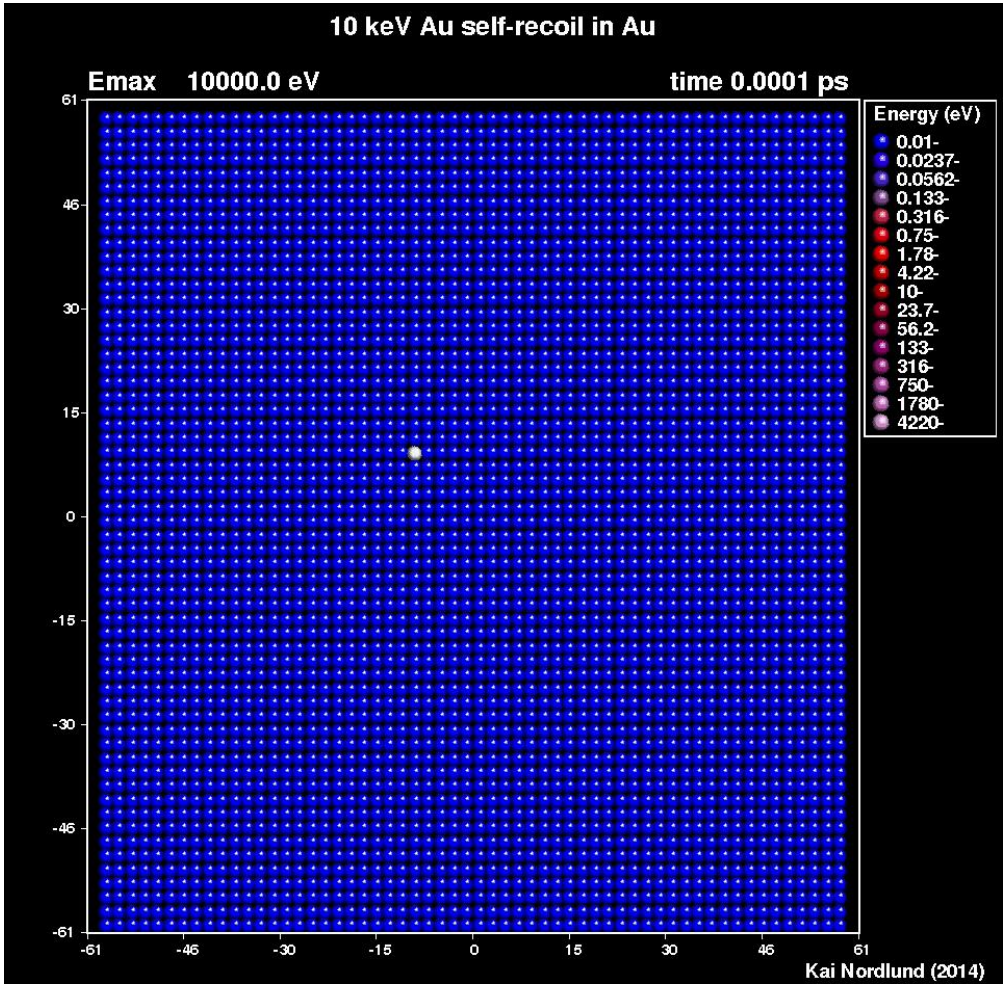
Damage from MD at about 10x threshold energy: 500 eV Au -> Cu



[Animation: au500.avi]

- Many-body collisional effects clearly visible
- Nota bene: this animation has actually been done for school visits, and hence to make it look better there is a minor physical cheat in there – can you figure out what?

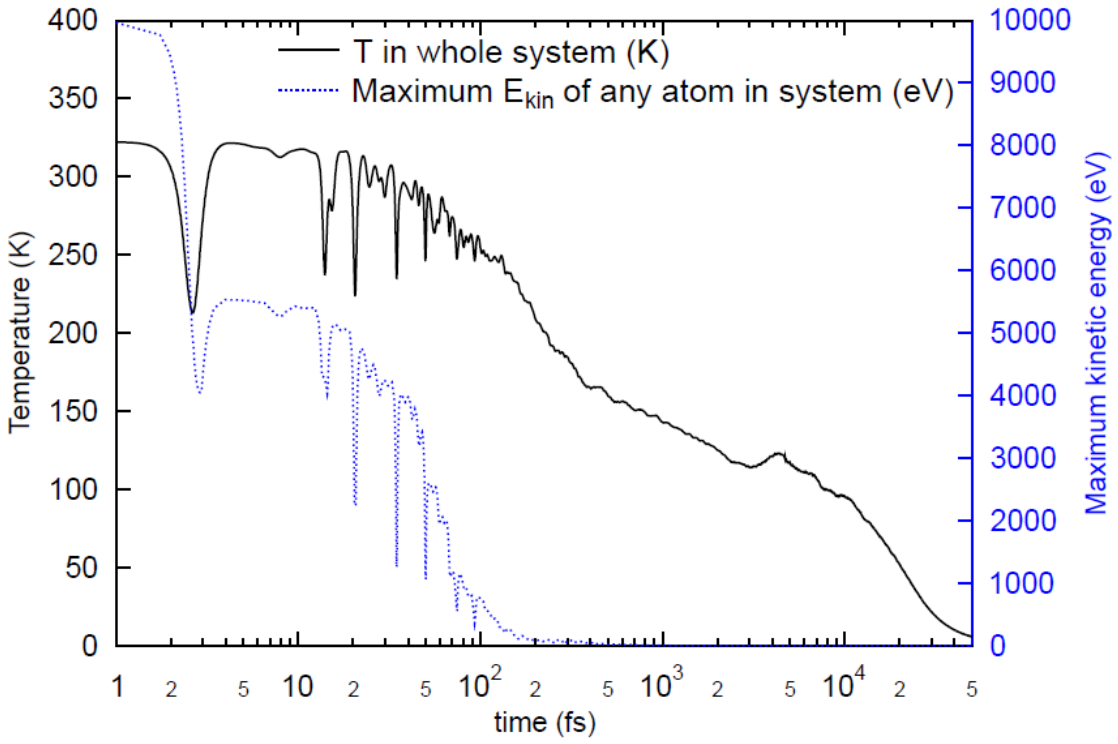
5.4. The dynamics of high-energy (keV) cascades from MD; Transition from ballistic collisions to thermodynamics: 10 keV recoil in Au



[Animation: 10kevau_au_slow_E.avi]

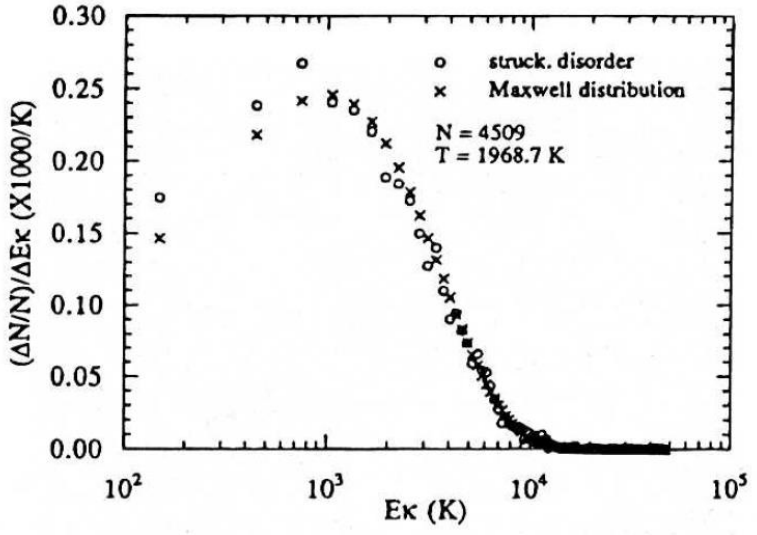
Development of maximum Ekin and T

- Plot of maximum energy of any atom in the system and the temperature in the system vs. time.
  - Note that there is of course a huge temperature gradient in the simulation system: the center is very hot, the edges close to 0 K
  - The dips in the beginning of the plots correspond to strong binary collisions: during the collision kinetic energy for a moment is converted into potential energy, decreasing the apparent temperature



Transition to thermodynamics

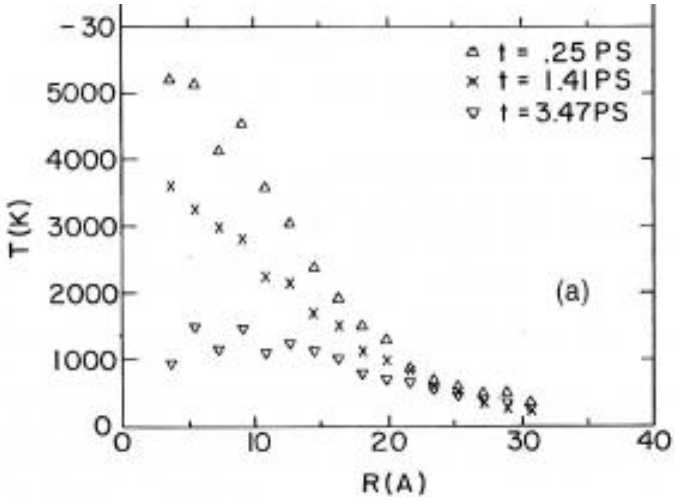
- Ergo: the initial stages of the cascade are a linear collision cascade that can be well treated with the binary collision approximation
- Towards the end, the system **thermalizes** (*termaliseras / termalisoituu*) and equilibrium thermodynamics comes into play
- A detailed analysis [Zhu et al; Phil. Mag. A 71 (1995) 735] showed that after roughly 1 ps, the kinetic energy of the atoms follows a Maxwell-Boltzmann distribution, i.e. the system is thermal!



Temperature in cascade

- After thermalization, the center of the cascade is initially still very hot, ~ 10000 K
- However, it cools down very rapidly, with a cooling rate of the order of 10^{15} K/s
- The structure factor of the material follows closely that of a liquid at the same temperature

5 keV cascade in Cu



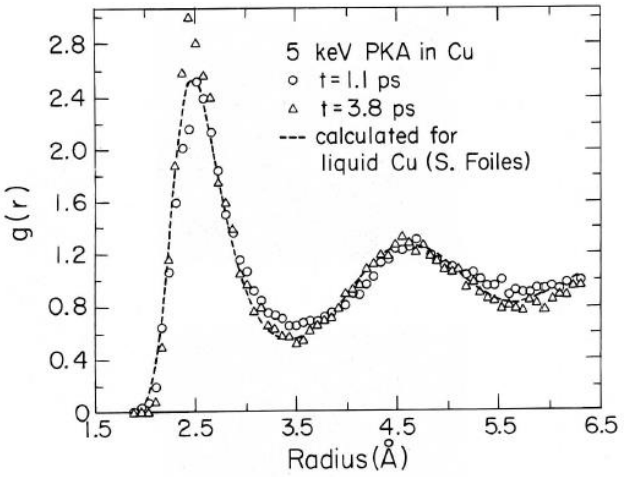


FIG. 22. Pair correlation function for atoms in the core of the cascade at 1.1 ps and 3.83 ps. Also shown is the pair correlation function for liquid Cu as calculated by Foiles. (After Ref. 78.)

[Picture sfrom Review article :Averback, Diaz de la Rubia, Solid State Physics 51 (1998) 281]

Cooling down mechanisms, 1

- The high temperature in the center (atoms with high kinetic energies) can cool down in the bulk by two mechanisms:
  - Lattice heat conductivity (phonons)
  - Electronic heat conductivity (free electrons)
- In addition, if a cascade intersects a surface, the sputtered particles will also carry away energy
- In case of a good insulator, the lattice heat conductivity of course dominates as there are no free electrons
  - The cascade itself may excite some electrons into the conduction band, but their contribution is likely small

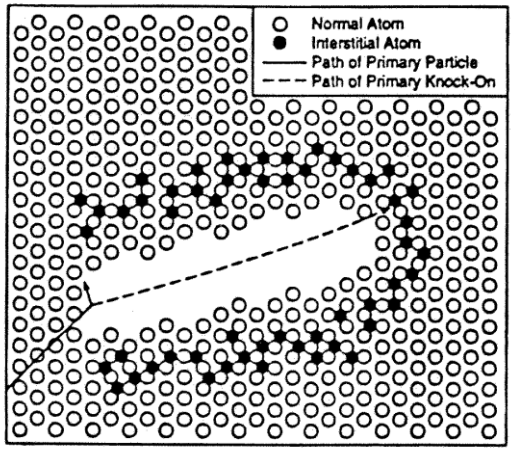
Cooling down mechanisms, 2

- However, in metals (and possibly semiconductors) some of the high lattice energy may transfer to the electrons via **electron-phonon coupling** (EPC) (elektroni-fononi-kytkentä/elektron-fonon-koppling) which may speed up the cooling down
  - This is because the electrons move much faster than atoms, and hence electronic heat conductivity is much more efficient than that of atoms
- The role of the EPC is not very clear, but the fact that ion beam mixing coefficients of atoms can be well reproduced by MD simulations without any EPC, indicates it is not overly important [K. Nordlund et al, Phys. Rev. B (Rapid Comm.) 57, 13965 (1998)]
  - However, there must be some fraction of EPC cooling in metals, and current research is trying to sort out its importance
    [A. M. Rutherford and D. M. Duffy, J. Phys. Cond. Matter, 19: 496201, 2007; C. Björkas and K. Nordlund, Nucl. Instr. Meth. Phys. Res. B, 267:1830--1836, 2009]

