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Tutorial: Molecular dynamics simulations for irradiation effects

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Greets from the white nights in Finland

 [Picture by Kai Nordlund, midsummer 2012, Kukkia lake at midnight seen from Kuohijoki village]

The ion beam simulation groups in Helsinki

Prof. Kai Nordlund
Principal investigator

Doc. Antti Kuronen
Principal investigator

Doc. Krister Henriksson
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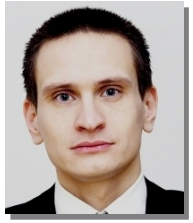
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Doc. Flyura Djurabekova*
Principal investigator

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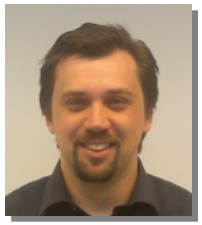
M Sc. Mohammad Ullah
Irradiation of GaN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M Sc Laura Bukonte
Fusion reactor mat'ls

M Sc Andrey Ilinov
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Nanowires

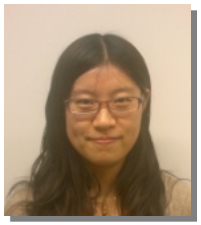
M Sc Stefan Parviainen
Particle physics mat'ls

M Sc Kostya Avchachov
Irradiation of metals

M Sc Aleksi Leino
Nanostructures in silica

MSc Harriet Åhlgren
Graphene

MSc Morten Nagel
Fusion reactor mat'ls


M´Sc Yi-Nan Liu
Fusion reactor mat'ls

M Sc Elnaz Safi
Fusion reactor mat'ls

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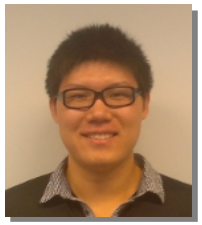
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Nanoclusters

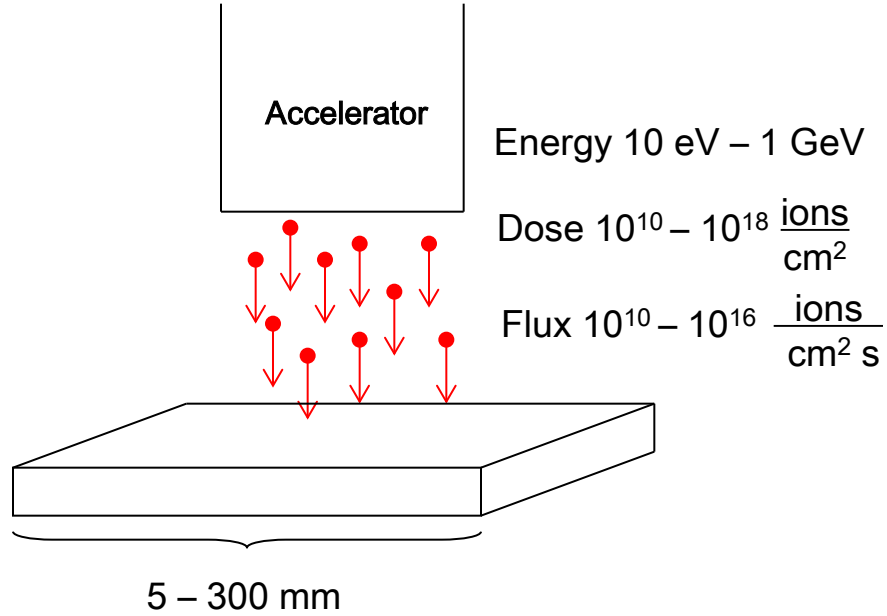
M Sc Anders Korsbäck
Particle physics materials
(CERN)

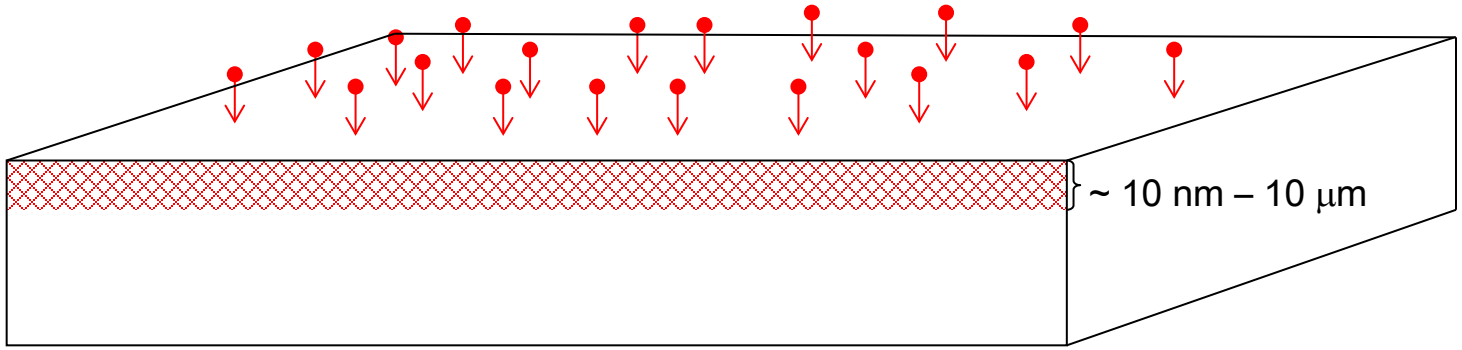
Contents

- Background
  - Irradiation effects in materials – brief summary of physics
  - The rich materials science emerging from ion irradiation
- Molecular dynamics
  - General approach
  - Features specific to ion irradiation and Irradiation effects
- Some examples of recent applications from our group
  - … of course many other groups also do excellent work …
- Extra slides at end on Binary Collision Approximation and Kinetic Monte Carlo
  - **Slides available below my web home page, google for "Kai Nordlund" and click on the "Tutorials…" link**

Background

- Materials modification with ion beams: ions from an accelerator are shot into a material
- Huge (~ G€) business in semiconductor industry!
- Extensively studied since 1950's or so.

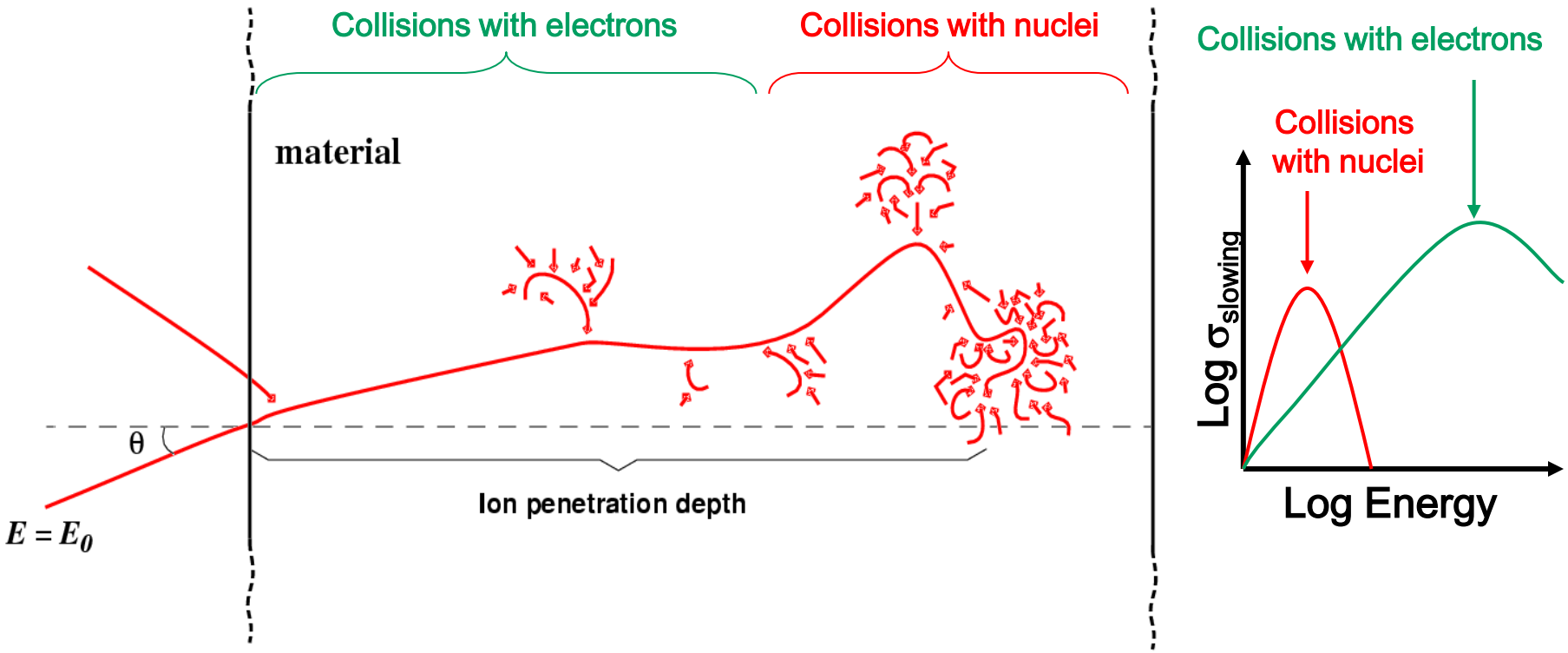




Irradiation effects:

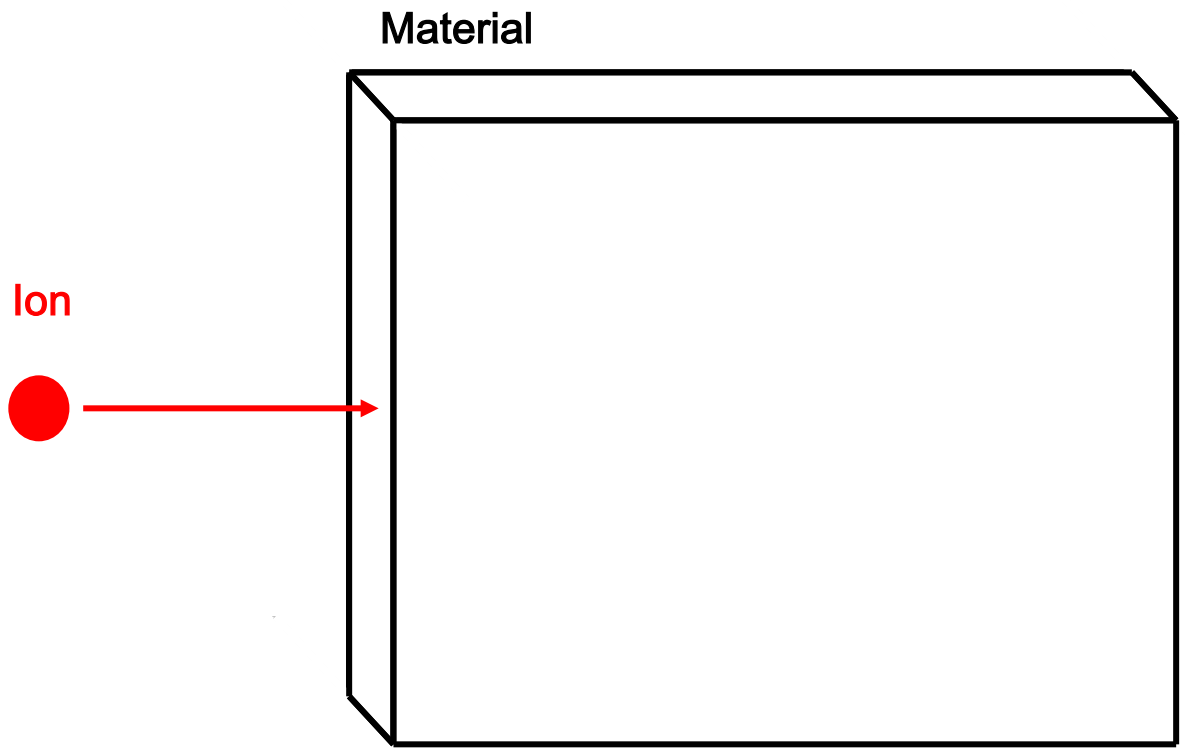
Basic physics

- Schematical illustration of the ion slowing-down process



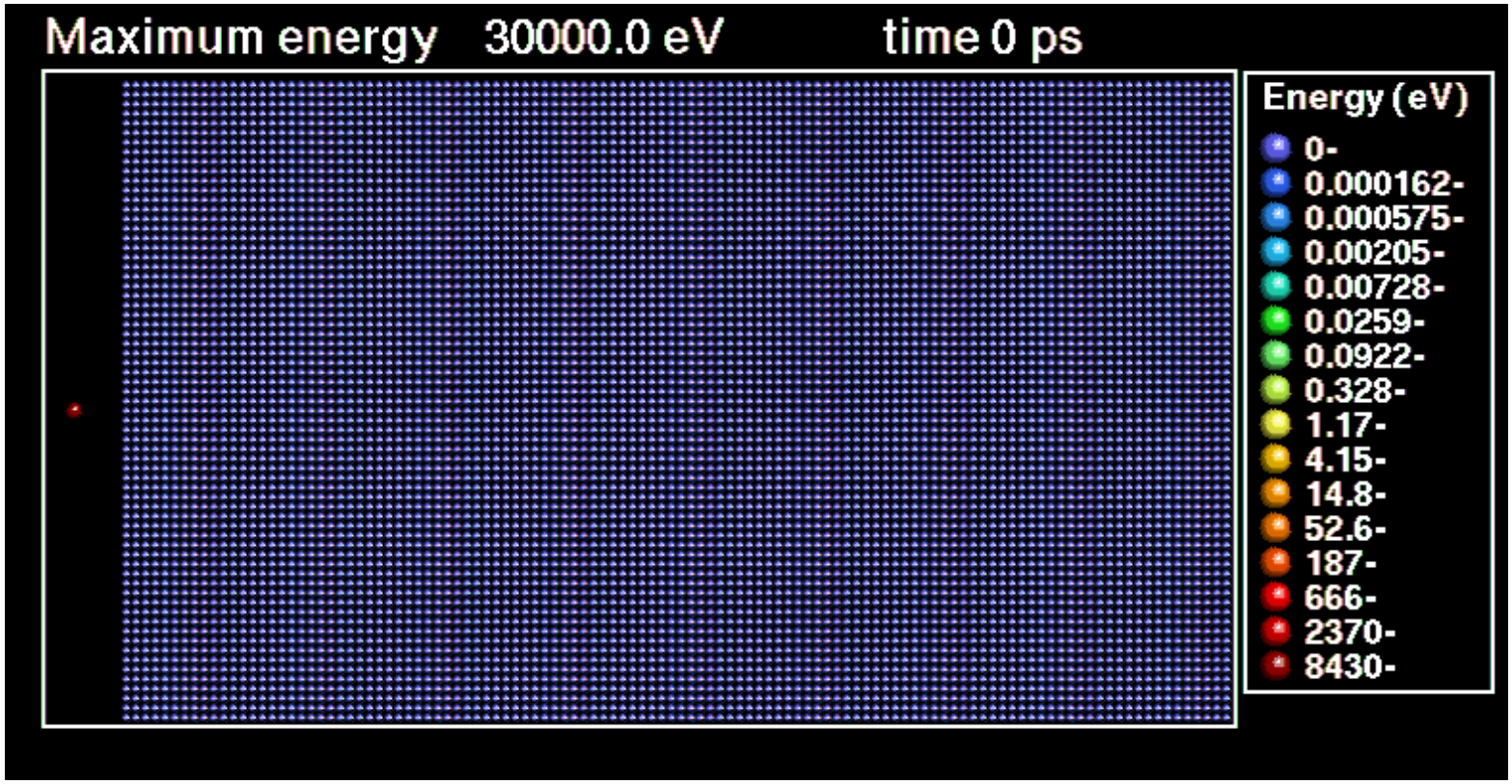
Animation view from MD

- A molecular dynamics (MD) simulation can make it much clearer what irradiation effects really looks like
- Cross sectional view common



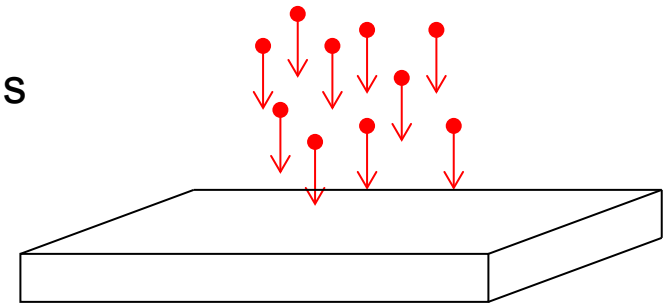
Irradiation effects:

Animation view



Ion beam and plasma energies and fluxes

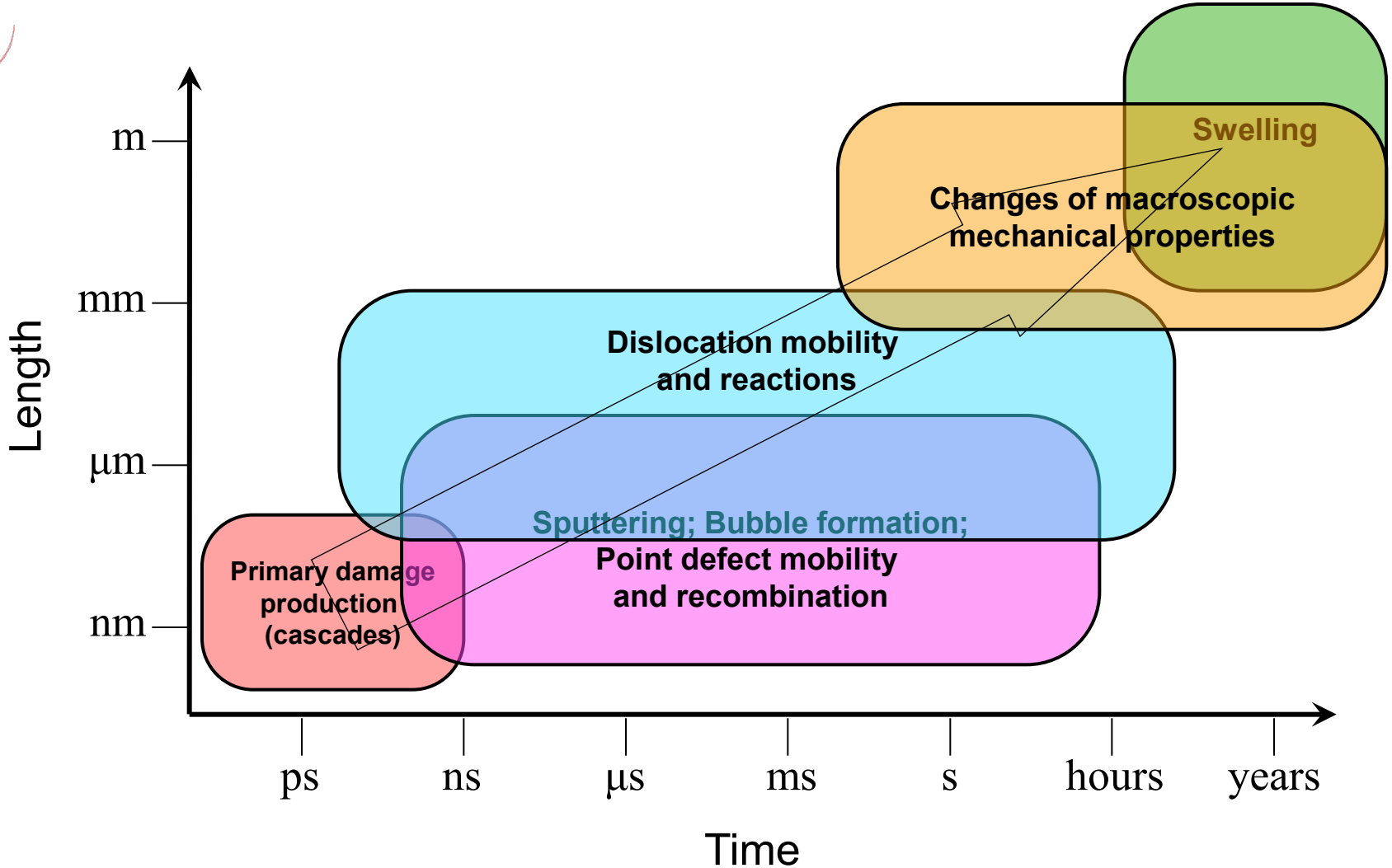
- How do ions hit a material?
- From an accelerator, with a well-defined single energy E_0 with very little energy spread
  - Time between impacts ~ μs – s on a nanometer scale => each impact independent of each other



- From a plasma more complex energy, wider energy spread, depends on kind of plasma
  - If fluxes large, impacts can be close to each other in time
  - In an arc plasma, collision cascades can actually be overlapping in place and time!
- For neutrons, recoils deep inside the material, after that physics the same except no surface effects!

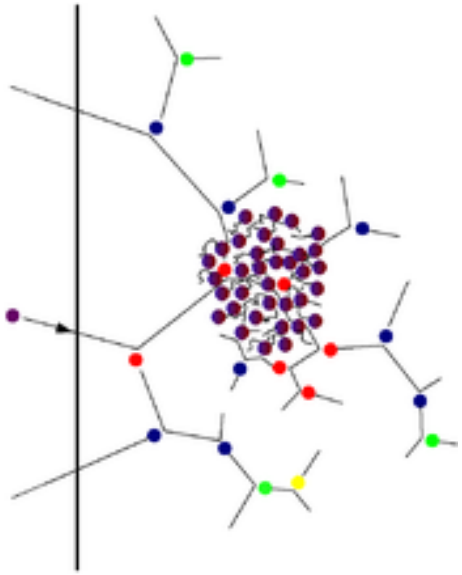
Irradiation effects:

What happens physically in the materials?

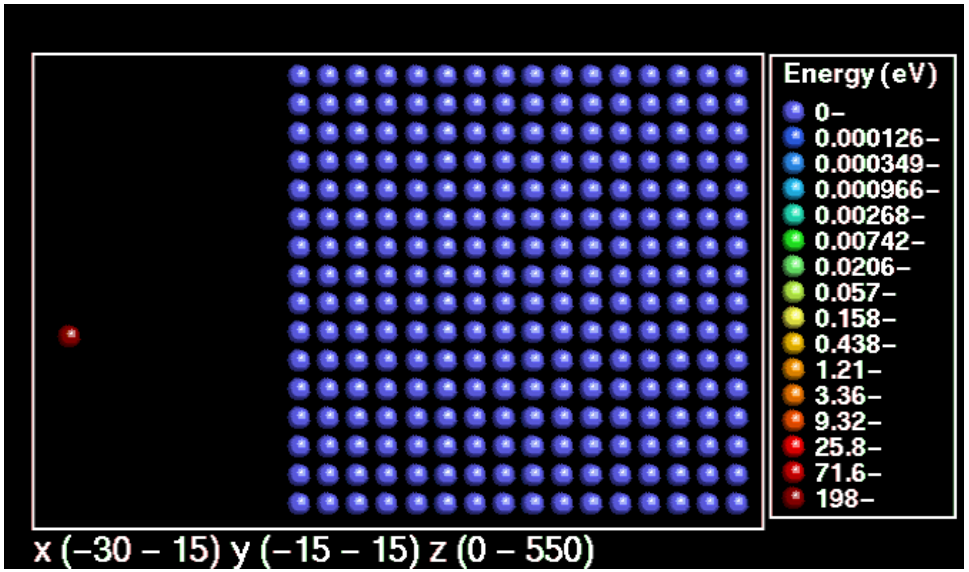


The rich materials science of irradiation effects

- This is a demanding (and hence fun! ☺) range of materials physics issues to work on.
- First stage: collision cascade by single incoming ion
- Simplified view:

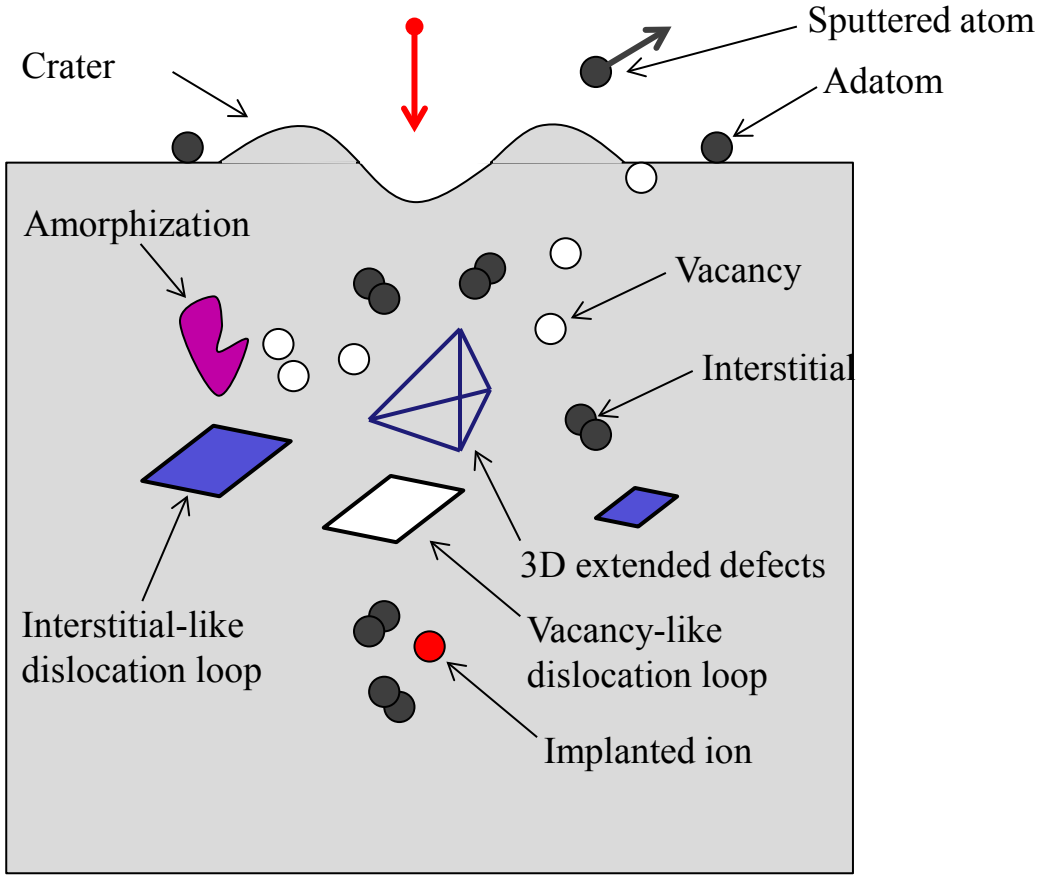


[Wikipedia by Kai Nordlund]