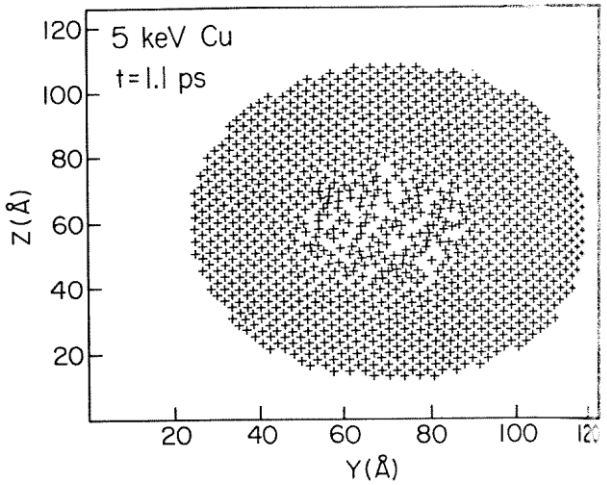
Concept of a thermal spike

- This very high temperature region is known as a **thermal spike** or **heat spike** (*termisk pik / kuumuuspiikki*)
  - Sometimes also as a Brinkman spike or displacement spike
- This was originally predicted in 1954(!) but whether they really exist was debated for a long time as it is difficult to determine the cooling rates of materials on nm length and ps time scales

Brinkman, 1954



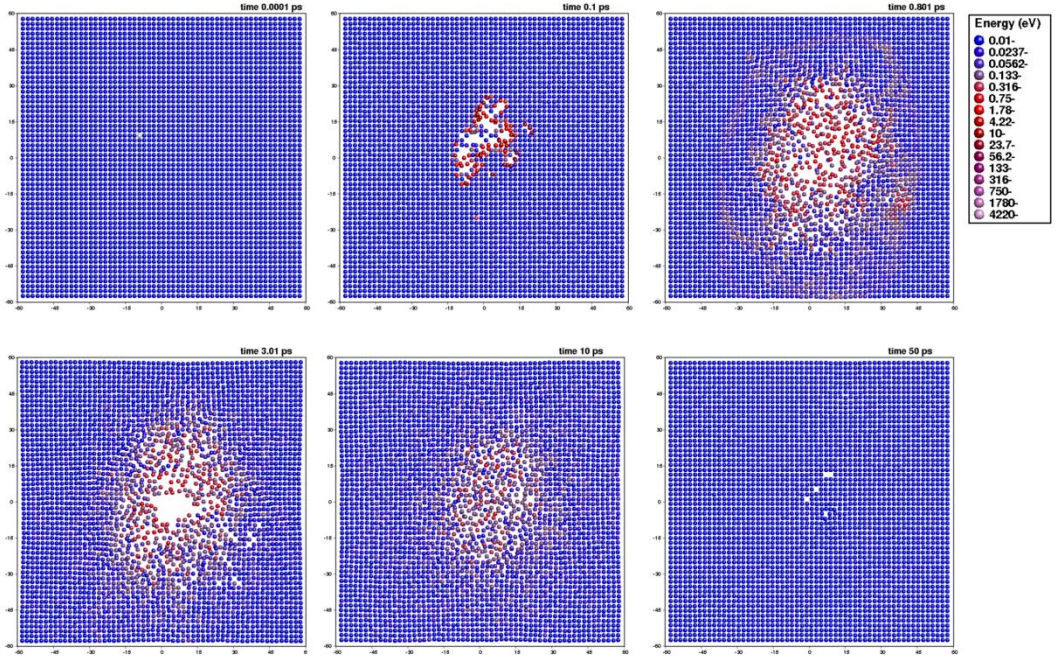
Diaz de la Rubia *et al.* , PRL 1987



Thermal spike is underdense in middle

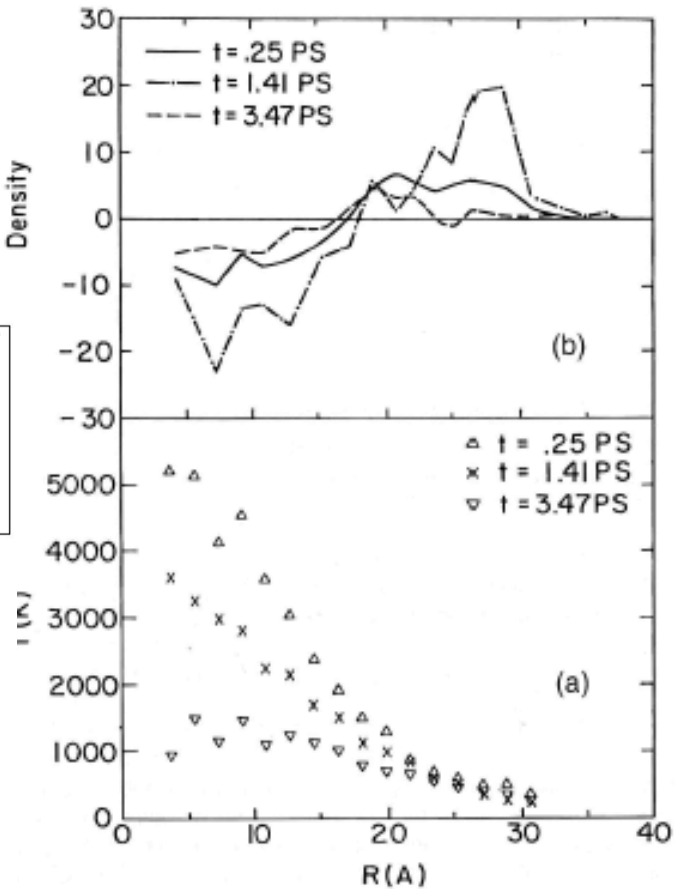
- Key evidence for thermal spikes came from molecular dynamics simulations
- These also showed the cascade core is underdense for a while, as predicted by Brinkman in 1954

10 keV cascade in Au



[Kai Nordlund]

5 keV cascade in Cu



[Picture from Review article :Averback, Diaz de la Rubia, Solid State Physics 51 (1998) 281]

Experimental evidence for thermal spikes

- Also several experiments provide strong evidence for the existence of thermal spikes. A couple of key examples:
- Experiments on irradiation of certain ceramics showed that after irradiation, new phases appear that are otherwise known to form only at high temperatures
  - [A. Meldrum, S. J. Zinkle, L. A. Boatner, and R. C. Ewing. A transient liquid-like phase in the displacement cascades in zircon, hafnon and thorite. Nature, 395:56--58, 1998.]
- A special nuclear physics measurement technique gave a lifetime of about 6 ps for a liquid phase in Fe
  - [A. E. Stuchbery and E. Bezakova, Thermal-spike lifetime from pico second-duration preequilibrium effects in hyperfine magnetic fields following ion implantation, Phys. Rev. Lett., 82(18):3637, 1999.]

Thermal spikes exist only in dense materials

- However, the thermal spikes are not always formed
- In very light materials (say Li or C) there is *never* a thermal spike in the sense of a pocket of metastable liquid material
- Spike formation probability depends on density and structure of material
- Example: comparison of hot atoms by 10 keV recoils in Si, Al, Ge, Au: much denser cascade in the FCC metal Al, Au than in the diamond-structured Si, Ge
  - Atomic packing fraction ~ ½ in diamond compared to FCC

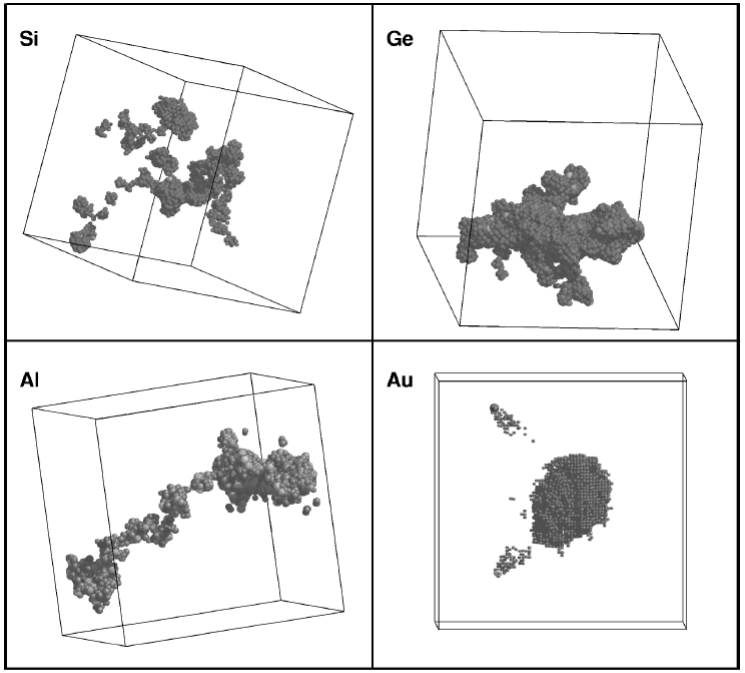
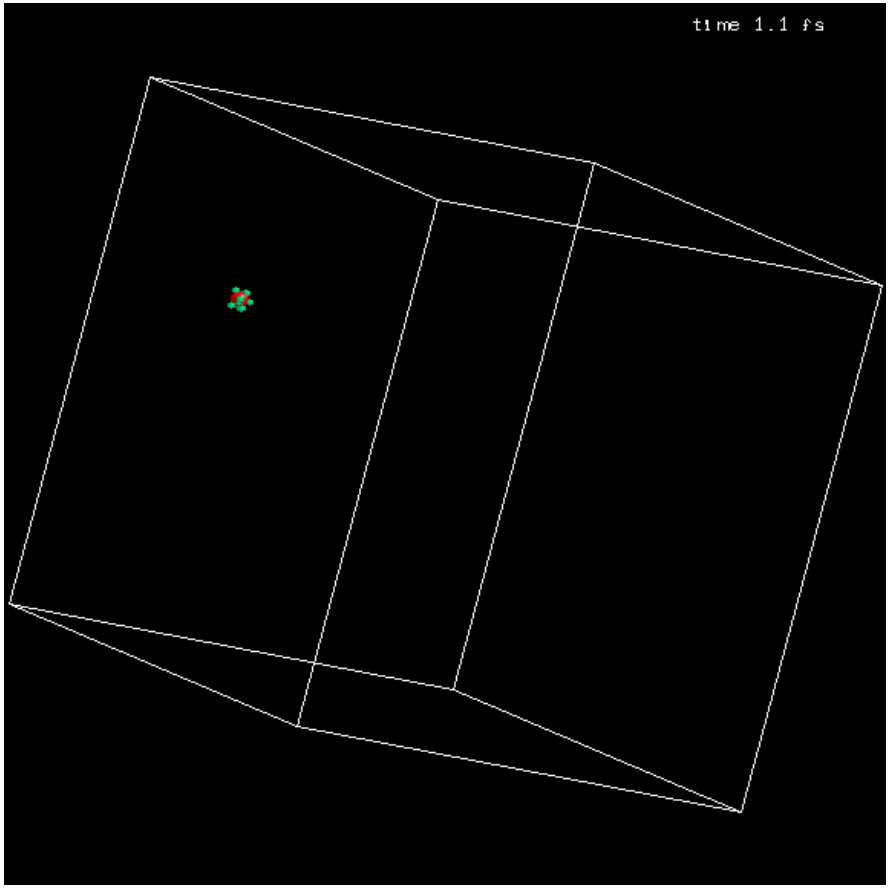


FIG. 2. Liquid atoms in 10 keV cascades in silicon (upper left), germanium (upper right), aluminum (lower left), and gold (lower right) (Ref. 61). The snapshots were chosen at times when the number of atoms in large continuous liquid regions was at a maximum.

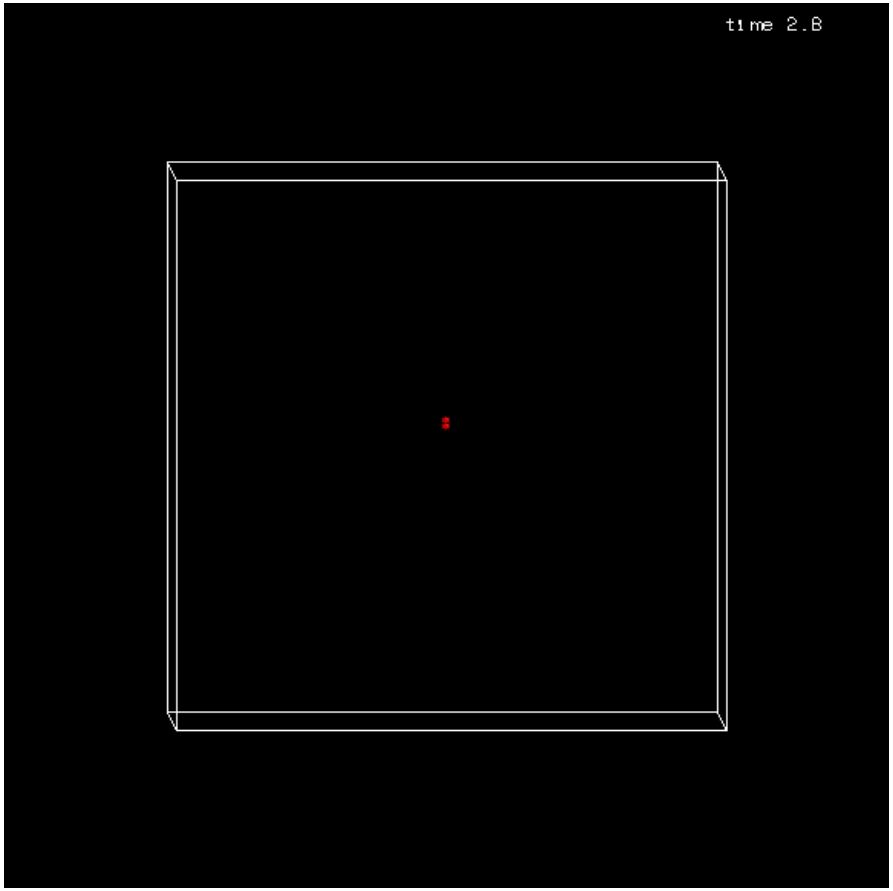
[Nordlund et al, Phys.Rev. B **57**, 7556 (1998)]

Cascade in Si vs. Au

- Widely different atomic mass and density
  - Colors and size are kinetic energy of atoms, red=hot



[Animation: si10kevanim3d.gif]

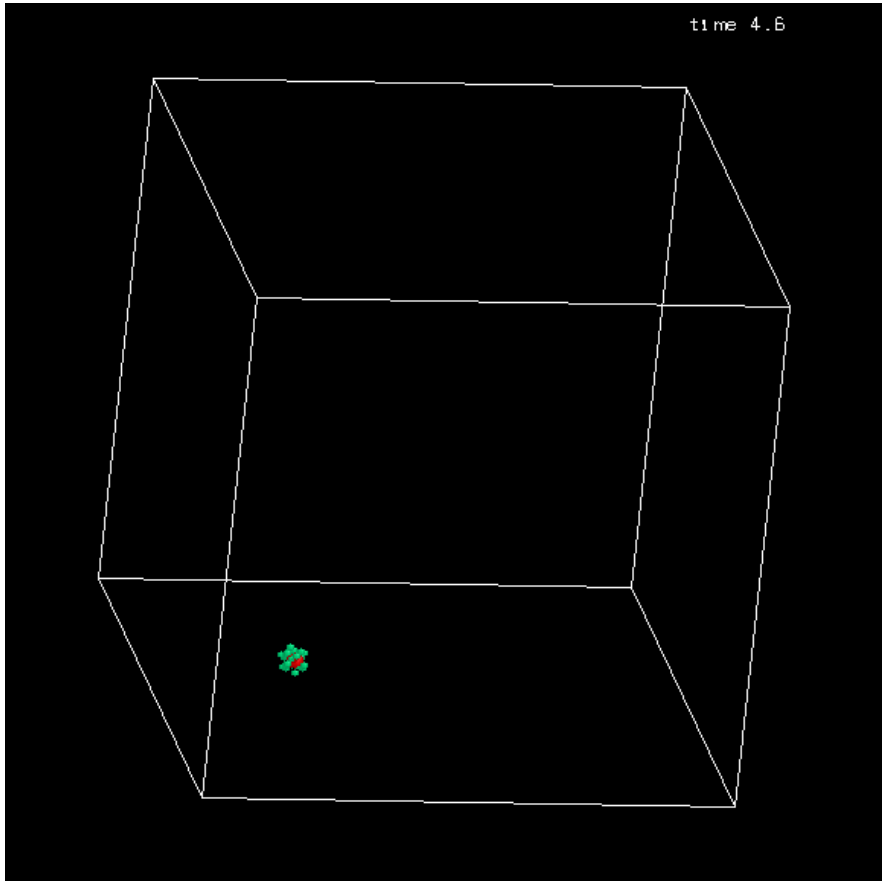


[Animation: au10kevanim3d.gif]

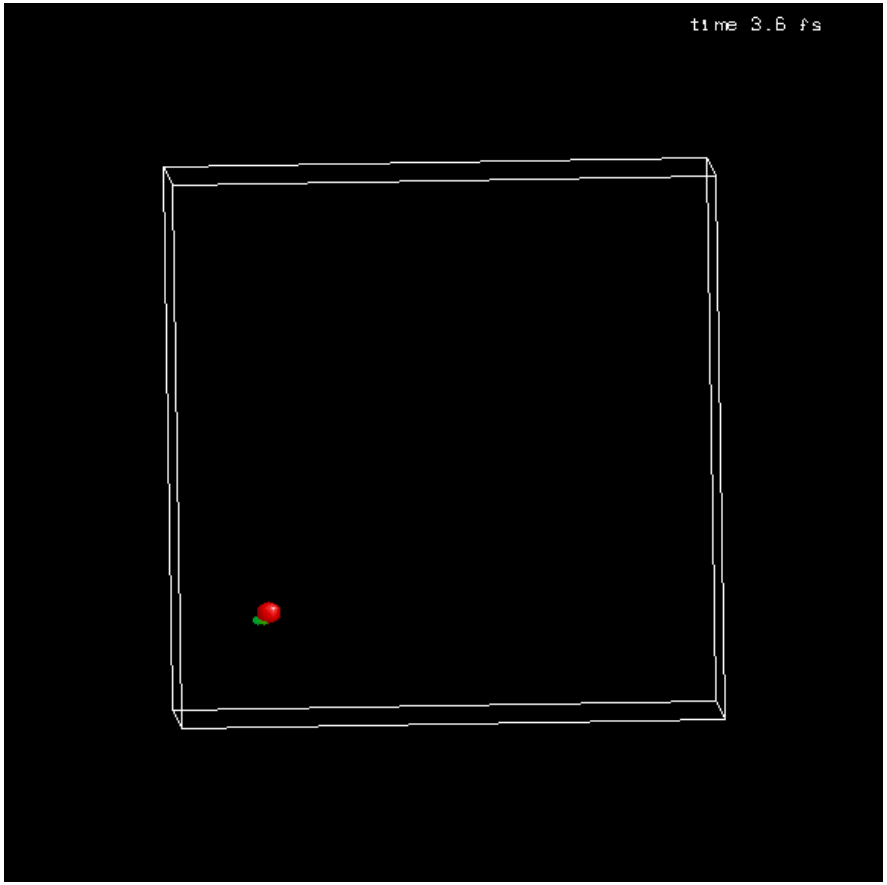
[Nordlund et al, Phys.Rev. B **57**, 7556 (1998)]

Cascade in Ge vs. Cu

- Almost same atomic mass, but different crystal structure and density



[Animation: ge10kevanim3d.gif]

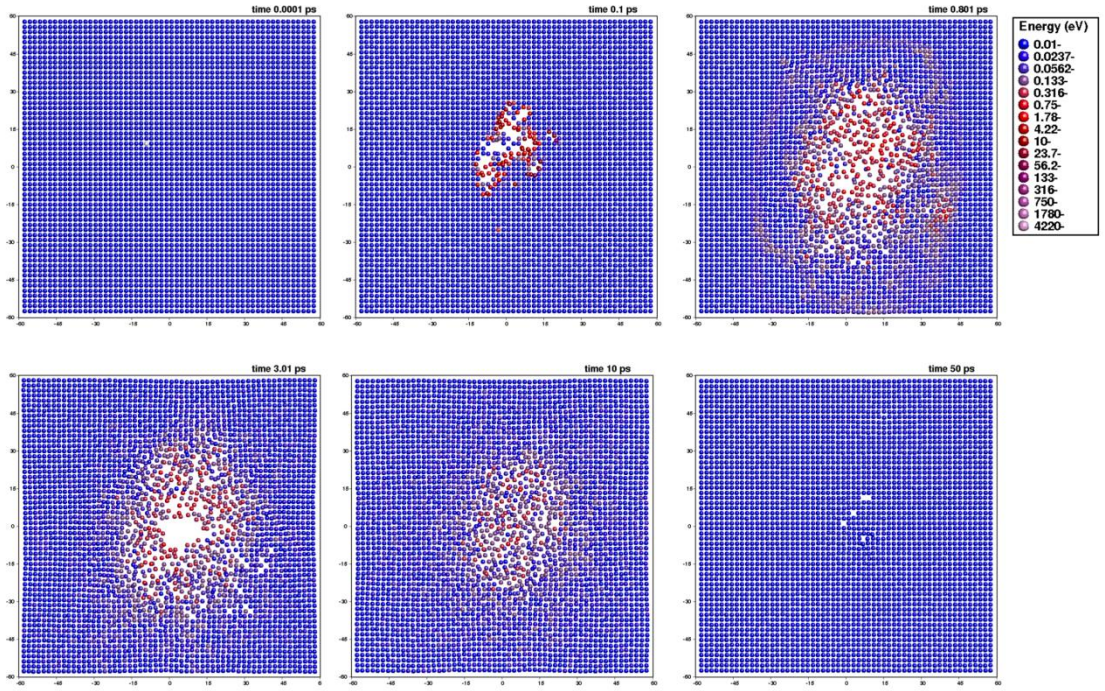


[Animation: cu10kevanim3d.gif]

[Nordlund et al, Phys.Rev. B **57**, 7556 (1998)]

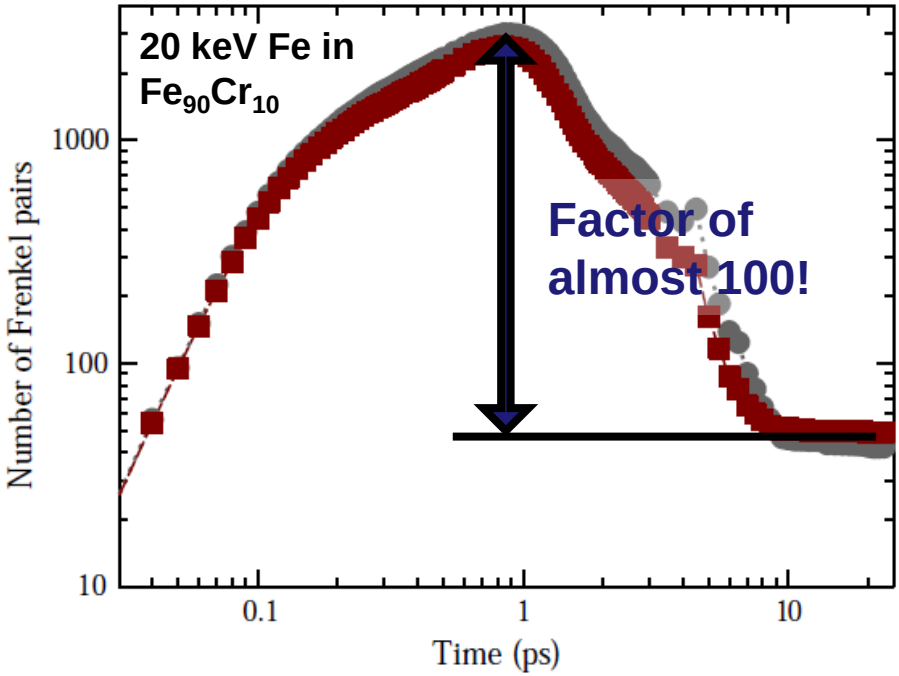
Damage recombination

- Looking at these animations, it appears that many of the liquid atoms regenerate into perfect crystal, i.e. do not produce damage!
  - E.g. from the figure below it is obvious there are hundreds of liquid atoms just in this cross section, but only a few small vacancies remain in the end



Damage recombination

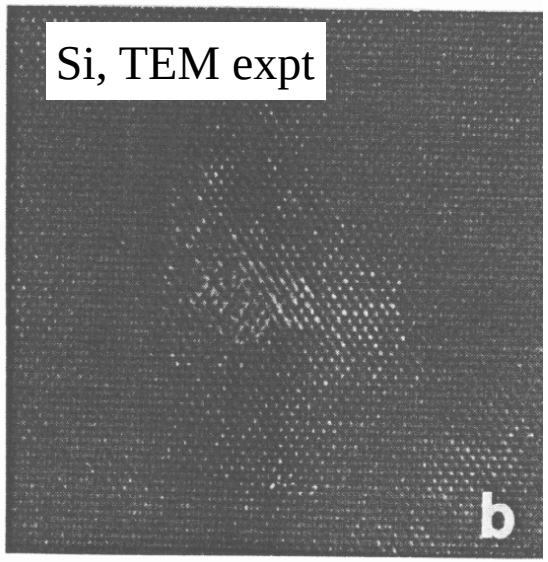
- Analysis of defects (e.g. by counting empty lattice sites) confirms this visual observation
  - The effect is known as **athermal defect recombination** (*atermisk defektrekombination / aterminen kidevirherekombinaatio*)
    - "athermal" means that the effect occurs without any thermal activation
- It is a very strong effect in metals!