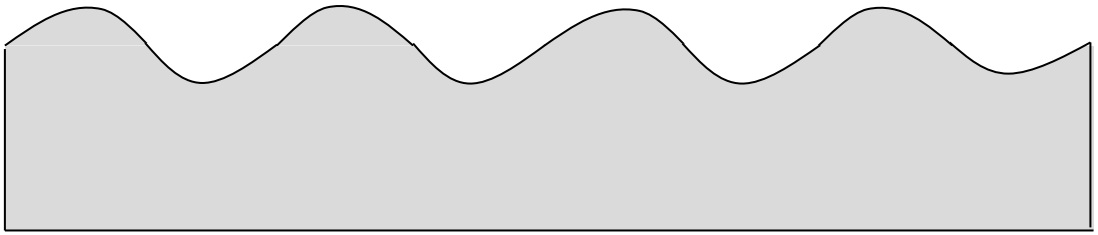
The rich materials science of Irradiation effects

- But actually much more is going on.
- Just for a single ion all of the below *may* be produced:



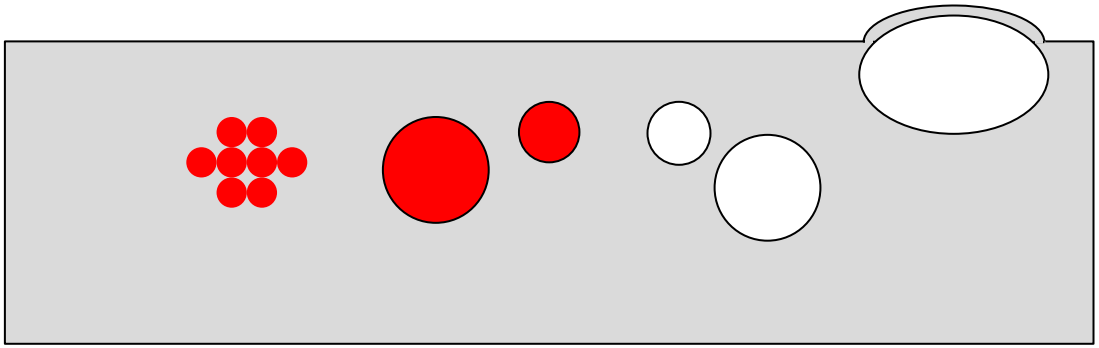
The rich materials science of Irradiation effects: high fluences

- In addition, for multiple ions i.e. prolonged irradiation many more things can happen, for instance:
  - Spontaneous roughening/ripple formation



[T. K. Chini, F. Okuyama, M. Tanemura, and K. Nordlund, Phys. Rev. B 67, 205403 (2003); Norris et al, Nature communications 2, 276 (2011)]

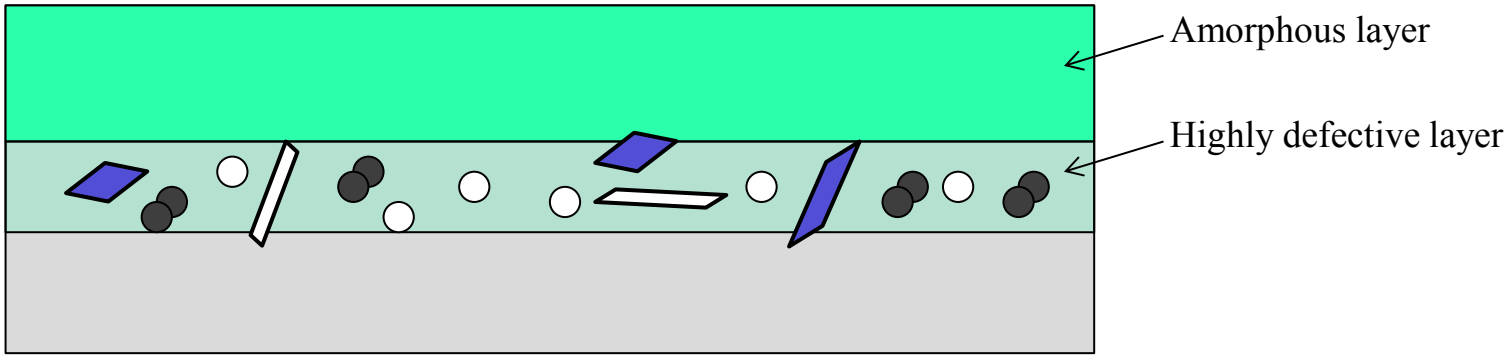
  - Precipitate/nanocluster, bubble, void or blister formation inside solid



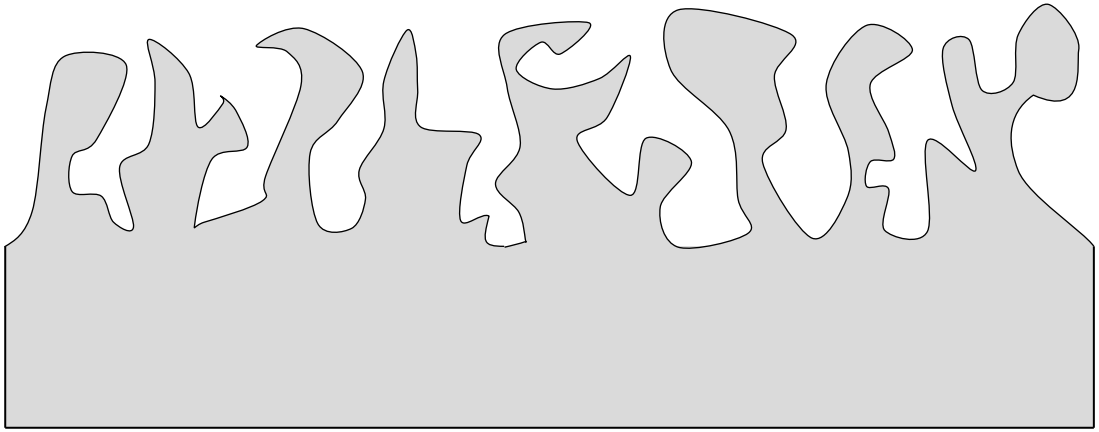
[Bubbles e.g: K. O. E. Henriksson, K. Nordlund, J. Keinonen, D, Physica Scripta T108, 95 (2004); Nanocrystals e.g. 75S. Dhara, Crit. Rev. Solid State Mater. Sci. 32, 1 [2007)]

The rich materials science of Irradiation effects: high fluences

- Phase changes, e.g. amorphization:

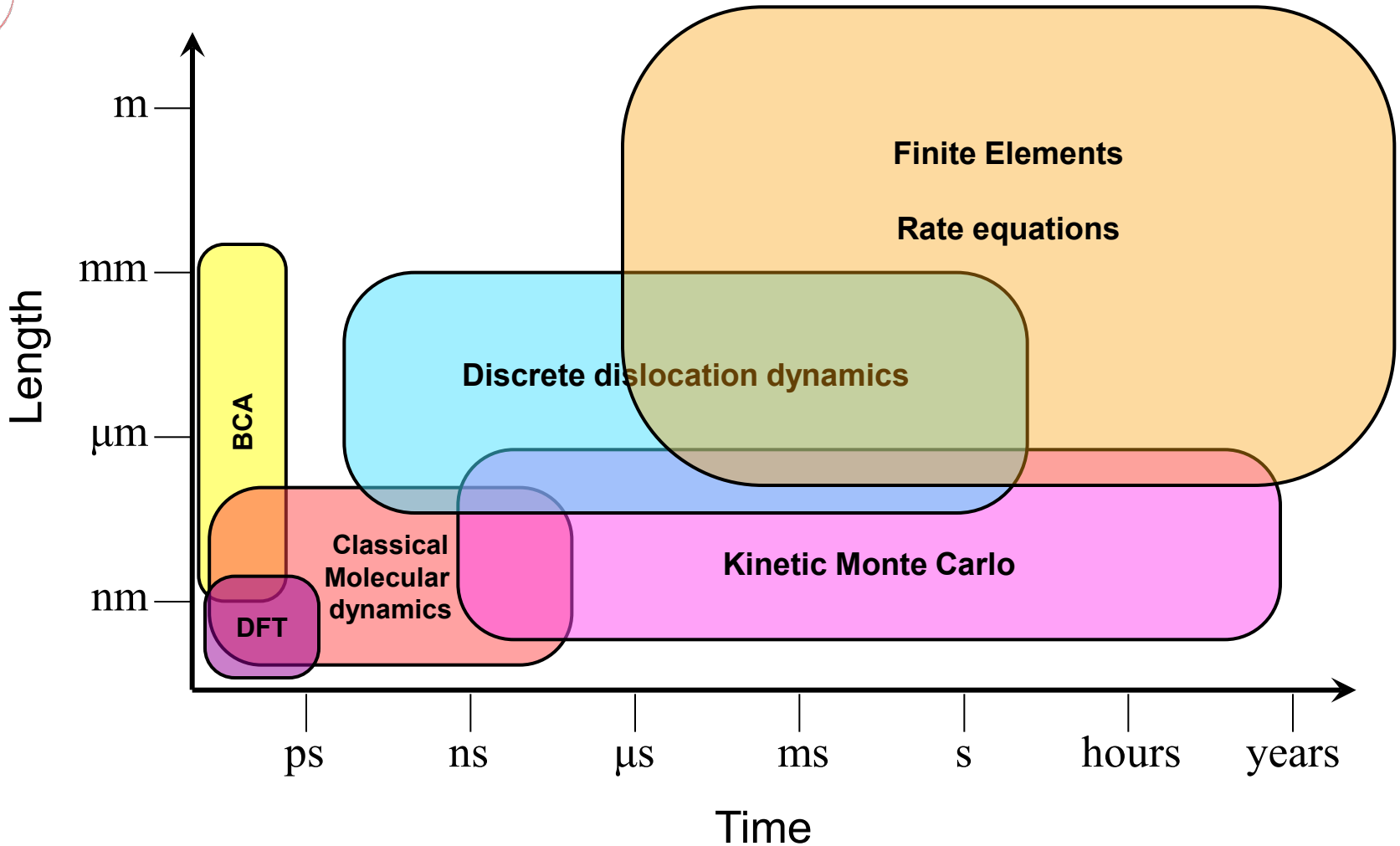


- Spontaneous porousness formation, “fuzz” (e.g. in Ge, W)



Irradiation effects:

What is needed to model all this?



Irradiation effects:

What is needed to model the atomic level?

- One needs to be able to handle:
  1) keV and MeV-energy collisions between nuclei
  2) Energy loss to electronic excitations
  3) Transition to high-pressure and high-T thermodynamics (E_{kin} ~ 1 eV)
  4) Realistic equilibrium interaction models
  5) Phase changes, segregation, sputtering, defect production…
  6) Long-term relaxation of defects
- Sounds daunting, but:
  - Steps 1 – 2 can be handled in a binary collision approximation simulation
  - Steps 1 – 5 can all be handled in the same molecular dynamics simulation
  - Step 6 requires kinetic Monte Carlo or rate theory

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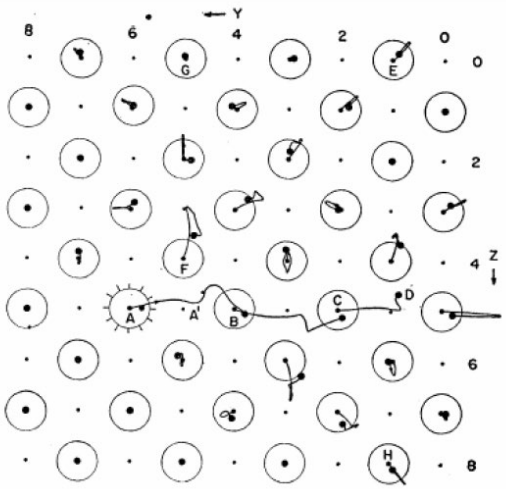
- Molecular dynamics
  - General approach
  - Features specific to ion irradiation and Irradiation effects
- Some examples of recent applications from our group
  - … of course many other groups also do excellent work …
- Extra slides at end on Binary Collision Approximation and Kinetic Monte Carlo

MD = 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!