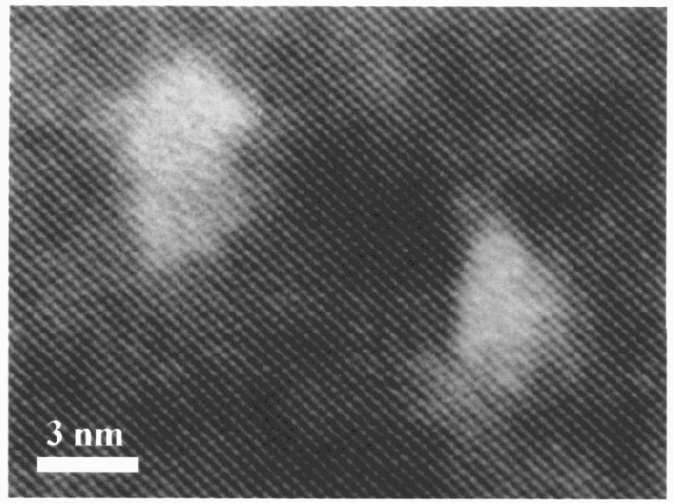
[Vörtler et al, J. Nucl. Mater. 382 (2008) 24–30]

Damage recombination

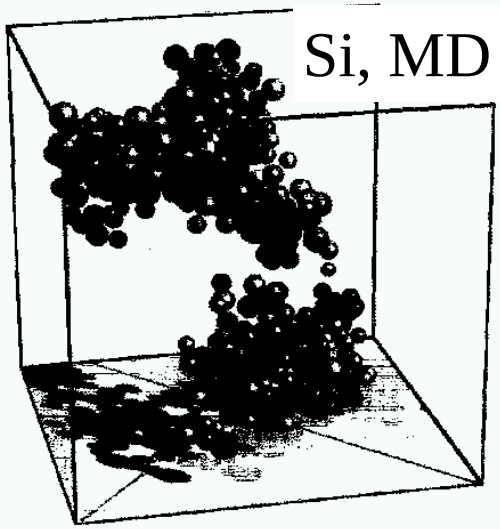
- The reason to the recombination can be understood to be simply recrystallization
- To what extent it occurs depends on the recrystallization rate of the material: if it is fast, the damage has time to recombine, if it is slower, not => liquid zone ‘freezes in’ into a disordered or amorphous region
- The latter is typical in semiconductors, and also seen experimentally in at least Si, Ge and GaAs



[Ruault et al, Phil. Mag A 50 (1984) 667]



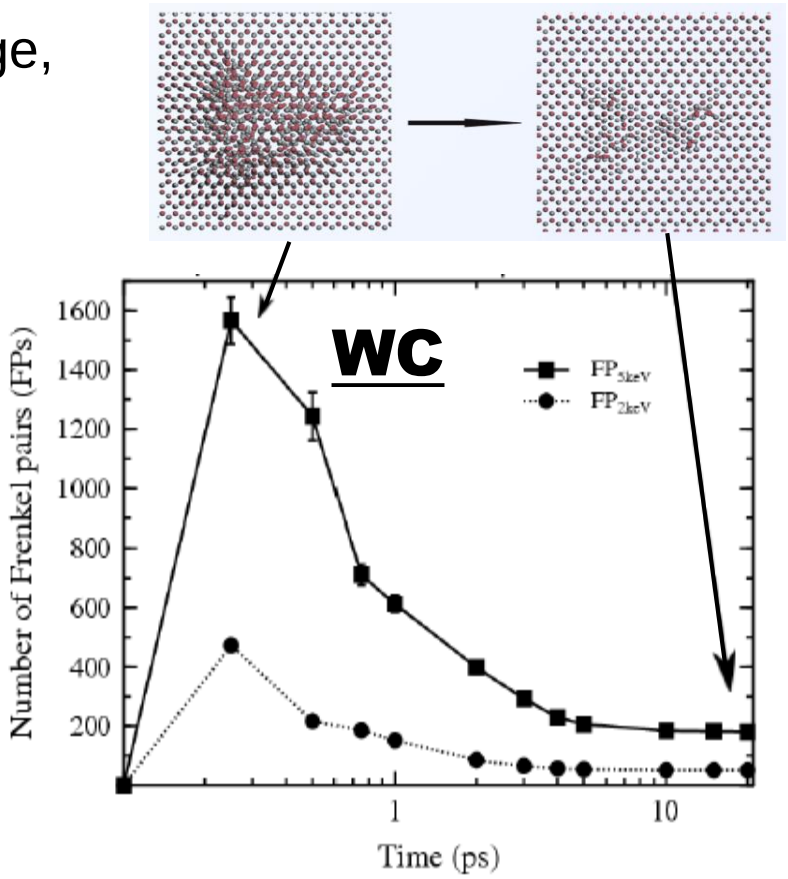
[Jencic, J.Appl.Phys. 2000]



[Diaz de la Rubia and Gilmer, Phys. Rev. Lett. 1995]

Damage recombination in ionic materials

- Ionic/ceramic materials are often somewhere in between metals and semiconductors
- Some recombination of damage, but disordered regions remain
- Large variations between different ionic materials!
  - Attempt to explain this: [Trachenko, Phys. Rev. B 73 (2006) 174207]

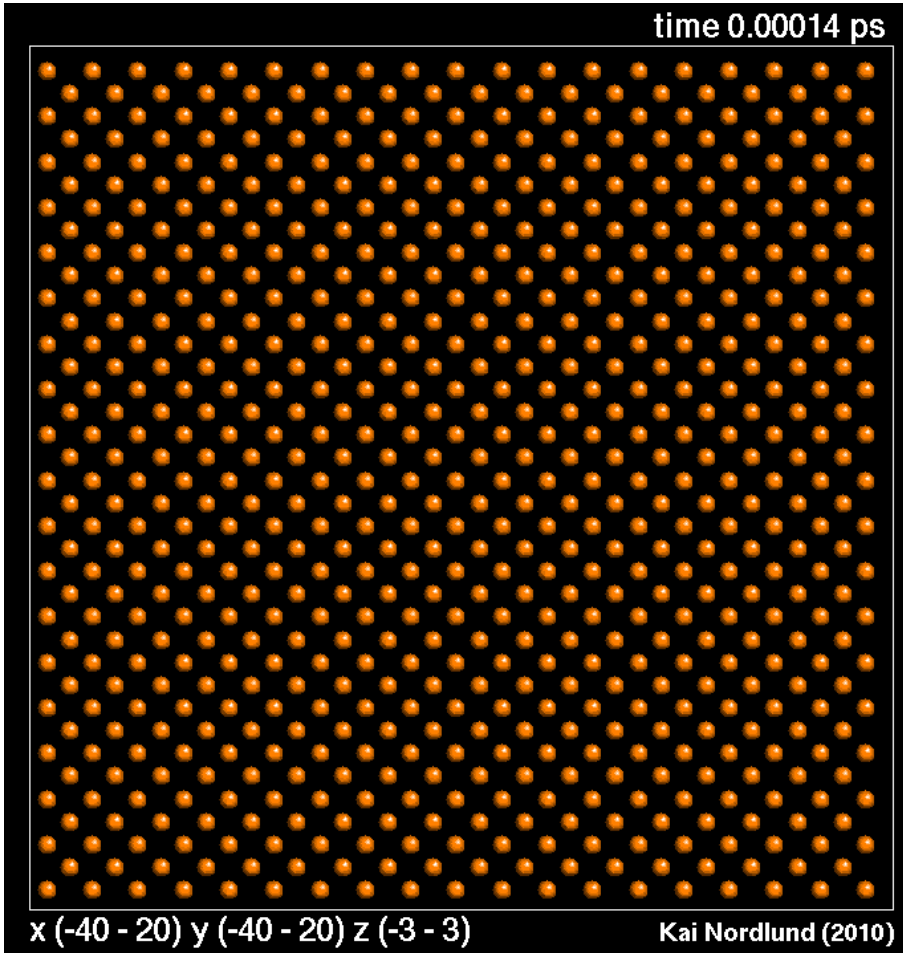


[Björkas et al, Phys. Rev. B 2006]

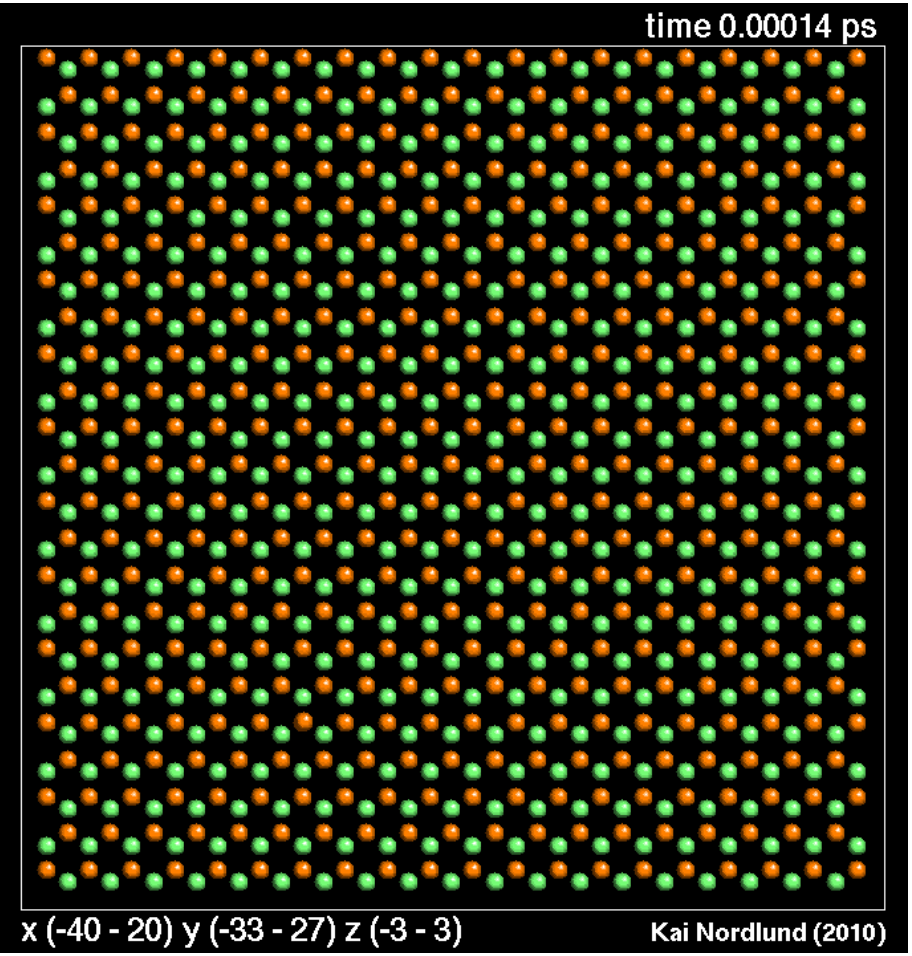
Damage in ceramics

Primary radiation damage in W vs. WC

W 5 keV



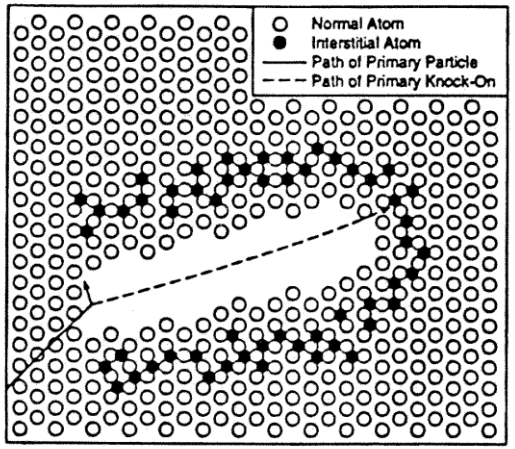
WC 5 keV



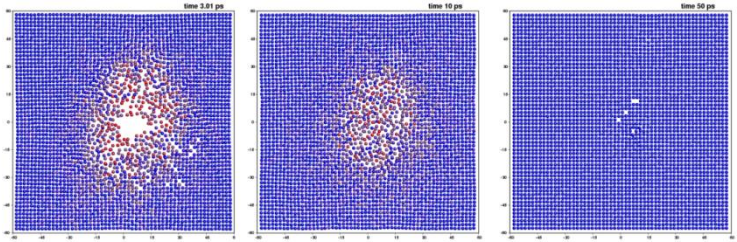
[Animation: w_vs_wccasc_5kev.avi]

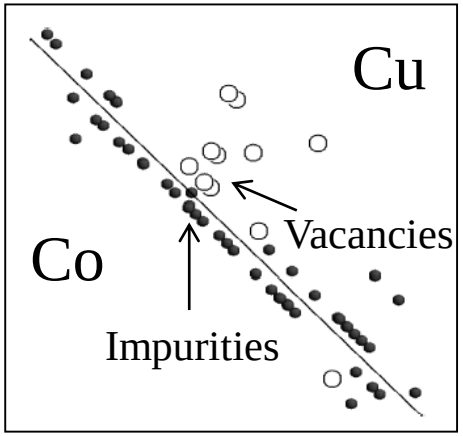
Vacancy clustering in center

Brinkman, 1954



- The original picture of Brinkman is valid in one respect: the ballistic processes do press interstitial atoms to the outside of the cascade
- At the end of the cascade, the behaviour can be understood by the recrystallization front of the cascade pressing the vacancies towards the center, resulting in the fact that one tends to have vacancy clusters in the center
- This was shown explicitly in simulations of a Co/Cu bilayer system; vacancies tend to go to the side with the lower melting point (Cu), impurities on the other side (Co)