MD algorithm

Give atoms initial $\boldsymbol{r}^{(t=0)}$ and $\boldsymbol{v}^{(0)}$, choose short Δt

↓

Get forces $\boldsymbol{F} = -\nabla V(\boldsymbol{r}^{(i)})$ *or* $\boldsymbol{F} = \boldsymbol{F}(\Psi)$ and $\boldsymbol{a} = \boldsymbol{F}/m$

↓

Move atoms: $\boldsymbol{r}^{(i+1)} = \boldsymbol{r}^{(i)} + \boldsymbol{v}^{(i)}\Delta t + {}^{1}/_{2}\,\boldsymbol{a}\,\Delta t^2$ + correction terms

Update velocities: $\boldsymbol{v}^{(i+1)} = \boldsymbol{v}^{(i)} + \boldsymbol{a}\Delta t$ + correction terms

↓

Move time forward: $t = t + \Delta t$

↓

Repeat as long as you need

MD – atom representations

- MD naturally needs atom coordinates (and velocities)
- Atom coordinates can simply be read in from an ASCII text file
- Simple but for atoms good enough format: .XYZ

```
  500
FCC cell made by makeFCC with a= 3.52 n= 5 5 5
Cu        -7.92        -7.92        -7.92 1
Cu        -6.16        -6.16        -7.92 1
Cu        -7.92        -6.16        -6.16 1
Cu        -6.16        -7.92        -6.16 1
Cu        -7.92        -7.92         -4.4 1
Cu        -6.16        -6.16         -4.4 1
```

- Arrays in an MD code, e.g.:

```
double precision :: x(MAXATOMS),y(MAXATOMS),z(MAXATOMS)
```

MD – Solving equations of motion

- The solution step $\boldsymbol{r}^{(i+1)} = \boldsymbol{r}^{(i)} + \boldsymbol{v}^{(i)}\Delta t + {}^1/_2\, \boldsymbol{a}\, \Delta t^2 +$ correction terms is crucial
- What are the "correction steps"?
- There is any number of them, but the most used ones are of the predictor-corrector type way to solve differential equations numerically:

Prediction: $\boldsymbol{r}^{(i+1),p} = \boldsymbol{r}^{(i)} + \boldsymbol{v}^{(i)}\Delta t + {}^1/_2\, \boldsymbol{a}\, \Delta t^2 +$ more accurate terms

↓

Calculate $\boldsymbol{F} = -\nabla\, V(\boldsymbol{r}^{(i)})$ and $\boldsymbol{a} = \boldsymbol{F}/m$

↓

Calculate corrected $\boldsymbol{r}^{(i+1),c}$ based on new $\boldsymbol{a}$

↓

MD – Solving equations of motion

- Simplest possible somewhat decent algorithm: velocity Verlet

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \Delta t \mathbf{v}(t) + \tfrac{1}{2}\Delta t^2 \mathbf{a}(t)$$

$$\mathbf{v}^{\mathrm{p}}\left(t+\tfrac{1}{2}\Delta t\right) = \mathbf{v}(t) + \tfrac{1}{2}\Delta t \mathbf{a}(t)$$

$$\mathbf{v}^{\mathrm{c}}(t+\Delta t) = \mathbf{v}^{\mathrm{p}}\left(t+\frac{1}{2}\Delta t\right) + \frac{1}{2}\Delta t \mathbf{a}(t+\Delta t).$$

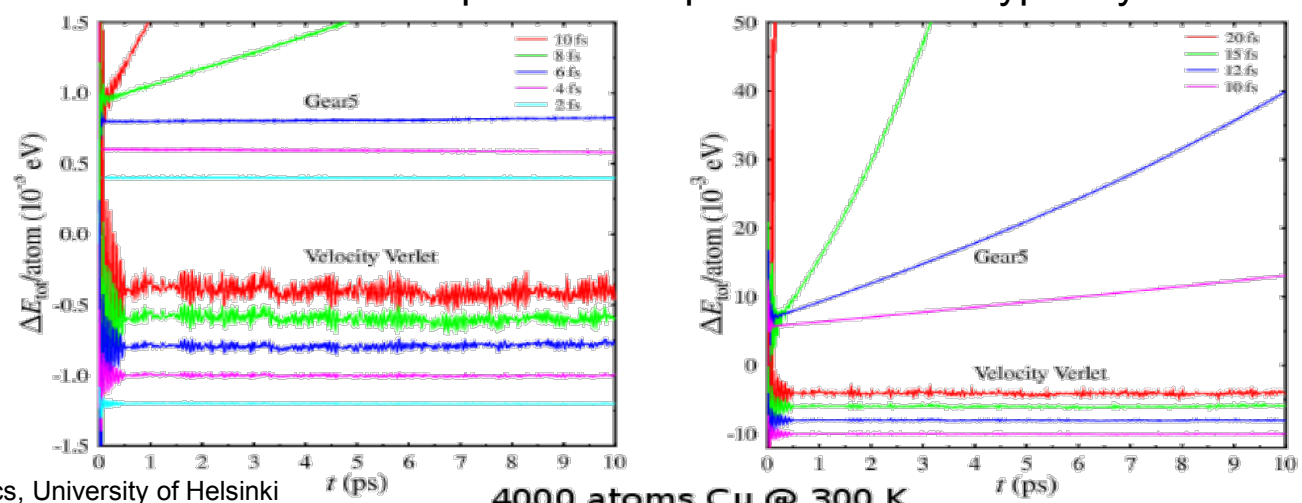
[L. Verlet, Phys. Rev. 159 (1967) 98]

- Another, much more accurate: Gear5, Martyna
  - I recommend Gear5, Martyna-Tuckerman or other methods more accurate than Verlet – easier to check energy conservation

[C. W. Gear, Numerical initial value problems in ordinary differential equations, Prentice-Hall 1971; Martyna and Tuckerman J. Chem Phys. 102 (1995) 8071]

MD – time step selection

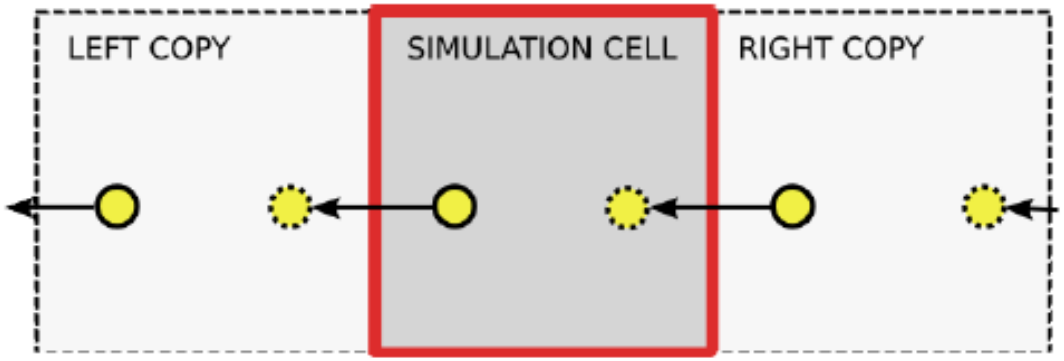
- Time step selection is a crucial part of MD
  - Choice of algorithm for solving equations of motion and time step are related
- Way too long time step: system completely unstable, “explodes”
- Too long time step: total energy in system not conserved
- Too short time step: waste of computer time
  - 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



4000 atoms Cu @ 300 K

MD – Periodic boundary conditions

- A real lattice can be extremely big
  - E.g. 1 cm of Cu: 2.1×10^{22} 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 our initial system “sees” another system, exactly like itself, in each direction around it. So, we’ve created a virtual infinite crystal.

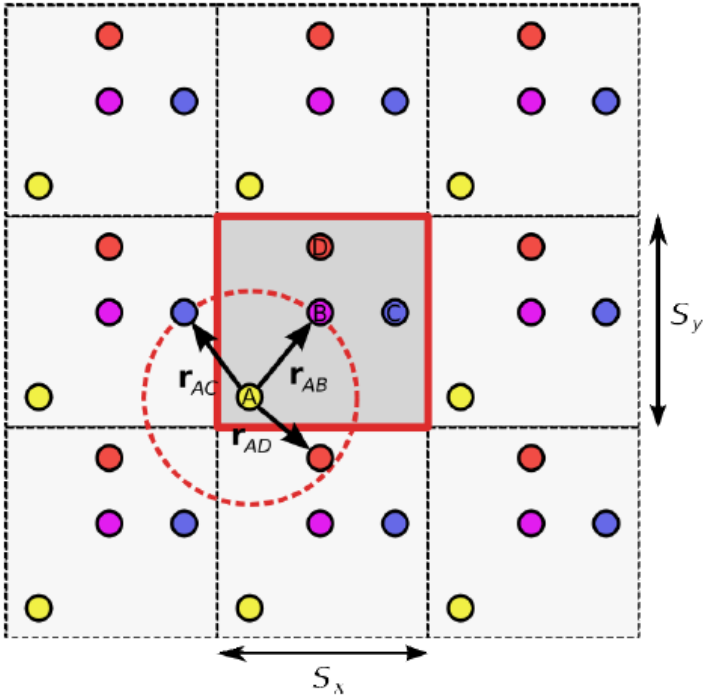


MD: periodics continued

- This has to also be accounted for in calculating distances for interactions
- “Minimum image condition”: select the nearest neighbour of an atom considering all possible 27 nearest cells
- Sounds tedious, but can in practice be implemented with a very simple comparison:

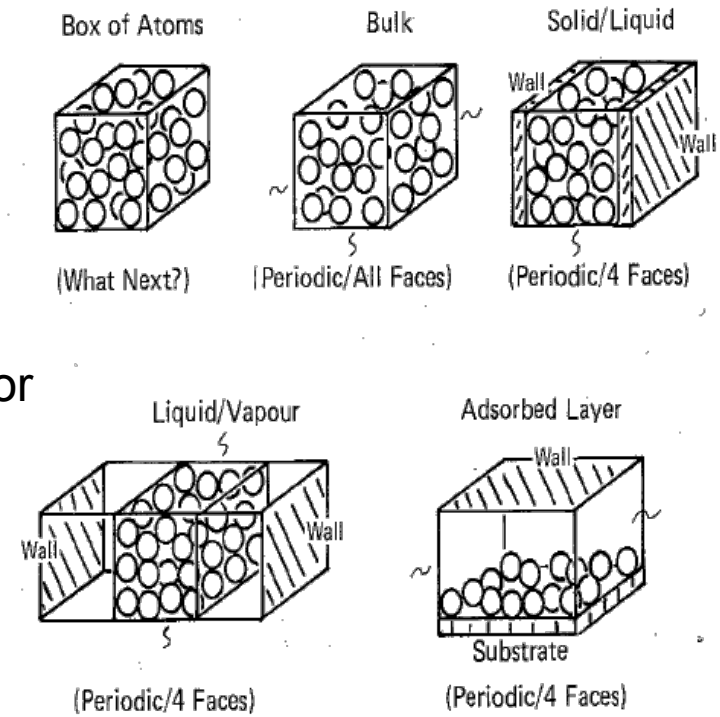
```
if (rijx > box(1)/2.0)  rijx=rijx-box(1)
if (rijy > box(2)/2.0)  rijy=rijy-box(2)
if (rijz > box(3)/2.0)  rijz=rijz-box(3)

if (rijx < -box(1)/2.0) rijx=rijx+box(1)
if (rijy < -box(2)/2.0) rijy=rijy+box(2)
if (rijz < -box(3)/2.0) rijz=rijz+box(3)
```



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

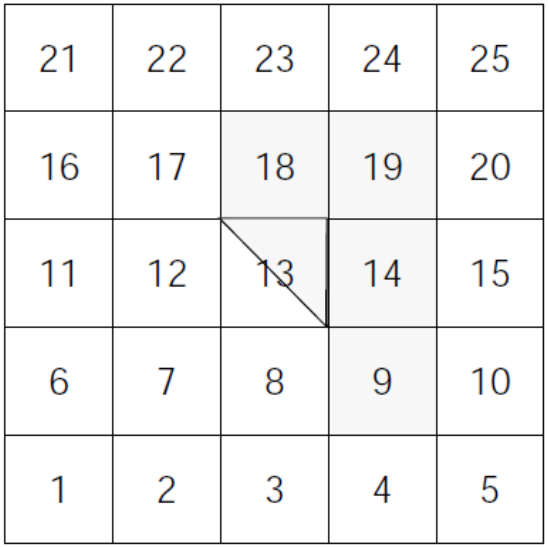


MD – Temperature and pressure control

- 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
  - Many algorithms exist, Nosé, Berendsen, …
  - Berendsen simple yet often good enough
- NPT ensemble simulation: both temperature and pressure is controlled
  - Many algorithms exist: Andersen, Nosé-Hoover, Berendsen
  - Berendsen simple yet often good enough

MD – cellular method and neighbour lists

- To speed up MD for large (> 100 or so) numbers of atoms, a combination of neighbour list and a cellular method to find the neighbours is usually crucial
- If one has N atoms, and want to find the neighbours for a finite-range potential, a direct search requires N^2 operations – killing for large N
- Solution: if potential cutoff = r_{cut}, divide atoms into boxes of size >= r_{cut}, search for neighbours only among the neighbouring cells
- Neighbour list: form a list of neighbours within $r_{cut} + r_{skin}$ and update this only when needed



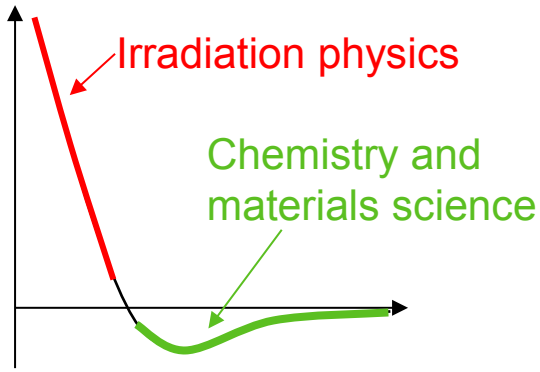
Nonequilibrium extensions – what else is needed to model nonequilibrium effects?

- The basic MD algorithm is 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 by us and others

What is needed to model irradiation effects?

1) 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
  - So called “Universal ZBL” potential accurate to ~5% and very easy to implement
- Simulating this gives the ***nuclear stopping*** explicitly!



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

What is needed to model irradiation effects?

1) keV and MeV-energy collisions between nuclei

- During the keV and MeV collisional phase, the atoms move with very high velocities
  - Moreover, they collide strongly occasionally
- To handle this, a normal equilibrium time step is not suitable
- On the other hand, as ion slows down, time step can increase
- Solution: adaptive time step

1) keV and MeV-energy collisions between nuclei

- Adaptive time step example:

$$\Delta t_{n+1} = \min\left(\frac{\Delta x_{\max}}{v_{\max}}\ ,\ \frac{\Delta E_{\max}}{F_{\max} v_{\max}}\ ,\ c_{\Delta t}\Delta t_n\ ,\ \Delta t_{\max}\right)$$

  Here Δx_{max} is the maximum allowed distance moved during any t (e.g. 0.1 Å), ΔE_{max} is the maximum allowed change in energy (e.g. 300 eV), v_{max} *and* F_{max} *are the* highest speed and maximum force acting on any particle at *t*, respectively. $c_{\Delta t}$ prevents sudden large changes (e.g. 1.1), and t_{max} is the time step for the equilibrated system.

- This relatively simple algorithm has been demonstrated to be able to handle collisions with energies up to 1 GeV accurately (by comparison with binary collision integral)

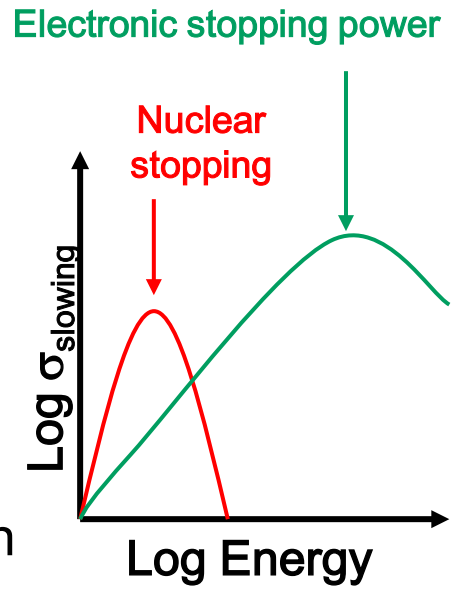
[K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)].

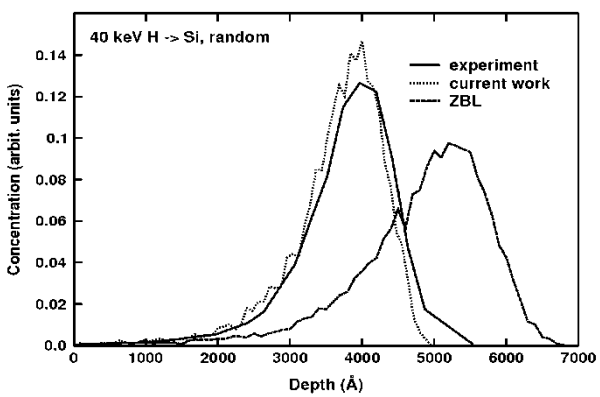
2) Energy loss to electronic excitations

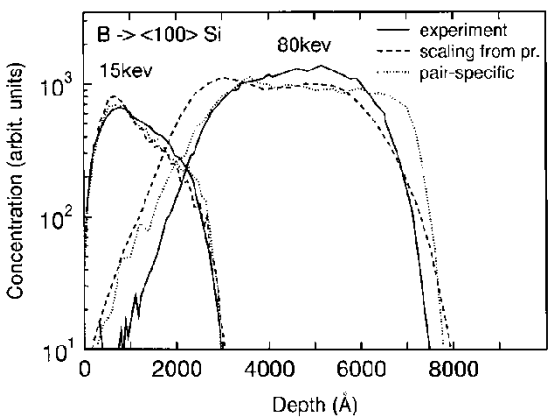
- The energy loss to electronic excitations = electronic stopping S can be included as a frictional force in MD simply as:

$$v^{(i+1)} = v^{(i)} - S(v)/m\Delta t$$

- The nice thing about this is that this can be compared directly to experiments via BCA or MD range or ion transmission calculations. Examples of agreement:







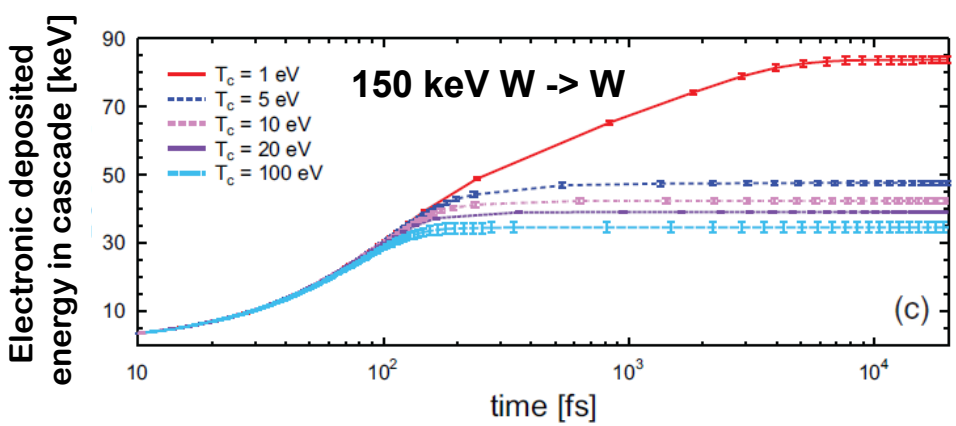
[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen,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

2) Energy loss to electronic excitations

- The issue of how to deal with electronic stopping is thus well established at high E, but very recently it was realized that how the low-E limit is handled has a biggish (~ factor of 2) effect on damage production, and bigger on clustering
- How should this be exactly treated? Electron-phonon coupling, weaker elstop (as shown by e.g. Arista et al), ???

[Valdes et al, Nuclear Instruments and Methods B 193 (2002) 43; Pruneda et al, PRL **99,** 235501 (2007]

  - Open issue to be solved – maybe ICACS community can help?

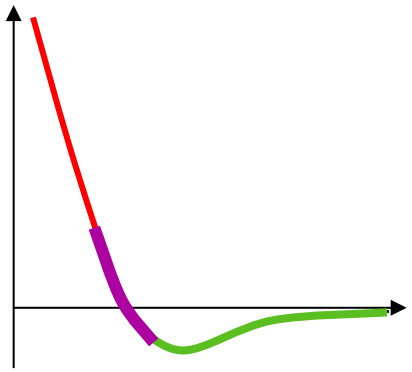


[A. E. Sand, S. L. Dudarev, and K. Nordlund,, EPL 103, 46003 (2013)]

What is needed to model irradiation effects?

3) Transition to high-pressure and high-T thermodynamics

- Requires realistic **intermediate part** in potential



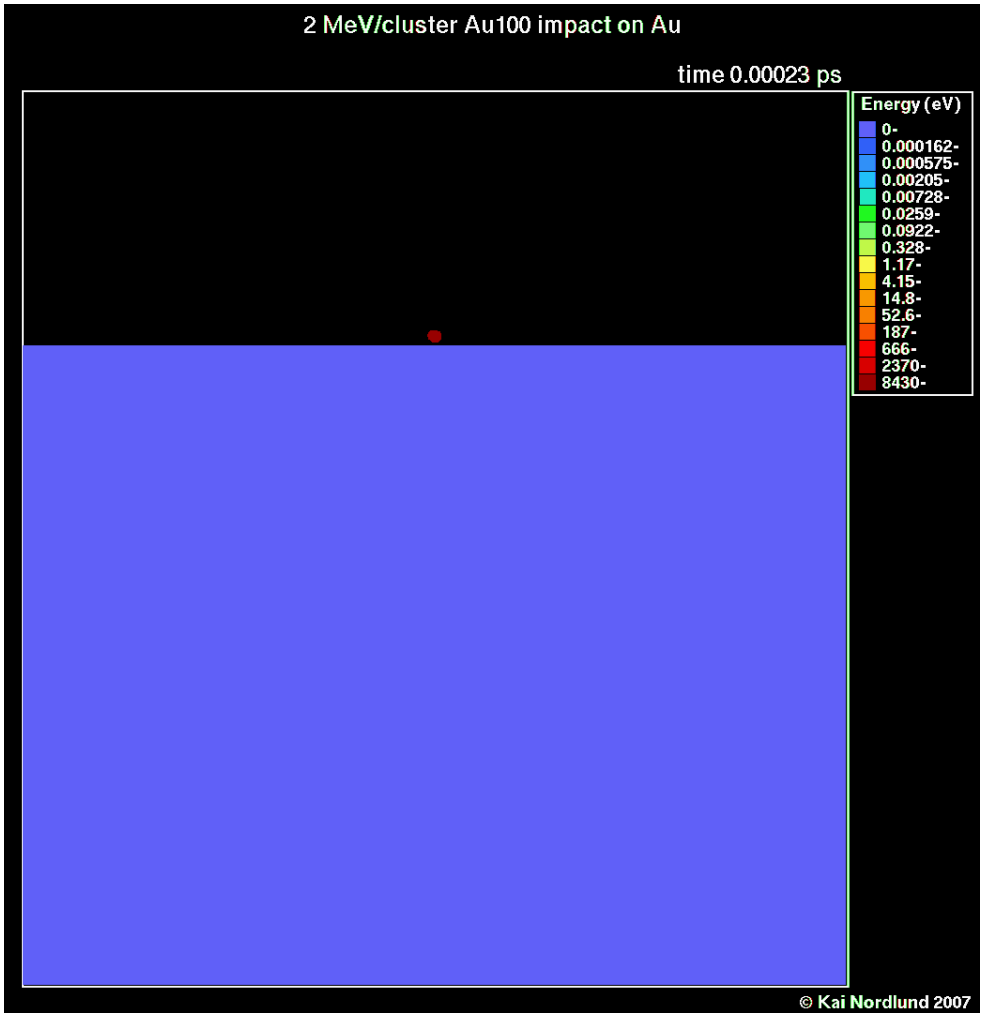
  - Can be adjusted to experimental high-pressure data and threshold displacement energies
    - Somewhat tedious ‘manual’ fitting but doable
  - Could also be fit to DFT database in this length range, although this rarely done

[K. Nordlund, L. Wei, Y. Zhong, and R. S. Averback, Phys. Rev. B (Rapid Comm.) 57, 13965 (1998); K. Nordlund, J. Wallenius, and L. Malerba. Instr. Meth. Phys. Res. B 246, 322 (2005); C. Björkas and K. Nordlund, Nucl. Instr. Meth. Phys. Res. B 259, 853 (2007); C. Björkas, K. Nordlund, and S. Dudarev, Nucl. Instr. Meth. Phys. Res. B 267, 3204 (2008)]

What is needed to model irradiation effects?

3) Transition to high-pressure and high-T thermodynamics

- The transition to thermodynamics occurs naturally in MD
- But boundary conditions a challenge due to heat and pressure wave emanating from a cascade

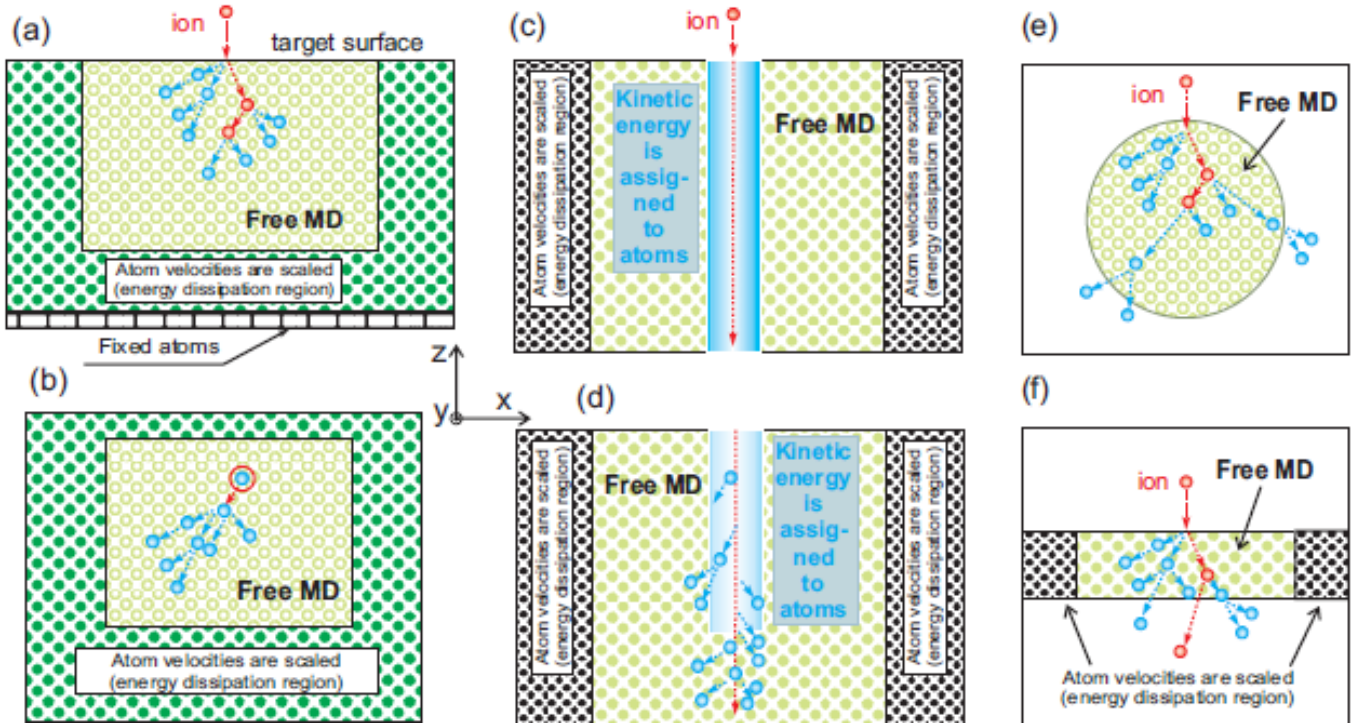


3) Transition to high-pressure and high-T thermodynamics:

MD irradiation temperature control

- Central part 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:

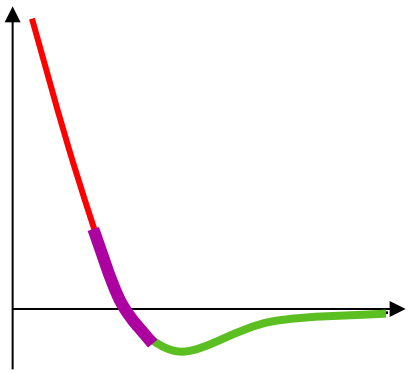
a) surface, b) bulk recoil, c-d) swift heavy ion, e) nanocluster, f) nanowire



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

4) Realistic equilibrium interaction models

- Finally one also needs the **normal equilibrium part** of the interaction model



- Since we start out with the extremely non-equilibrium collisional part, all chemical bonds in system can break and reform and atoms switch places
  - **Conventional Molecular Mechanics force fields are no good at all!**
- More on potentials in a few slides

5) Long-term relaxation of defects

- The long-time-scale relaxation phase after the collisional stage can take microseconds, seconds, days or years
  - Microseconds important in semiconductors
  - Years important in nuclear fission and fusion reactor materials
- This is clearly beyond the scope of molecular dynamics
- Several groups have recently taken into use Kinetic Monte Carlo (KMC) to be able to handle all this
- Also rate theory (numerical solution of differential equations) can be extremely useful in this regard
- Outside the scope of this talk, but KMC slides added at end

[K. O. E. Henriksson, K. Nordlund, A. Krasheninnikov, and J. Keinonen, Appl. Phys. Lett. 87, 163113 (2005); K. O. E. Henriksson, K. Nordlund, A. Krasheninnikov, and J. Keinonen, Fusion Science & Technology 50, 43 (2006); [Ahl12] T. Ahlgren, K. Heinola, K. Vörtler, and J. Keinonen. J. Nucl. Mater., 427:152--161, 2012]

Whence the interactions?

- Recall from the MD algorithm:

$$\text{Get forces } \boldsymbol{F} = -\nabla V(\boldsymbol{r}^{(i)}) \text{ or } \boldsymbol{F} = \boldsymbol{F}(\Psi) \text{ and } \boldsymbol{a} = \boldsymbol{F}/m$$

- This is the crucial physics input of the algorithm!
  - In the standard algorithm all else is numerical mathematics which can be handled in the standard cases to arbitrary accuracy with well-established methods (as outlined above)
- Forces can be obtained from many levels of theory:
  - Quantum mechanical: Density-Functional Theory (DFT), Time-dependent Density Functional theory (TDDFT)
    - Limit: ~1000 atoms for DFT, ~100 atoms for TDDFT
  - Classically: various interatomic potentials
    - Limit: ~ 100 million atoms!
    - Most relevant to irradiation effects

Equilibrium potentials

- For classical MD the often only physical input is the potential
- Originally simple 2-body potentials, but by now these are almost completely out of use except for noble gases
- Dominant are 3-body potentials, and increasingly 4-body are used
- Two major classes of potentials:
- Tersoff-like:

$$V_i = \sum_{\text{neighbours}} \left[V_{\text{repulsive}}(r_{ij}) + b_{ijk}(r_{ij}, r_{ik}, \theta_{ijk}) V_{\text{attractive}}(r_{ij}) \right]; \; b_{ijk} \propto \frac{1}{\sqrt{\text{coordination of } i}}$$

- Embedded-atom method-like (EAM)

$$V_i = \sum_{\text{neighbours}} V_{\text{repulsive}}(r_{ij}) + F_i\left(\sum_j \rho(r_{ij}) \right)$$

- Both can be motivated in the second momentum approximation of tight binding (“extended Hückel approximation” if you are a chemist)
  - Related to Pauling’s theory of chemical binding

[K. Albe, K. Nordlund, and R. S. Averback, Phys. Rev. B 65, 195124 (2002)]

Potential development aims

- First consider a potential for a pure element A.
- To be able to handle the effects described above, the potential should give:
  - The correct ground state: cohesive energy, crystal structure etc.
  - Describe all phases which may be relevant
  - Describe melting well
  - Describe defect energetics and structures well
- If we further consider irradiation of a compound AB:
- For high-dose irradiation the compound may segregate, so we need good models for elements A and B separately!
  - Fulfills all the requirements just given for a pure element
  - Describes well the heat of mixing of the compound
  - Describes defects involving atom types A and B well

Potential development approach

- We start by obtaining information on as many coordination states as possible:
  - Usually at least:

Z:	1	3	4	6	8	12
	dimer	graphite	diamond	SC	BCC	FCC

  - Data from experiments or DFT calculations
- Cohesive energy, lattice constant, bulk modulus for all Z
  - Elastic constants for most important
- Fitting done in systematic approach introduced by Prof. Karsten Albe (TU Darmstadt)

"Albe" fitting formalism

- Use Tersoff potential in Brenner form (unique mathematical transformation)

$$E = \sum_{i>j} f_{ij}(r_{ij}) \left[V_R^{ij}(r_{ij}) - \underbrace{\frac{b_{ij} + b_{ji}}{2}}_{\overline{b_{ij}}} V_A^{ij}(r_{ij}) \right]$$

$$V_R(r) = \frac{D_o}{S-1} \exp\left(-\beta\sqrt{2S}(r - r_o)\right)$$

$$V_A(r) = \frac{SD_o}{S-1} \exp\left(-\beta\sqrt{2/S}(r - r_o)\right)$$

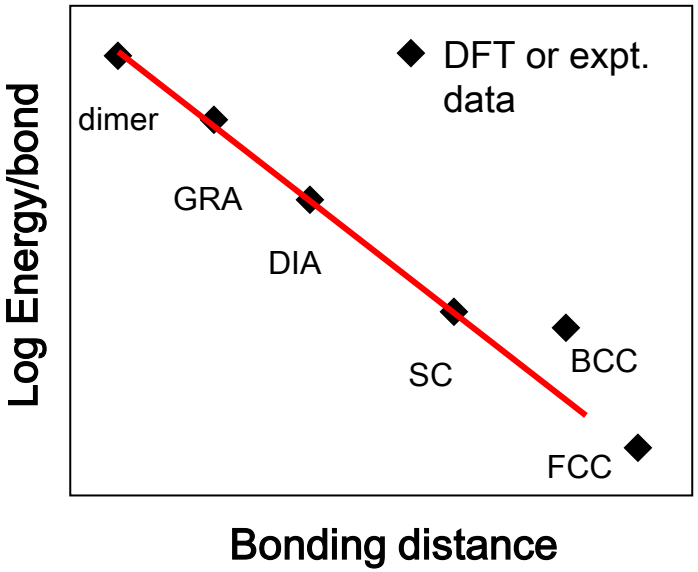
  - The 3 parameters r_0, D_0 and β can be set directly from the experimental dimer interatomic distance, energy and vibration frequency!

"Albe" fitting formalism

- Key idea:
  - In nn formulation, if material follows Pauling theory of chemical bonding,

$$E_b = -D_o \exp\left(-\beta\sqrt{2S}(r_b - r_o)\right)$$

for all coordinations



[Albe, Nordlund and Averback, Phys. Rev. B **65** (2002) 195124]

"Albe" fitting formalism

- Pair-specific A-B interaction
- Three-body part modified from Tersoff form

Second-moment approximation exponential

No power of 3

$$b_{ij} = (1 + \chi_{ij})^{-1/2}$$

$$\chi_{ij} = \sum_{k(\neq i,j)} f_{ik}(r_{ik}) g_{ik}(\theta_{ijk}) \exp[2\mu_{ik}(r_{ij} - r_{ik})]$$

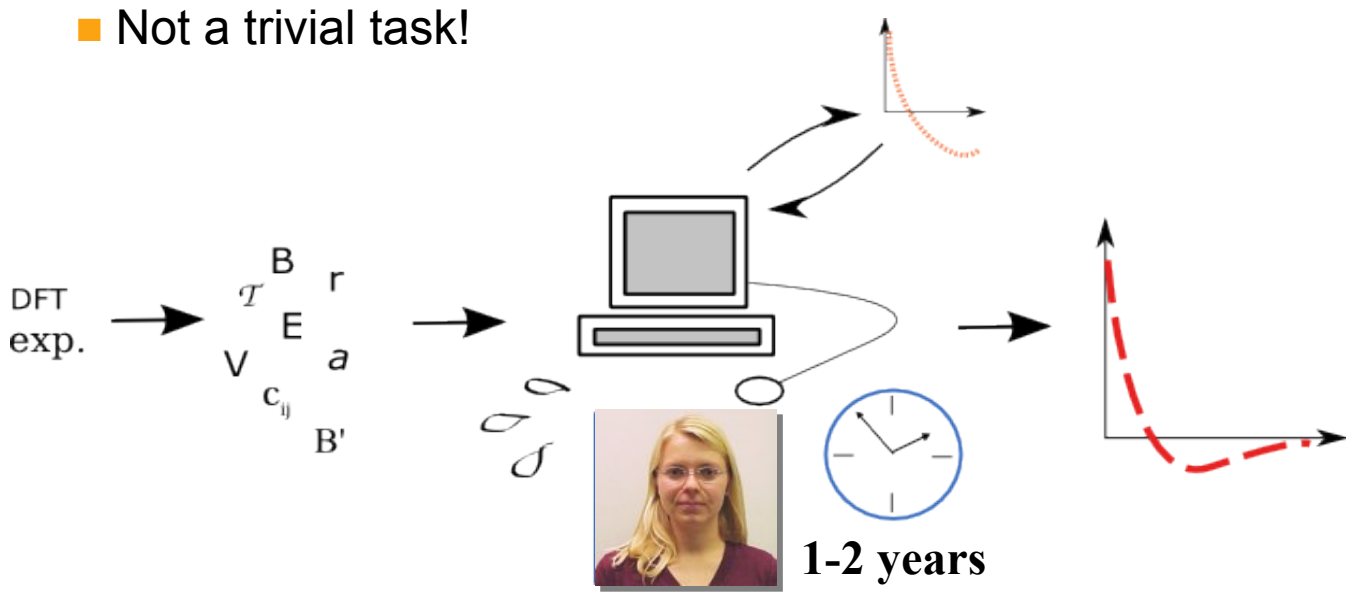
ik-dependent angular term

- This form for b_{ij} conforms exactly to $b_{ijk} \propto \frac{1}{\sqrt{\text{coordination of } i}}$

[Albe, Nordlund and Averback, Phys. Rev. B **65** (2002) 195124]

The “blood, sweat and tears” part

- There are all in all 11 parameters that must be specified
- Constructing a good potential means finding suitable values for these
  - This is done by fitting to different experimental or density-functional theory values of ground state and hypothetical phases – also for other functional forms than Tersoff
  - Not a trivial task!



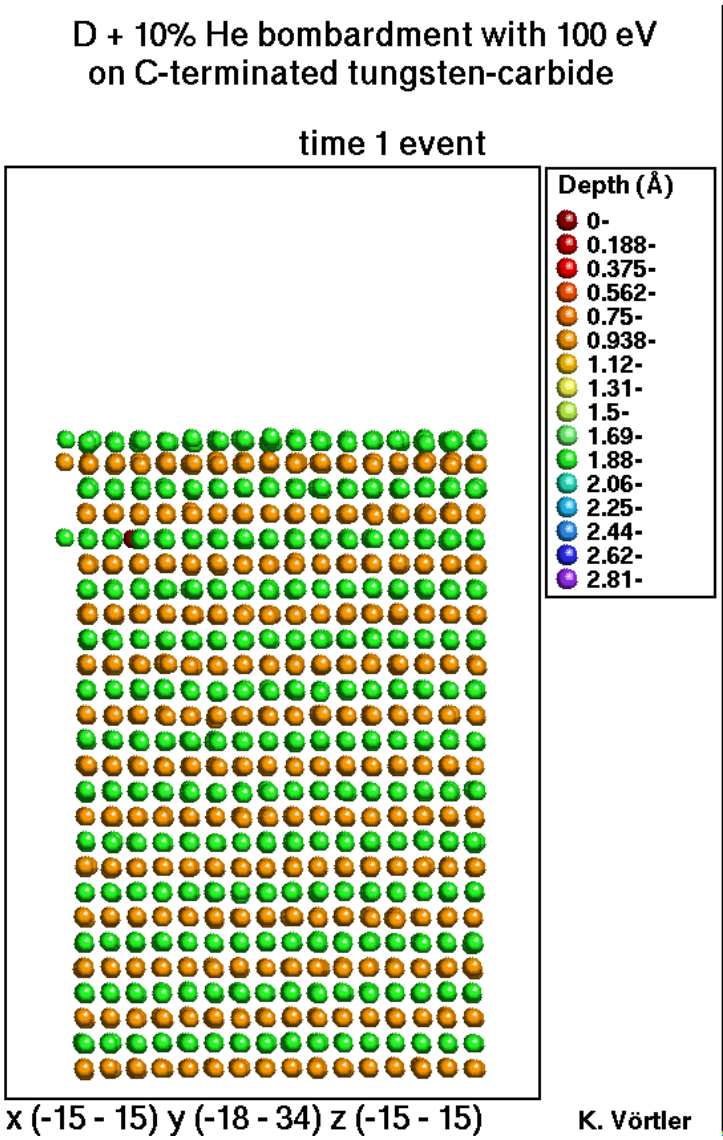
[Schematic courtesy of Dr. Carolina Björkas]