[**K. Nordlund** and R. S. Averback, Phys. Rev. B **59**, 20 (1999)]

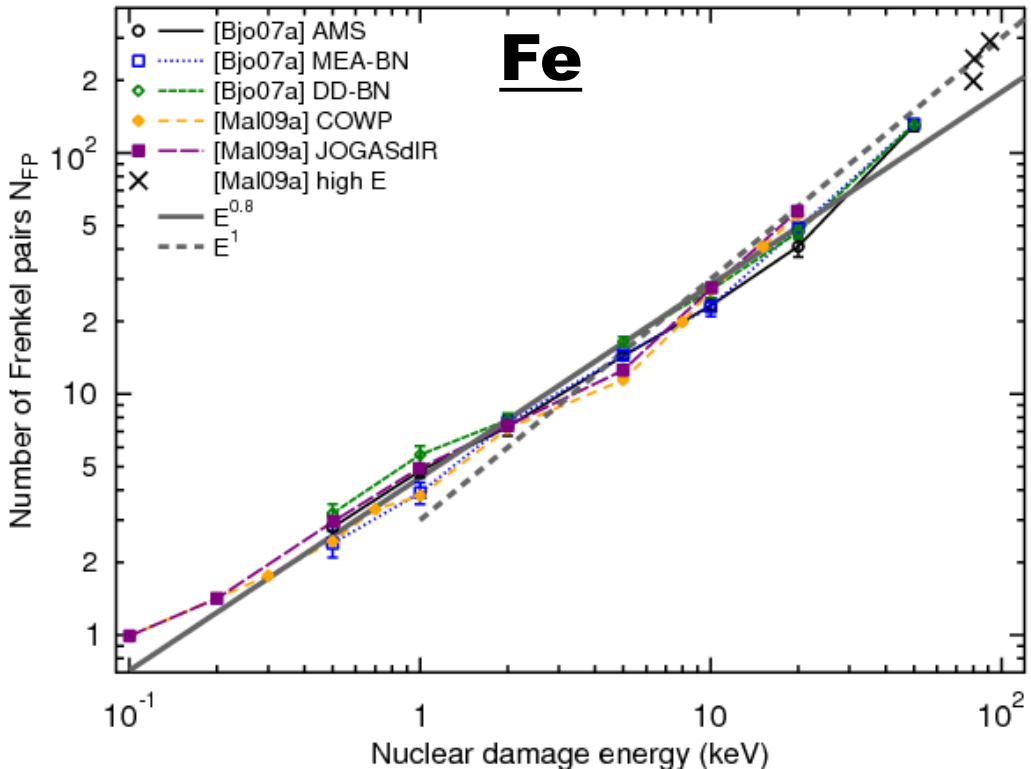
Vacancy and interstitial clustering

- Thus there is a natural mechanism for vacancy clustering
- Interstitials also tend to cluster, but not as clearly
- Both vacancies and interstitial clusters can in some materials collapse directly into dislocation structures (more on these later)
- Now we can finally understand what is going on in this animation:

[Animation: irradiation.avi]

5.5. Resulting damage production

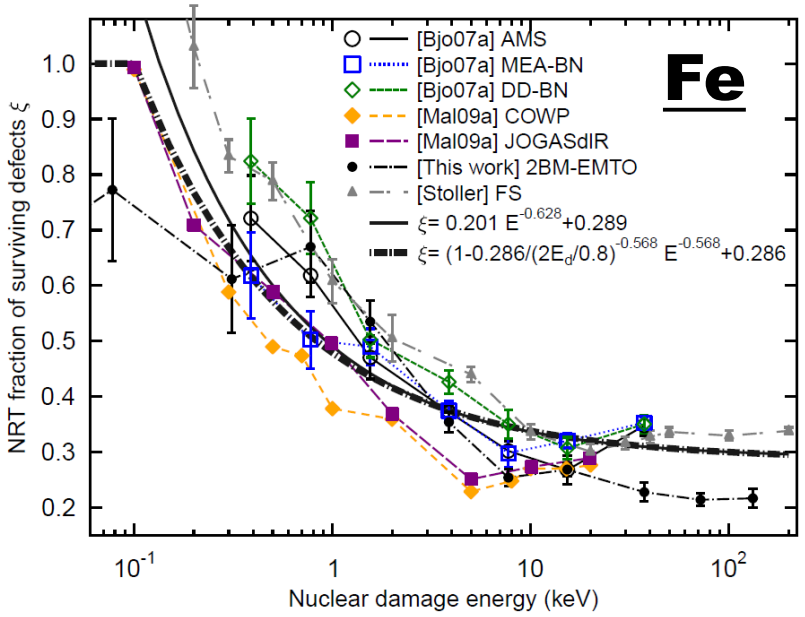
- If the damage production is counted purely by number of defects, it increases with nuclear damage energy (=recoil energy minus energy lost to electronic stopping)
- But due to recombination, increase is initially sublinear:



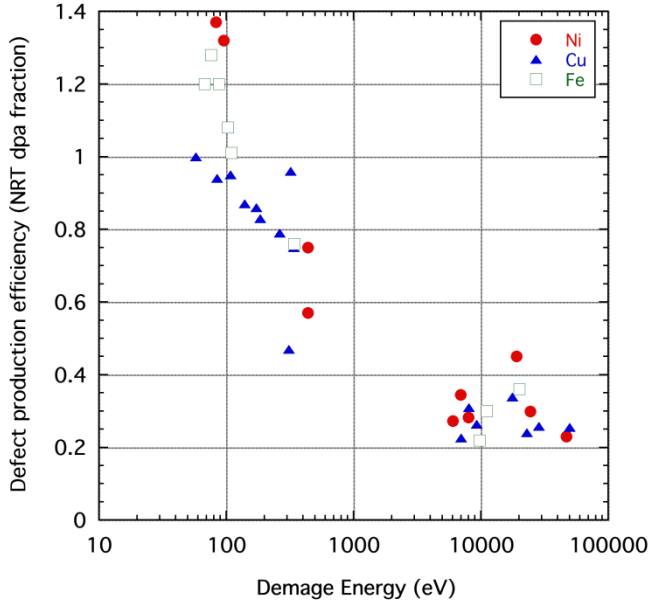
Resulting damage production

- Due to the athermal recombination, the damage production in metals is at high energies typically ~ a factor of 3 lower than that given by the Kinchin-Pease / NRT equations
- This explains the behaviour shown in section 4:

Simulations



Experiments



[Nordlund, Zinkle, et al. Nature communications **9**, 1084 (2018)]

Damage efficiency

- The difference between the true damage production and the NRT prediction is known as the cascade efficiency
- The new arc-dpa equation describes exactly this

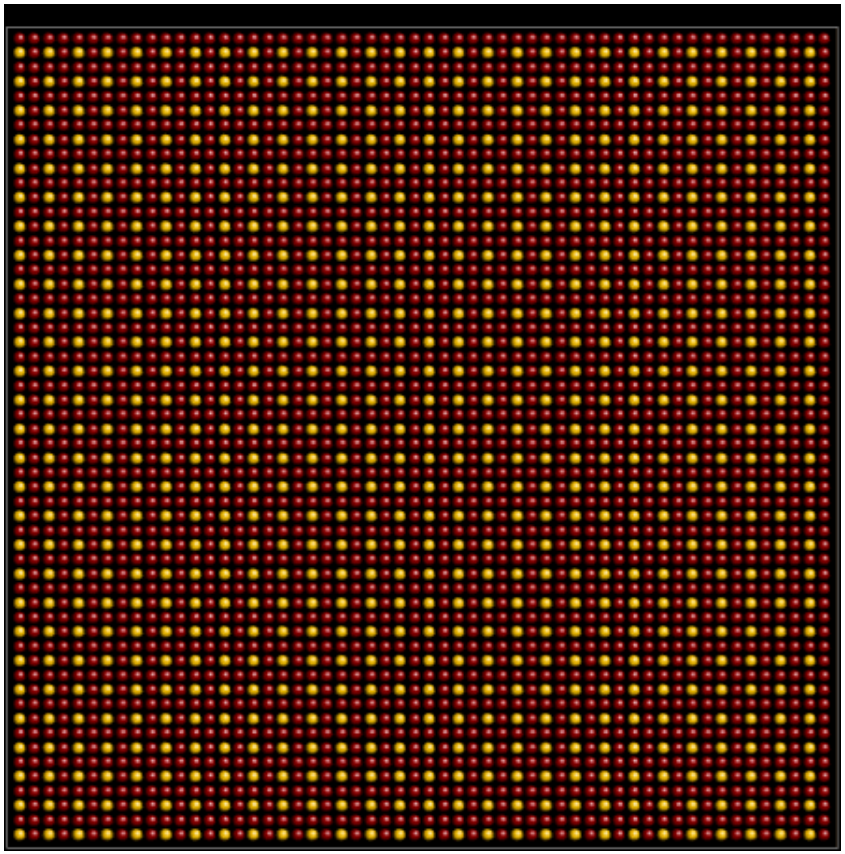
$$N_{d,arcdpa}(E) = \begin{cases} 0 & \text{when} \quad E < E_d \\ 1 & \text{when} \quad E_d < E < 2E_d / 0.8 \\ \dfrac{0.8E}{2E_d}\xi(E) & \text{when} \quad 2E_d / 0.8 < E < \infty \end{cases}$$

$$\xi(E) = \frac{1 - c_{arcdpa}}{(2E_d / 0.8)^{b_{arcdpa}}} E^{b_{arcdpa}} + c_{arcdpa}$$

[Nordlund, Zinkle, et al. Nature communications **9**, 1084 (2018)]

5.6 Ion beam mixing/radiation mixing

- In an alloy, the heat spike can cause lots of mixing: it is very improbable that a liquid atom returns to it original position. If it does not, this is called ion beam or radiation **mixing** (*blandning / sekoitus*)
- This also applies to perfect crystal: an atom in one perfect place can be replaced by another one
- Example: 10 keV cascade in initially ordered Cu_3Au alloy



[Animation: cu3aucasc.avi]

Mixing vs. damage production

- The result is that a cascade displaces a huge lot of atoms, but creates fairly few actual defects
- The NRT value disagrees with both in metals!
  - The name “displacements-per-atom” for dpa is highly misleading, as it does not correspond to either damage or actual displaced atoms

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

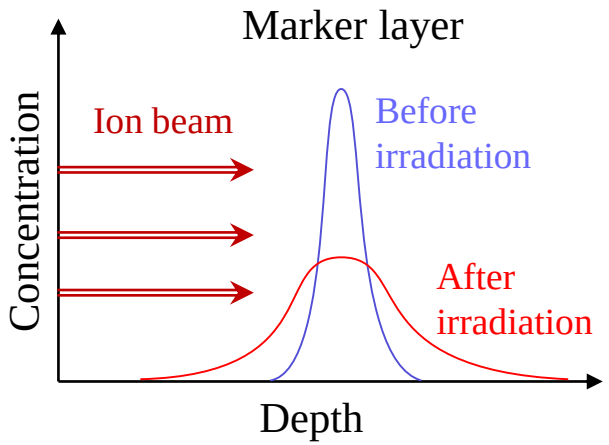
Factor of 8 difference!

Factor of 200 difference!

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

Marker layer experiments for ion beam mixing

- In perfect elemental crystals, ion beam mixing is in principle meaningless as it does not matter whether atoms are replaced by another one
  - And hence also not a measurable quantity



- However, it can be very significant for interface broadening and inclusion dissolution
- The ”pure” elemental mixing can also be observed measured by using very thin initially sharp marker layers, and measuring their broadening
- The radiation mixing is considered to cause a set of random atom displacements, i.e. a random walk
- This gives a clear analogy to diffusion, which is a random walk [A. Einstein, Ann. Phys. 17 (1905) 549]

Ion beam mixing coefficient: experiment

- In the experiments, the mixing coefficient Q can be obtained using the relation

$$Q = \frac{\langle Dt \rangle}{\Phi F_D}$$

- Here $\langle Dt \rangle$ is the ”diffusion” i.e. radiation-caused random walk, t is the irradiation time, Φ the irradiation fluence, and F_D the nuclear deposited energy/depth interval at the marker layer
- In practise, the $\langle Dt \rangle$ can be obtained by measuring the broadening of a Gaussian marker layer variance Ω^2 before and after irradiation using $\langle Dt \rangle = \frac{1}{2}(\Omega^2_{\text{irradiatied}} - \Omega^2_{\text{unirradiatied}})$
- Q has the funny units of Å^5/eV

[Klatt, Averback, Peak, Appl. Phys. Lett. 55 (1989) 1295]

Ion beam mixing coefficient: simulation

- From BCA or MD simulations, one can obtain an ion beam mixing coefficient that is in principle exactly the same as the experimental one using

$$Q = \frac{\langle Dt \rangle}{n_0 E_D} = \frac{\sum_i [R_i(t) - R_i(t=0)]^2}{6\, n_0 E_D}$$

- Here the time t is the time in an individual cascade event, R_i is the position of an atom, and the sum runs over all atoms i in a simulation. The relation between $\langle Dt \rangle$ and R_i comes from the Einstein relation for diffusion. Φ the irradiation fluence, and E_D the nuclear deposited energy in the simulation event

[Diaz de la Rubia et al, Phys. Rev. Lett. 59 (1987) 1930]

Experimental and simulation results on heat spikes

- The mixing efficiency has been measured in a large number of metals with marker layer experiments
- The Q values have later been well reproduced with MD simulations of heat spikes

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]

[Nordlund et al, Phys. Rev. B 57 (1988) R13965]

TABLE I. Ion-mixing data for different matrix materials. Irradiation conditions and symbols in table are given in text.