Potentials developed in general

- In general, potentials suitable for irradiation effects exist:
  - For almost all pure elements
  - For the stoichiometric state of a wide range of ionic materials
    - But these do not always treat the constituent elements sensibly, e.g. in many oxide potentials O-O interactions purely repulsive => predicts O_2 cannot exist => segregation cannot be modelled
  - For a big range of metal alloys
- Not so many potentials for mixed metal – covalent compounds, e.g. carbides, nitrides, oxides in non-ionic state
- Extremely few charge transfer potentials
- For organics only ReaxFF for CNOH, extended Brenner for COH systems
- NIST maintains a potential database, but pretty narrow coverage – one often really needs to dig deep in literature to find them

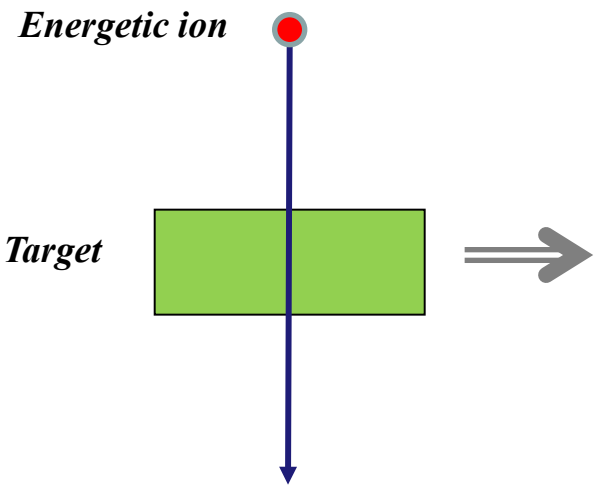
Potentials developed by us

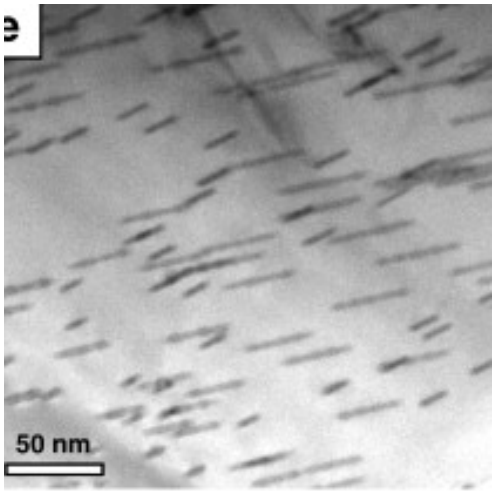
- We, and/or the Albe group, have so far developed potentials for:
  - BN, PtC, GaAs, **GaN**, SiC, **ZnO,** FePt, BeWCH, FeCrC, FeCH
    + He with pair potentials
  - All these potentials include all the pure elements and combinations!
  - Fitting code “pontifix” freely available, contact Paul Erhart
- Just to give a flavor of complexity that can be modelled: prolonged irradiation of WC by H and He



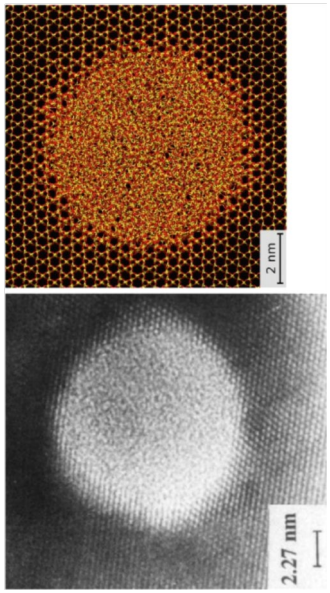
Something new: swift heavy ions by MD

- Swift heavy ions (i.e. MeV and GeV ions with electronic stopping power > 1 keV/nm) produce tracks in many insulating and semiconducting materials





[M. Lang et al, Earth and Planetary Science Letters 274 (2008) 355]



What happens physically: excitation models

- The value of the electronic stopping is known pretty accurately
  - Thanks to a large part to work in the ICACS community!
- But even the basic mechanism of what causes the amorphization is not known; at least three models are still subject to debate:
  1. Heat spikes: electronic excitations translate quickly into lattice heating that melts the lattice and forms the track
     - "Two-temperature model"; Marcel Toulemonde, Dorothy Duffy, …
  2. Coulomb explosion: high charge states make for an ionic explosion, high displacements make for track
     - Siegfried Klaumünzer, …
  3. Cold melting: ionization changes interatomic potential into antibonding one, repulsion breaks lattice and forms track
     - Alexander Volkov, …

How to model it

- Any of the models eventually translate into an interatomic movement, which can be handled by MD
- Linking the electronic excitations stages can be implemented as a concurrent multiscale scheme

Conventional MD

Get forces $\boldsymbol{F} = -\nabla V(\boldsymbol{r}(n))$ and $\boldsymbol{a} = \boldsymbol{F}/m$

↓

Solve: $\boldsymbol{r}(n+1) = \boldsymbol{r}(n) + \boldsymbol{v}(n)\,\Delta t + 1/2\,\boldsymbol{a}\,\Delta t2 + \ldots$
$\boldsymbol{v}(n+1) = \boldsymbol{v}(n) + \boldsymbol{a}\,\Delta t + \ldots$

↓

Move time forward: $t = t + \Delta t$; ; $n=n+1$

↓

Repeat

MD + antibonding or Coulomb

Get modified interatomic potentials $V^*i(\boldsymbol{r}(n),Se,t)$

↓

Get forces $\boldsymbol{F} = -\nabla V^*i(\boldsymbol{r}(n))$ and $\boldsymbol{a} = \boldsymbol{F}/m$

↓

Solve: $\boldsymbol{r}(n+1) = \boldsymbol{r}(n) + \boldsymbol{v}(n)\,\Delta t + 1/2\,\boldsymbol{a}\,\Delta t2 + \ldots$
$\boldsymbol{v}(n+1) = \boldsymbol{v}(n) + \boldsymbol{a}\,\Delta t + \ldots$

↓

Move time forward: $t = t + \Delta t$; $n=n+1$

↓

Repeat

How to model it

- Any of the models eventually translate into an interatomic movement, which can be handled by MD
- Linking the electronic excitations stages can be implemented as a concurrent multiscale scheme

Conventional MD

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↓

Solve: $\boldsymbol{r}(n+1) = \boldsymbol{r}(n) + \boldsymbol{v}(n)\,\Delta t + 1/2\,\boldsymbol{a}\,\Delta t2 + \ldots$
$\boldsymbol{v}(n+1) = \boldsymbol{v}(n) + \boldsymbol{a}\,\Delta t + \ldots$

↓

Move time forward: $t = t + \Delta t$; ; $n=n+1$

↓

Repeat

MD + heat spike model

Get forces $\boldsymbol{F} = -\nabla V{*}i(\boldsymbol{r}(n))$ and $\boldsymbol{a} = \boldsymbol{F}/m$

↓

Solve: $\boldsymbol{r}(n+1) = \boldsymbol{r}(n) + \boldsymbol{v}(n)\,\Delta t + 1/2\,\boldsymbol{a}\,\Delta t2 + \ldots$
$\boldsymbol{v}(n+1) = \boldsymbol{v}(n) + \boldsymbol{a}\,\Delta t + \ldots$

↓

Modify velocities: $\boldsymbol{v}(n+1) = \boldsymbol{v}(n+1) + \boldsymbol{v}{*}\boldsymbol{i}(Se,t)$

↓

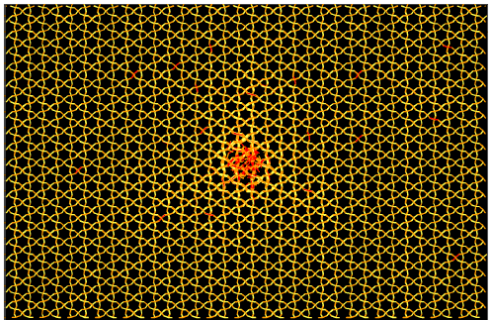
Move time forward: $t = t + \Delta t$; $n=n+1$

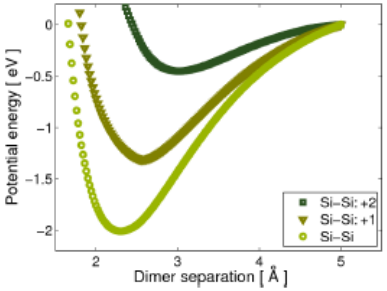
↓

Repeat

How to model it

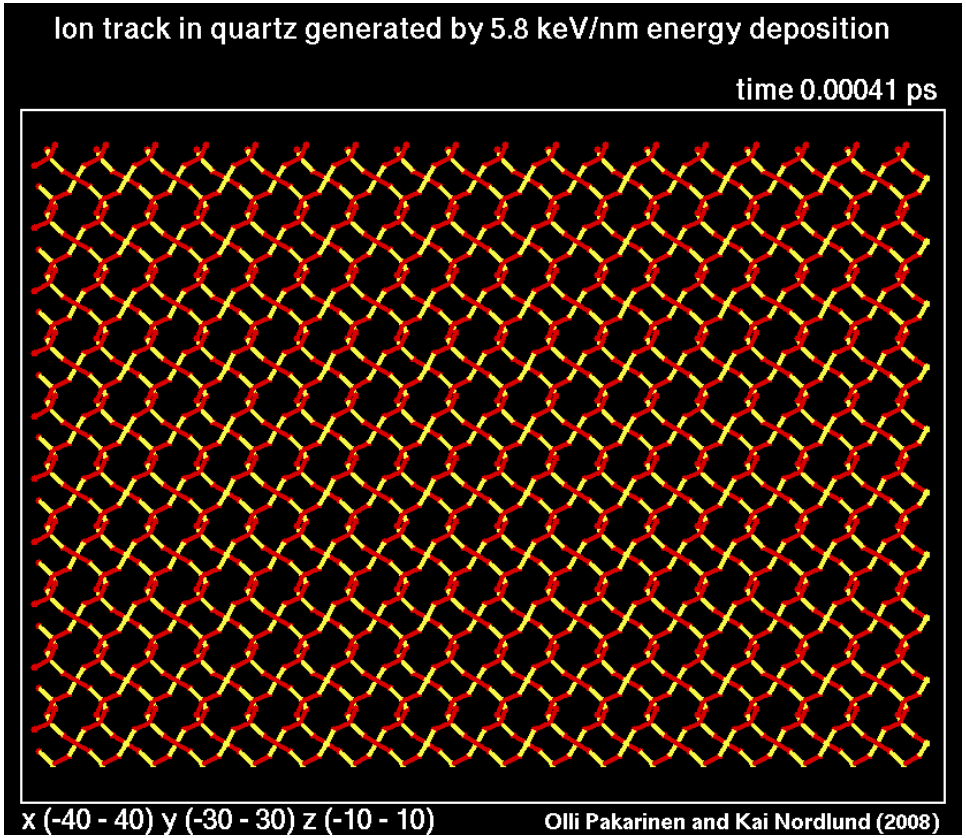
- The concurrent multiscale models give a way to test the excitation models against experiments
- We have implemented the heat-spike model and variations of cold melting models into our MD code
- Basic result is that both heat-spike (Toulemonde) models and cold melting models give tracks in SiO_2
  - Heat spike models give better agreement with experiments, but the cold melting models cannot be ruled out – huge uncertainties in how to modify potential

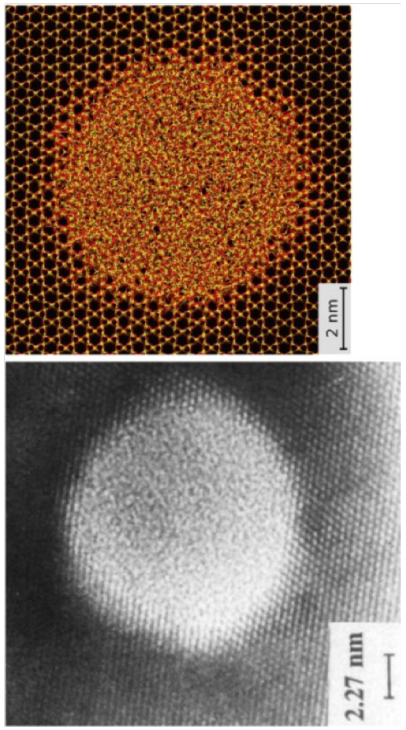




Sample result

- The two-temperature model in MD creates well-defined tracks in quartz very similar to the experimental ones





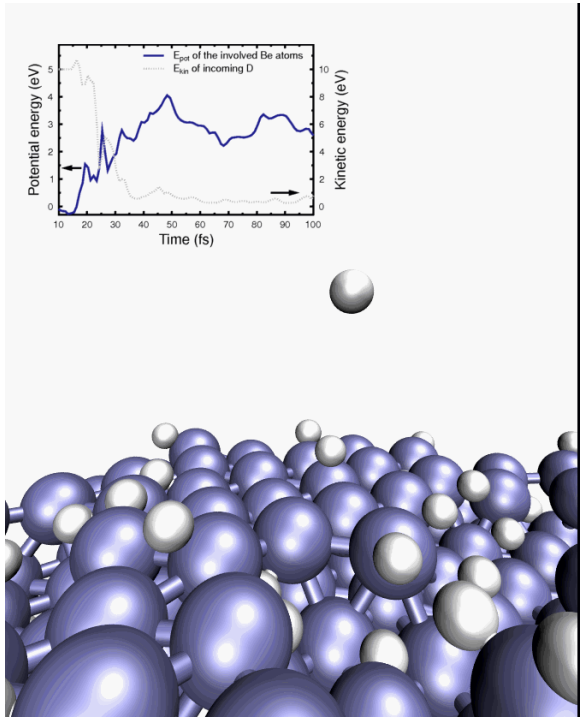
[O. H. Pakarinen et al, Nucl. Instr. Meth. Phys. Res. B **268**, 3163 (2010)]