Matrix	Marker	E_{irr} (keV)	F_D (eV)	$Dt/\phi F_D$ (Å^5/eV)	$T_{1/2}$ (keV)	E_r (keV)	V_t (Å^3)	ΔH_{coh} (eV/atom)	δ (kJ/mol)
C	Ni	500	81.2	2.60	10	5.6	883 401 655	7.36	
C	Ag	500	81.2	2.30	10	5.6	883 401 655	7.36	
C	Au	500	81.2	2.70	10	5.6	883 401 655	7.36	
Al	Ag	650	58.4	20.70	28	17.1	11 494 920	3.33	−22
Al	W	650	58.4	22.50	28	17.1	11 494 920	3.33	−8
Al	Pt	650	58.4	12.70	28	17.1	11 494 920	3.33	−185
Ti	Mo	500	107.4	4.50	50	32.1	7 436 669	4.87	−16
Ti	Hf[a]	300	118.7	11.00	50	32.1	7 436 669	4.87	+1
Ti	Pt[a]	300	118.7	3.30	50	32.1	7 436 669	4.87	−337
Fe	Pt	650	117.0	4.50	65	41.8	2 179 690	4.31	−59
Fe	Au	650	117.0	4.60	65	41.8	2 179 690	4.31	+38
Ni	Pt	650	210.0	5.00	65	42.0	1 434 996	4.44	−22
Ni	Au	650	210.0	7.80	65	42.0	1 434 996	4.44	+34
Cu	Pt	650	189.0	23.20	65	42.6	1 035 344	3.50	−32
Cu	Au	650	189.0	27.40	65	42.6	1 035 344	3.50	−29
Mo	Al	500	197.0	5.80	80	54.6	1 668 422	6.81	−20
Mo	Ti	500	135.0	1.65	80	54.6	1 668 422	6.81	−16
Mo	Pt	650	198.0	6.00	80	54.6	1 668 422	6.81	−115
Ru	Au	500	236.0	7.40	82	56.3	1 018 853	6.74	+65
Ag	Al	650	197.0	93.4	85	58.6	1 751 618	2.96	−21
Ag	Pt	650	197.0	59.0	85	58.6	1 751 618	2.96	−1
Hf	Ti	750	207.0	12.7	110	82.0	2 112 571	6.44	+1
Hf	Ni	750	207.0	17.2	115	82.0	2 112 571	6.44	−147
Ta	Fe	1000	207.0	7.6	115	82.1	1 151 776	8.10	−54
Ta	Ni	1000	207.0	10.4	115	82.1	1 151 776	8.10	−104
Ta	Y	1000	207.0	3.5	115	82.1	1 151 776	8.10	+127
W	Fe	1000	243.0	7.5	115	82.2	719 143	8.66	0
W	Ni	1000	243.0	17.9	115	82.2	719 143	8.66	−11
W	Y	1000	243.0	2.2	115	82.2	719 143	8.66	+110
Pt	Fe	1000	271.5	23.9	110	79.0	479 170	5.85	−47
Pt	Ni	1000	271.5	14.2	110	79.0	479 170	5.85	−17
Au	Ni	1000	271.5	58.0	110	79.4	654 839	3.80	+25
Au	Cu	1000	271.5	142.0	110	79.4	654 839	3.80	−20
Au	Cu	1000	271.5	165.0	110	79.4	654 839	3.80	−20

[a]These samples were irradiated at 77 K and analyzed at 300 K.

[Kim et al, Phys. Rev. B 37 (1988) 38]

Mechanisms of ion beam mixing

- The large variation in the mixing coefficients has several reasons, but two basic ones are well understood:
- In light, low-dense materials the mixing is low because there are no heat spikes/melting, and hence no contribution from melting to the random walk
- Comparing metals with very similar mass and atomic density like Cu vs. Ni and Au vs. Pt, one can still see fairly large differences
  - This difference is because Cu and Au have much lower melting points than Ni and Pt: the heat spike molten zone is larger and cools down slower

TABLE I. Ion-mixing data for different matrix materials.

Matrix	Marker	E_{irr} (keV)	F_D (eV)	$Dt/\phi F_D$ (Å^5/eV)
C	Ni	500	81.2	2.60
C	Ag	500	81.2	2.30
C	Au	500	81.2	2.70
Al	Ag	650	58.4	20.70
Al	W	650	58.4	22.50
Al	Pt	650	58.4	12.70
Ti	Mo	500	107.4	4.50
Ti	Hf[a]	300	118.7	11.00
Ti	Pt[a]	300	118.7	3.30
Fe	Pt	650	117.0	4.50
Fe	Au	650	117.0	4.60
Ni	Pt	650	210.0	5.00
Ni	Au	650	210.0	7.80
Cu	Pt	650	189.0	23.20
Cu	Au	650	189.0	27.40
Mo	Al	500	197.0	5.80
Mo	Ti	500	135.0	1.65
Mo	Pt	650	198.0	6.00
Ru	Au	500	236.0	7.40
Ag	Al	650	197.0	93.4
Ag	Pt	650	197.0	59.0
Hf	Ti	750	207.0	12.7
Hf	Ni	750	207.0	17.2
Ta	Fe	1000	207.0	7.6
Ta	Ni	1000	207.0	10.4
Ta	Y	1000	207.0	3.5
W	Fe	1000	243.0	7.5
W	Ni	1000	243.0	17.9
W	Y	1000	243.0	2.2
Pt	Fe	1000	271.5	23.9
Pt	Ni	1000	271.5	14.2
Au	Ni	1000	271.5	58.0
Au	Cu	1000	271.5	142.0
Au	Cu	1000	271.5	165.0

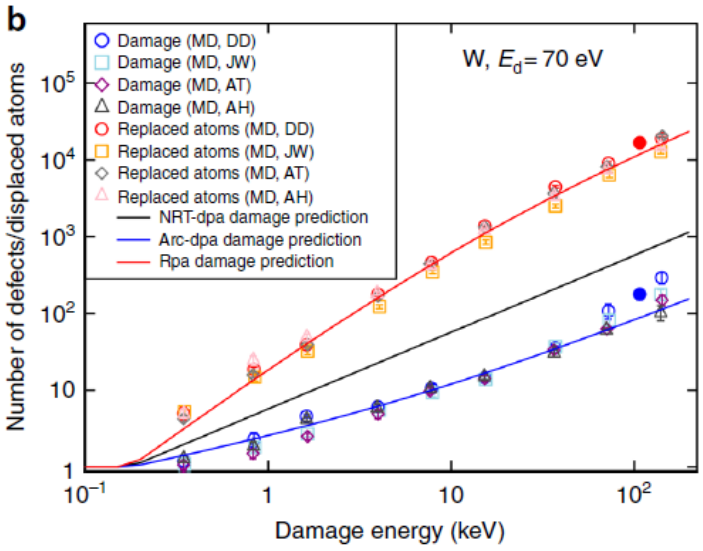
[Nordlund et al, J. Appl. Phys. 83 (1998) 1238]

Rpa equation for mixing

- The number of atoms dispaced by mixing in metals can be fairly well described with the ”replacements-per-atom” **(rpa)** equation
- It modified the NRT-dpa similar to the arc-dpa, but in a different functional form and direction:

$$\xi_{\mathrm{rpa}}(T_{\mathrm{d}}) = \left(\frac{b_{\mathrm{rpa}}^{c_{\mathrm{rpa}}}}{(2E_{\mathrm{d}}/0.8)^{c_{\mathrm{rpa}}}} + 1 \right) \frac{T_{\mathrm{d}}^{c_{\mathrm{rpa}}}}{b_{\mathrm{rpa}}^{c_{\mathrm{rpa}}} + T_{\mathrm{d}}^{c_{\mathrm{rpa}}}}.$$

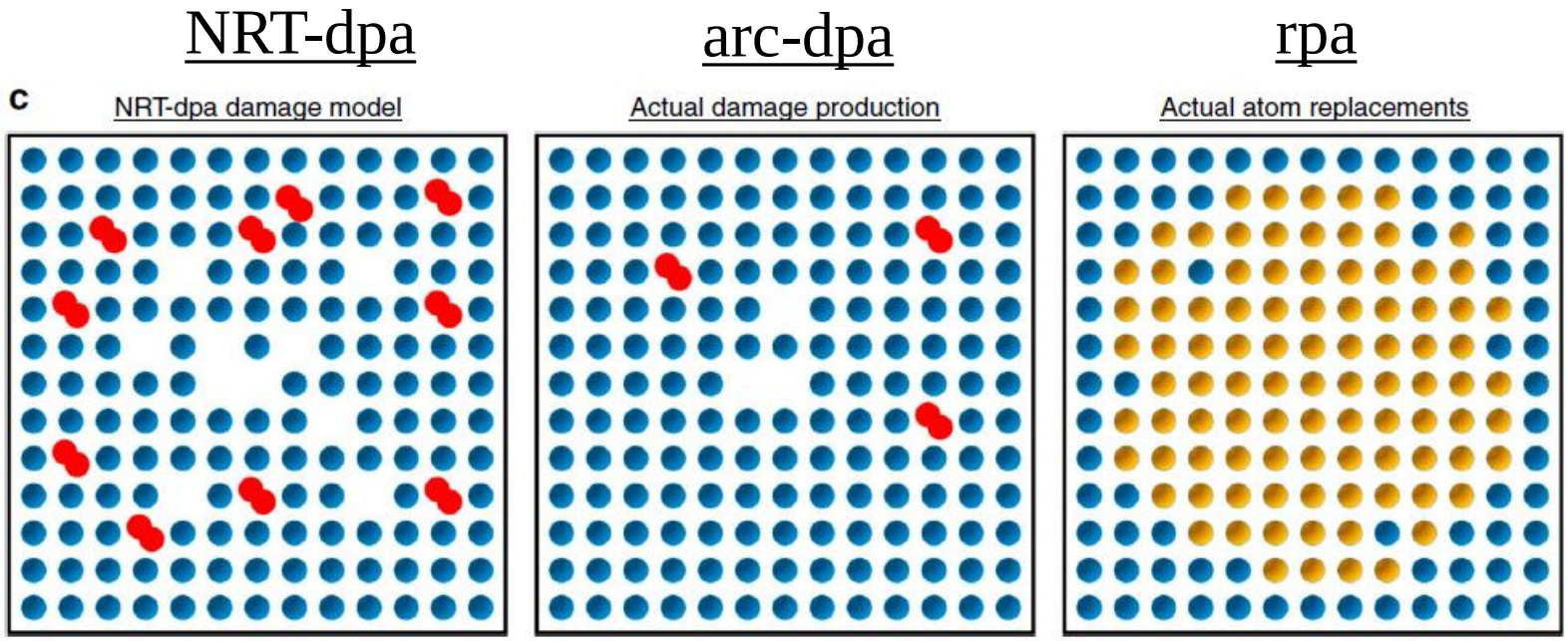
- The rpa also gives very good agreement with MD data



[Nordlund, Zinkle, et al. Nature communications **9**, 1084 (2018)]

Schematic comparison of NRT-dpa, arc-dpa and rpa

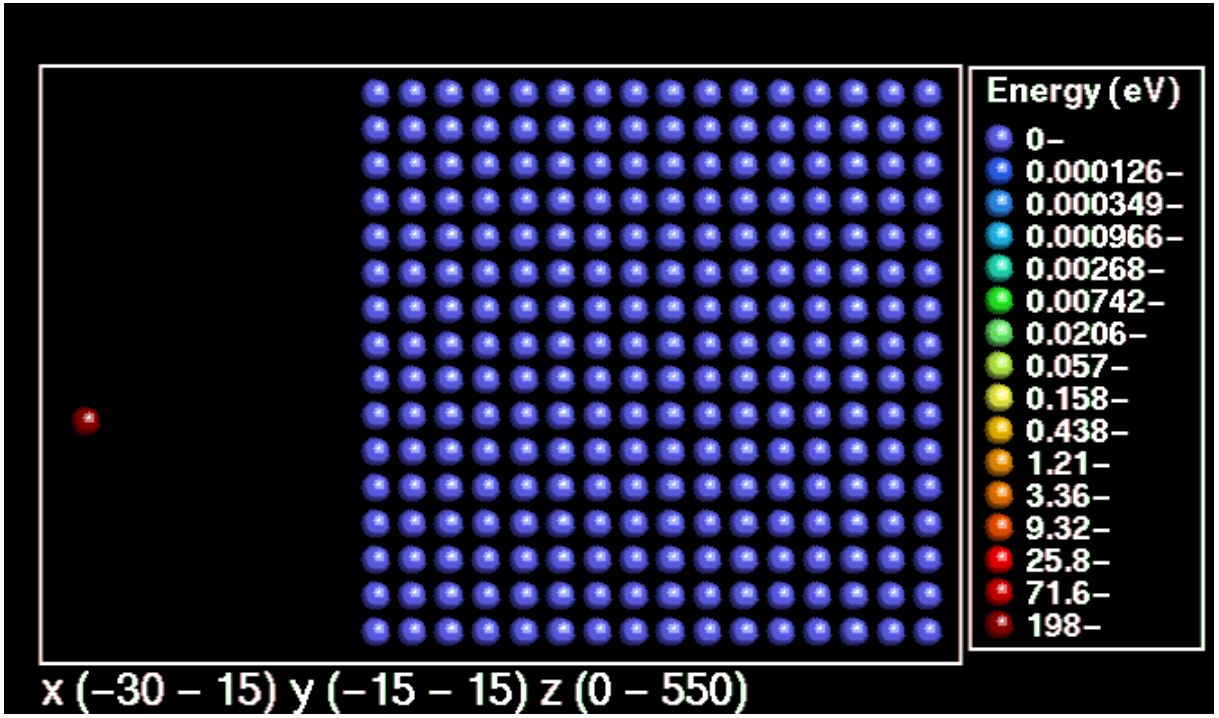
- The differences of the three dpa quantities and their physical meaning can be illustrated like this (a 2D cross section of end result of a heat spike)



[Nordlund, Zinkle, et al. Nature communications **9**, 1084 (2018)]

5.7 Surface effects: adatoms and sputtering

- For any irradiation event near surface, a recoiling atom can instead of going into an interstitial atom, become an extra atom on the surface, an **adatom** (adatom/adatomi), or leave the material, **sputter** (*förstoftas / sputrautua*)
- Both effects are visible here:



[Animation: au500.avi]

Sputtering

- The study of sputtering is a big topic in itself, and this is actually the oldest known radiation effect; it was first reported in [W. R. Grove. On the electro-chemical polarity of gases. Phil. trans. Roy. Soc. London, 142:87, 1852] and occurred regularly in cathode-ray tubes already in the 1800's
- The sputtering is described by the sputtering yield

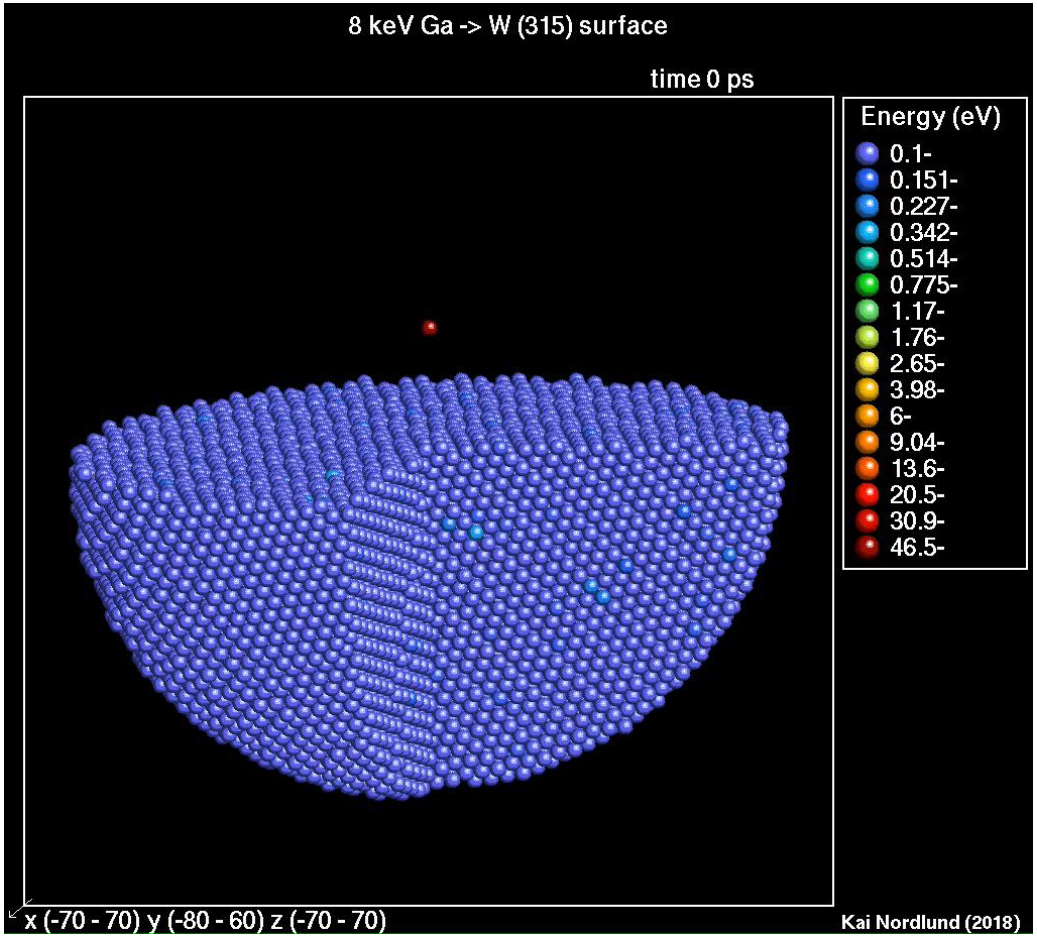
$$Y = \frac{\text{Number of outcoming atoms}}{\text{Number of incoming particles}}$$

(cf. section 2)

- Sputtering can also occur by electrons, especially in ionic materials, and even neutrons (although then the yields are extremely small)
- Sputtering is in regular industrial use e.g. for making coatings.
- Sputtering can be modelled well by BCA when there are no heat spikes, and MD when there are

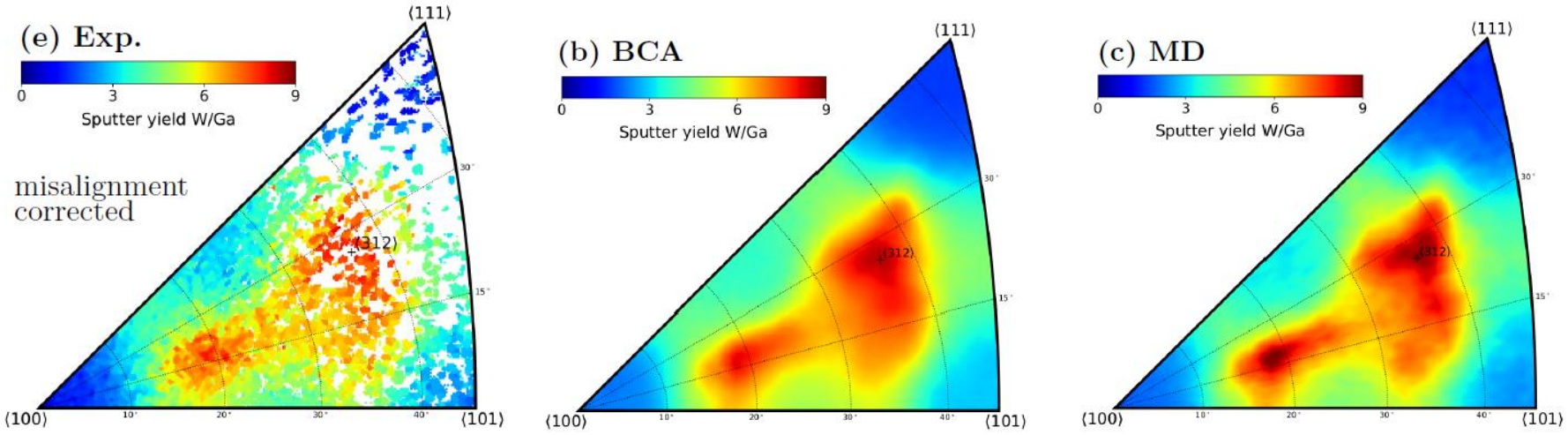
Example of sputtering simulation

- Sputtering by 8 keV Ga atoms on W (315 surface orientation)



Crystal direction dependence of sputtering

- In crystalline materials, the sputtering yield depends strongly on the crystal surface orientation
  - The reason is related to channeling
- Results for 30 keV Ga ions on W
  - Note that there is a > factor 5 difference, and no wide regime of constant yields!

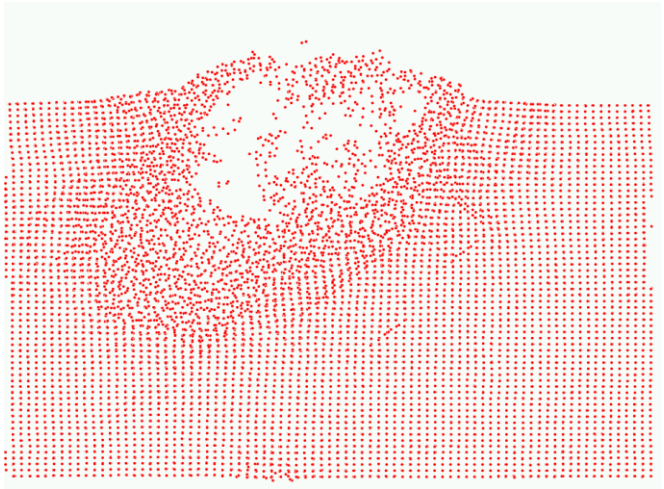


[K. Schlueter et al, (2020) to be submitted for publication]

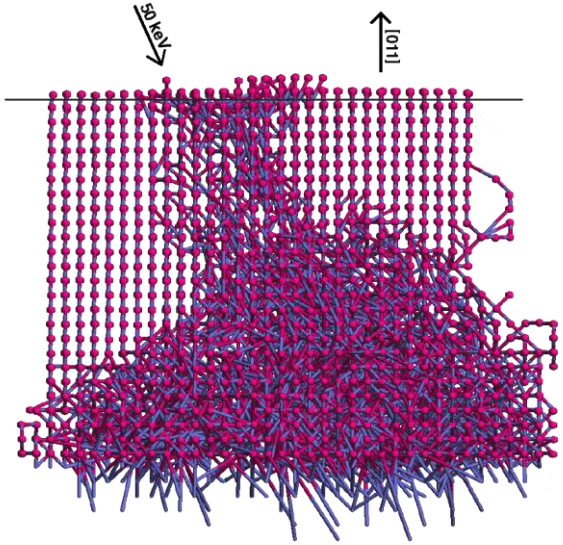
Surface effects by heat spikes

- If a heat spike intersects a surface, this can cause liquid flow of matter to the surface, and sputtering of massive clusters
  - It can also cause cratering or coherent displacement of atoms (dislocation loop punching towards the surface)

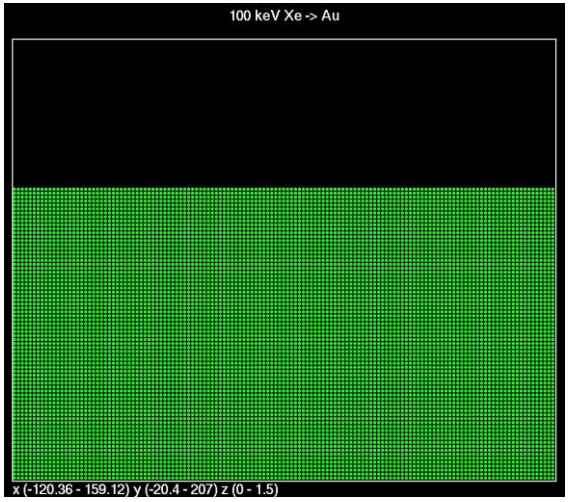
Ghaly and Averback, PRL 1994



Nordlund *et al*., Nature 1999



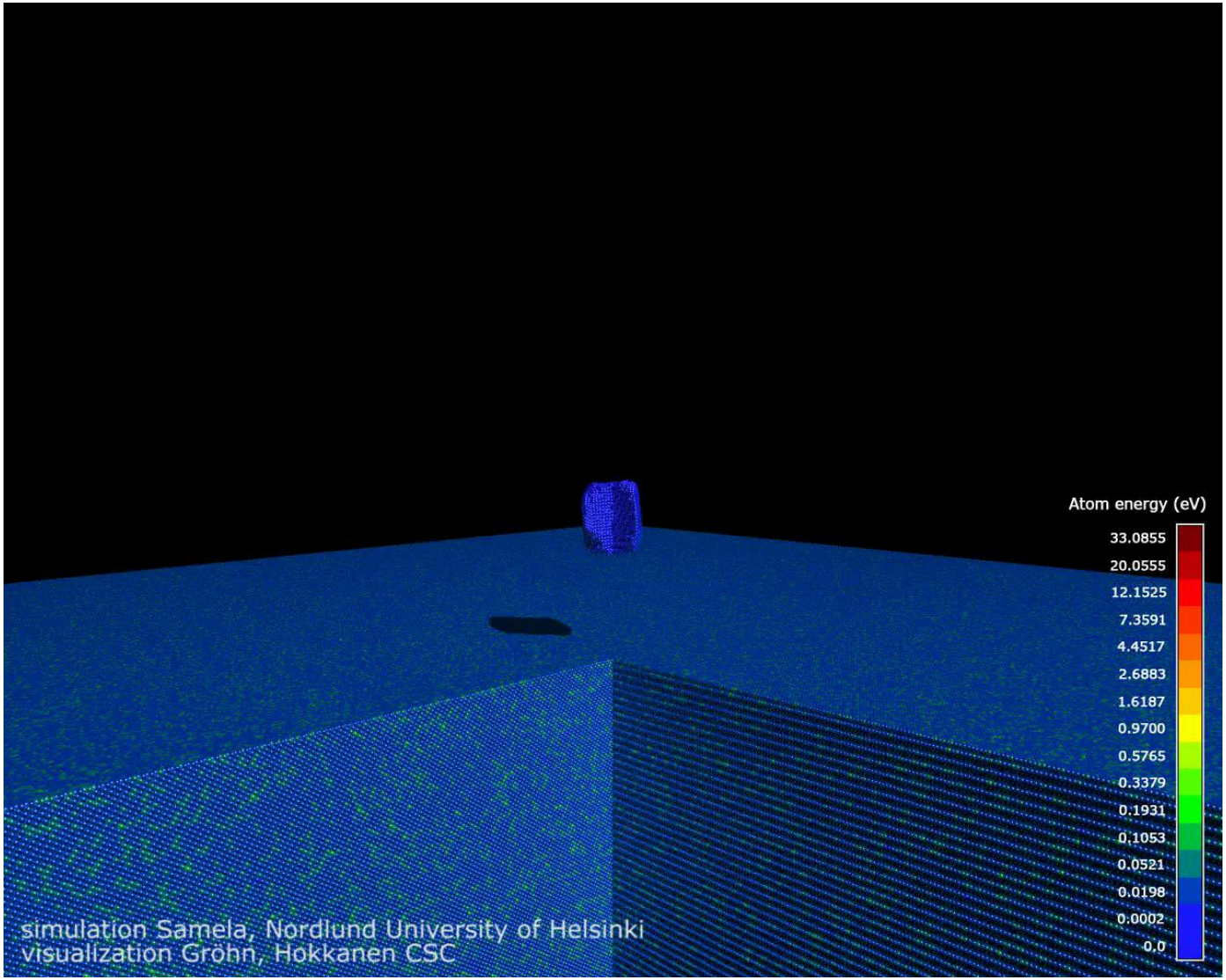
Nordlund, Physics World 2001



[Animation: 100kevxeauanim.avi]

Surface effects by clusters

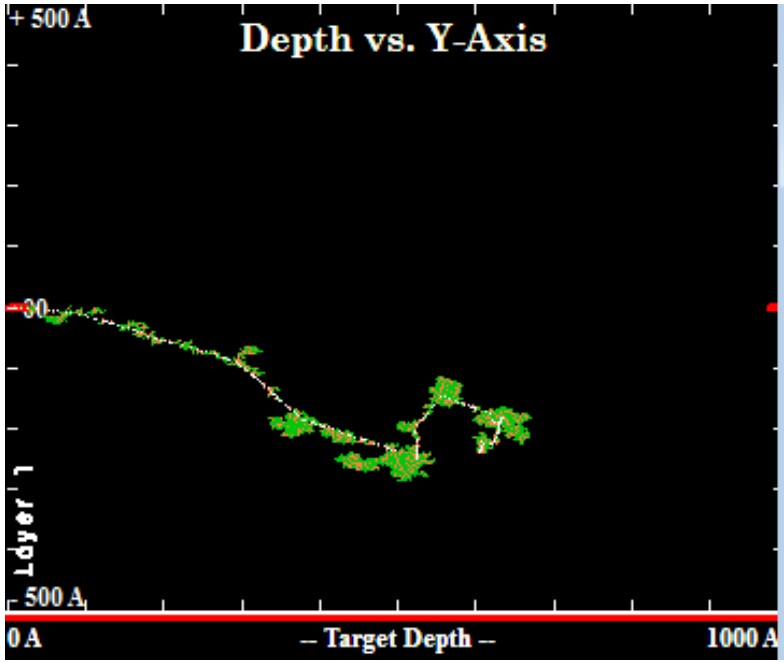
- Cluster ion irradiation can lead to truly massive cratering



[Animation: Crater_with_credits …. mpg]

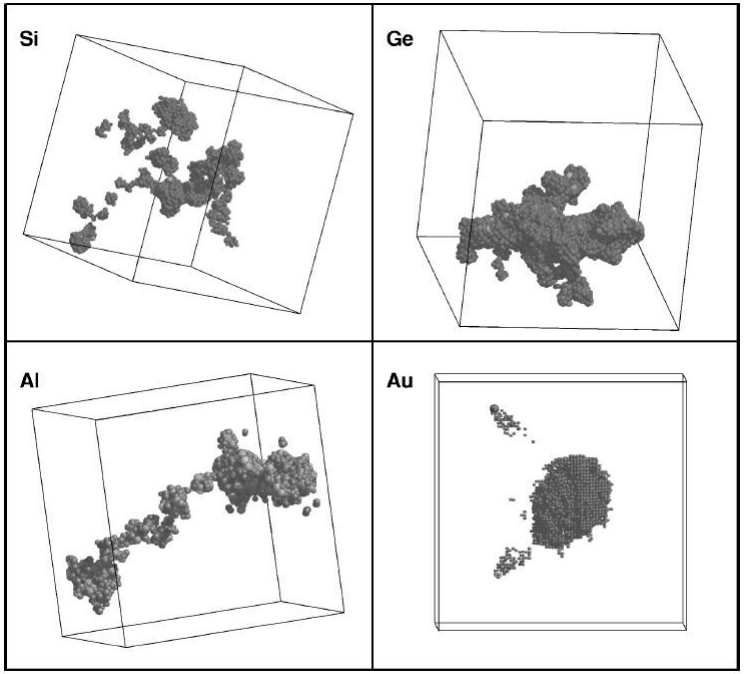
5.8 Breakup into subcascades

- Finally, when the ion energy increases, the ion path starts to be so long due to the decreasing cross section, that there are regions with virtually no damage
- This behaviour is known as subcascade formation, and can also be deduced from BCA simulations
- Example: SRIM simulation of a single 100 keV Ar ion impact on Au, with a threshold energy of 10 eV
- Green regions are subcascades. in between very little damage



Subcascade breakdown threshold?

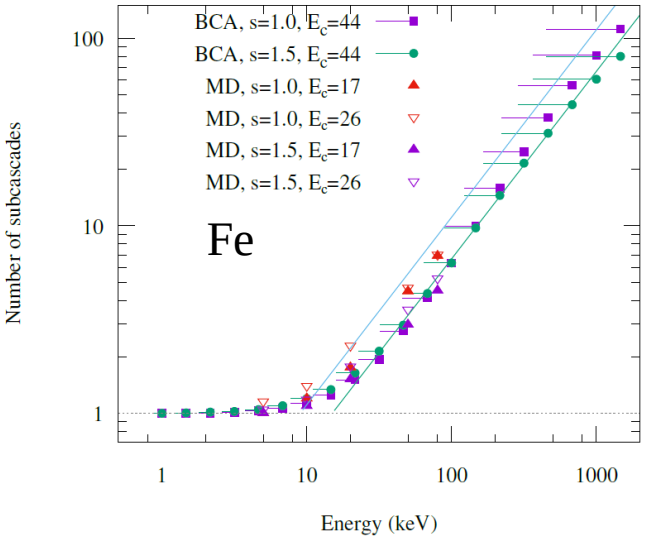
- The energy at which cascades supposedly fully break up into subcascades is known as the subcascade threshold energy
- It is not entirely well defined, is stochastic, and depends on melting point and what quantity is measured (e.g. mixing or damage)
- In general, however, it clearly increases with density of material: e.g. in Si already 10 keV cascades are split into subcascades, whereas in W or Pt the threshold may be >~ 100 keV



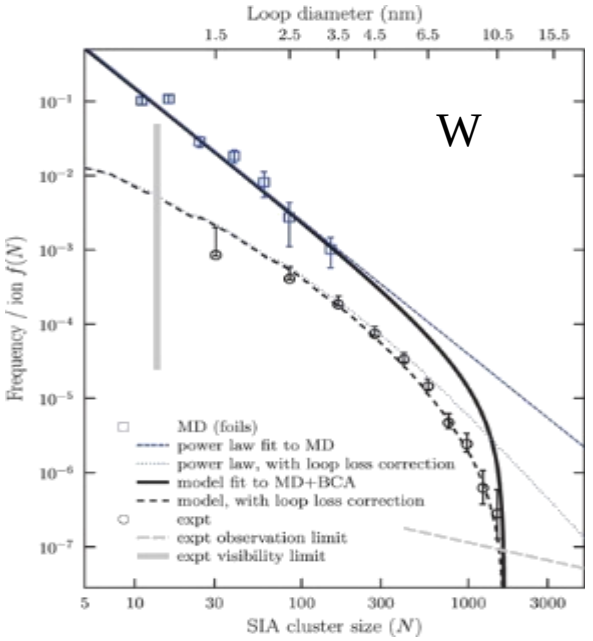
[E. Zarkadoula et al, J. Phys. Condens. Matt. **25**, 125402 (2013)]

Model for subcascade breakdown threshold

- Several models have been made for the subcascade breakdown energy, typically based on analyzing BCA simulations
  - More recently also combinations of BCA and MD
- The most recent models agree on that there is no single sharp threshold, but the transition from cascades to subcascades occurs over about 1 order of magnitude in energy



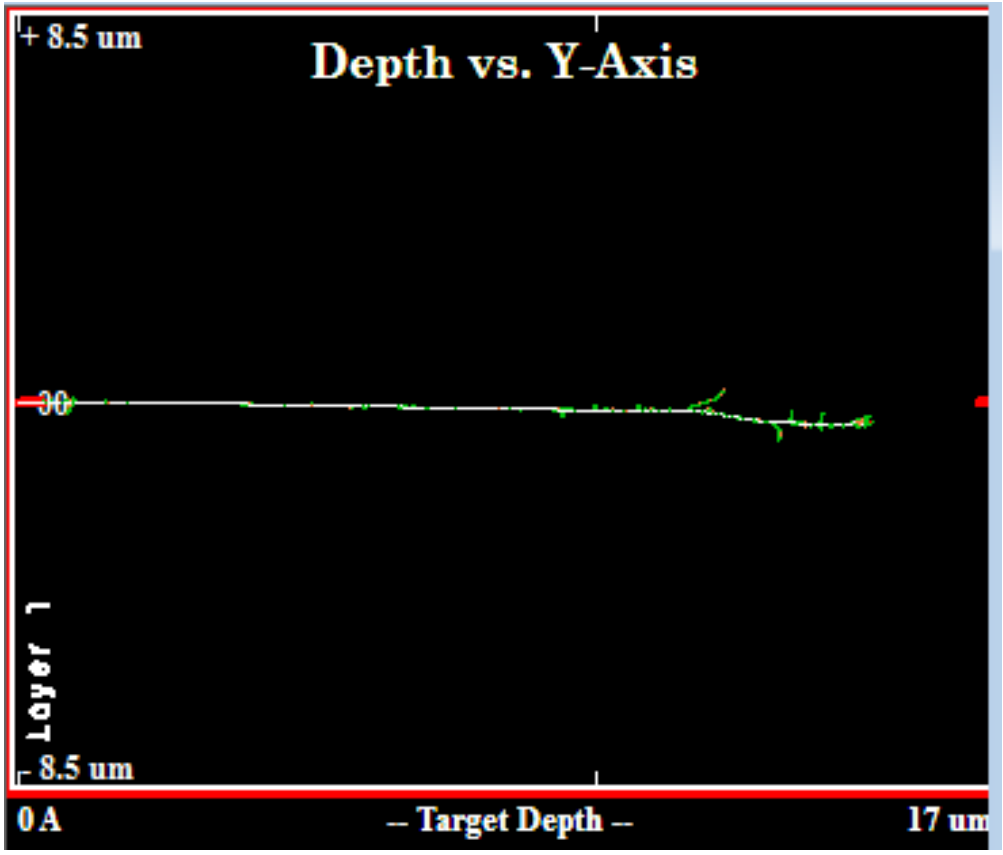
[A. De Backer et al, J. Phys.: Cond. Matter 30 (2018) 405701]



[Sand et al, Mater. Res. Lett. 5 (2017) 357]

Swift heavy ion regime

- Finally, when the ion energy gets to the 100 keV/amu range
- Example: 100 MeV Xe -> Au, single SRIM trajectory
  - The swift heavy ion damage mechanism is dominated by the electronic stopping, and was discussed in section 4.



What should you have learned from this section?

- You understand how many-body collisions can be simulated with molecular dynamics (MD)
- You understand the basics of the MD algorithms
- You understand how many-body collisions lead to damage production
- You know the concept of thermal spikes and how damage is produced and recombined in them
- You understand qualitatively how damage is produced in different energy ranges
- You know the concepts of mixing, sputtering and surface cratering
- You know what subcascades are