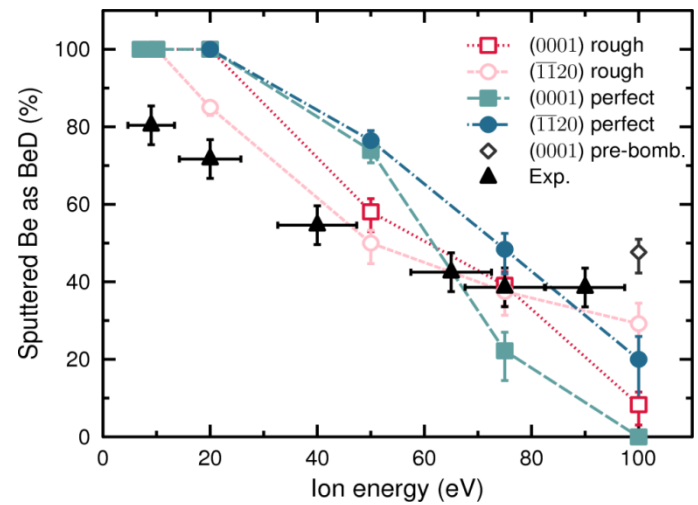
Contents

- Background
  - Irradiation effects in materials – brief summary of physics
  - The rich materials science emerging from ion irradiation
- Molecular dynamics
  - General approach
  - Features specific to ion irradiation and Irradiation effects
- Some examples of recent applications from our group
  - … of course many other groups also do excellent work …
- Extra slides at end on Binary Collision Approximation and Kinetic Monte Carlo

1. Chemical sputtering of metals

- Using classical molecular dynamics and experiments, we showed that pure metals can sputter chemically
  - Light metals under H bombardment sputter by breaking bonds!





[Björkas et al, New J. Phys. 11, 123017 (2009); Nordlund et al, NIM B 269, 1257 (2011)]

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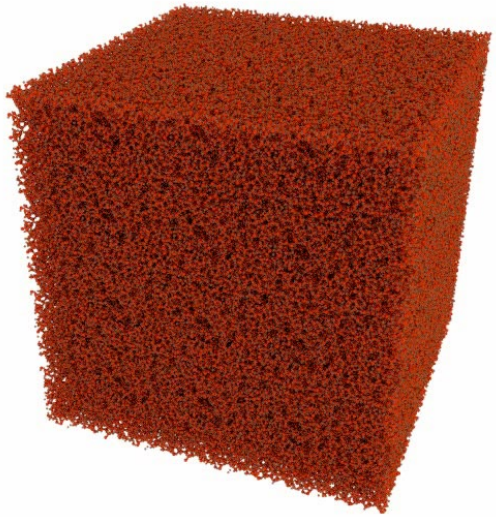
2. Swift heavy ion effects on materials

- Swift heavy ions (E_{kin} > 100 keV/amu) can be used to fabricate and modify nanostructures in materials
- We are using multiscale modelling of electronic energy transfer into atom dynamics to determine the effects of swift heavy ions on materials

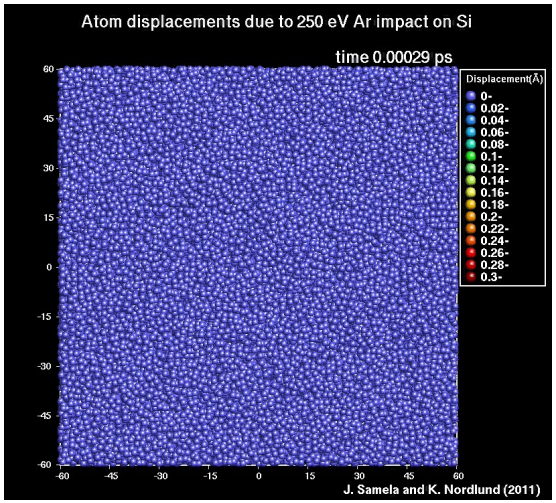
➢ **We have explained the mechanism by which swift heavy ions create nanostructures in silicon, silica and germanium and change nanocrystal shapes**

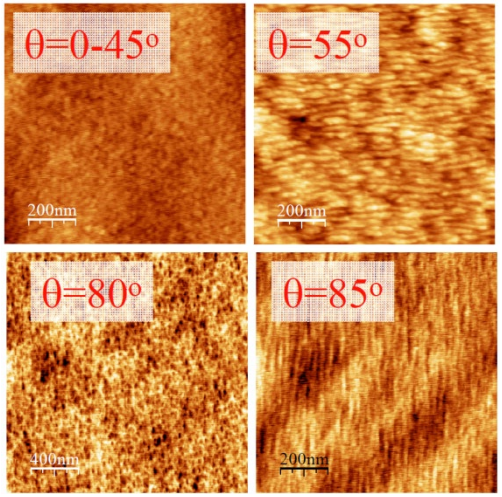


[Ridgway et al, Phys. Rev. Lett. 110, 245502 (2013); Leino et al, Mater. Res. Lett. (2013)]

3. Surface nanostructuring

- Together with Harvard University, we are examining the fundamental mechanisms of why prolonged ion irradiation of surfaces leads to formation of ***ripples*** (wave-like nanostructures)
  - **We overturned the old paradigm that ripples are produced by sputtering and showed ab initio that they can in fact be produced by atom displacements in the sample alone**

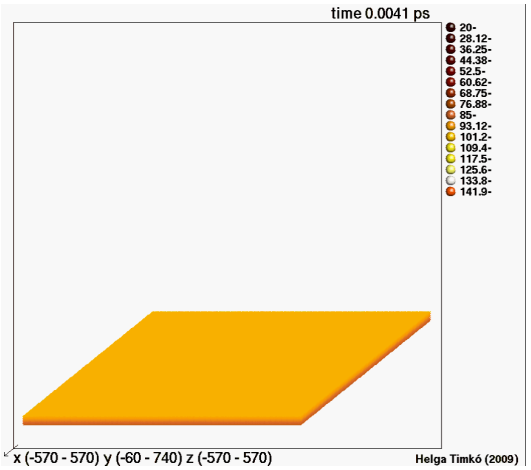


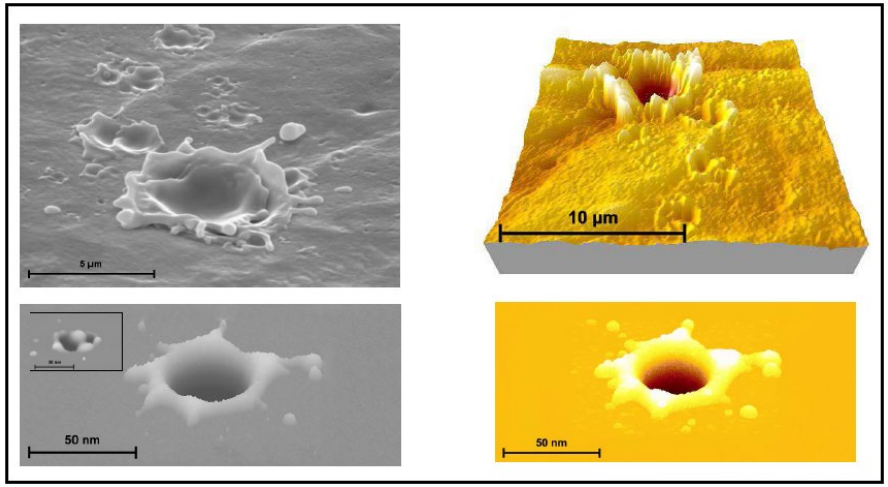


[Norris et al, Nature commun. 2 (2011) 276]

4. Modelling of arc cratering

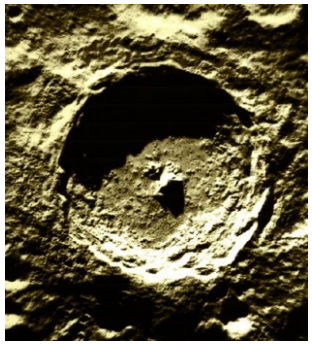
- We have developed new concurrent multiscale modelling methods for treating very high electric fields at surfaces
- Using it we are examining with a comprehensive multiscale model the onset of vacuum electric breakdown
  - **We have shown that the complex crater shapes observed in experiments can be explained as a plasma ion irradiation effect – multiple overlapping heat spikes**



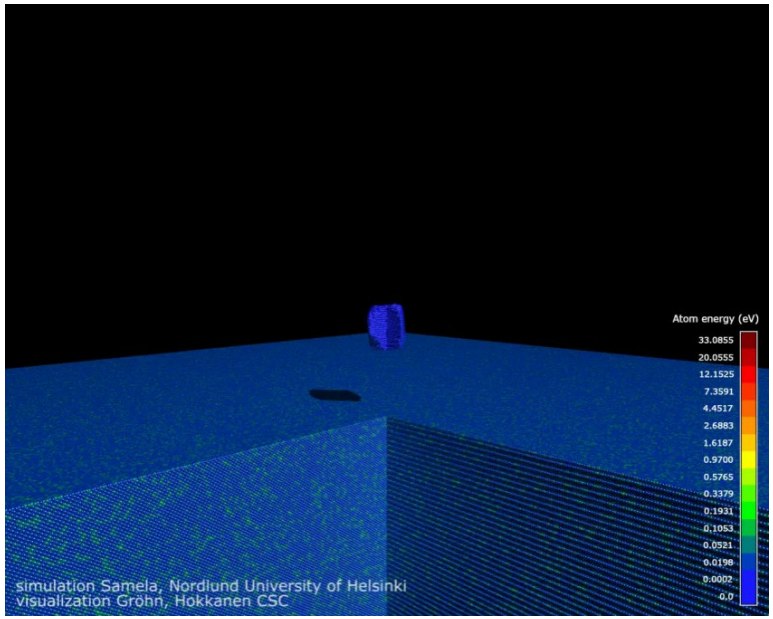


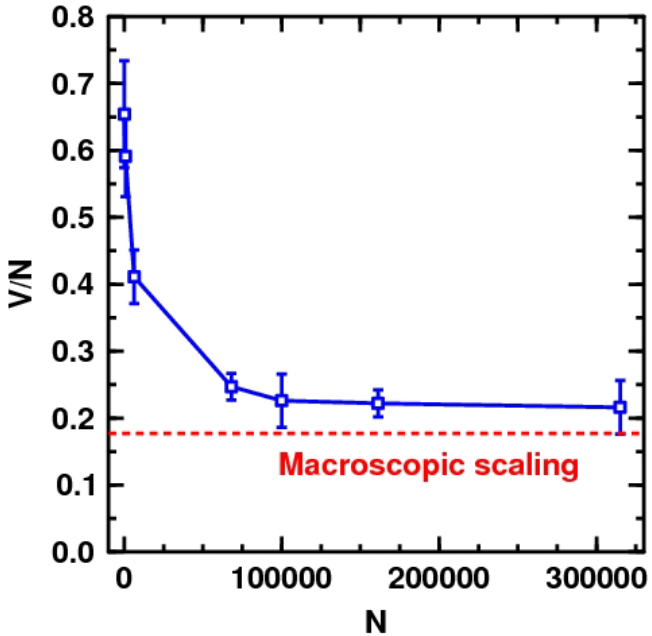
[H. Timko et al, Phys. Rev. B 81 (2010), 184109]

5. Cluster cratering over 40 orders of magnitude



- Using classical MD, we demonstrated that at a size ~ 10000 atoms, cluster bombardment starts producing craters with the same mechanism as meteorites on planets
  - 100 million atom simulations with statistics





[J. Samela and K. Nordlund, Phys. Rev. Lett. 101 (2008) 27601, and cover of issue 2]

Summary

- ***Molecular dynamics is a powerful tool for modelling irradiation effects***
  - ***– when you know what you are doing!***

And a lot of fun! ☺

Open positions: Experimental Tenure Track Professor and Simulation postdoc and PhD student

The University of Helsinki, Department of Physics
is soon opening a

Tenure track professor position
in
Experimental materials (ion beam) physics

(Applicant must be within 10 years of finishing PhD)

and groups of Kai Nordlund+Flyura Djurabekova now opening a

2+1.5 year postdoc on and 2+2 year PhD student position on simulation and theory of ripple formation

- *Professorship, postdoc starting Jan 2015, PhD student September 2014*
- *Knowledge of Finnish not required!*

Further reading

- General:
  - Classic book: Allen-Tildesley, Molecular dynamics simulations of liquids, Oxford University Press, 1989.
  - Newer book: Daan Frenkel and Berend Smit. Understanding molecular simulation: from algoritms to applications. Academic Press, San Diego, second edition, 2002
- Ion irradiation-specific reviews:
  - K. Nordlund and F. Djurabekova, *Multiscale modelling of irradiation in nanostructures*, J. Comput. Electr. **13**, 122 (2014).
  - K. Nordlund, C. Björkas, T. Ahlgren, A. Lasa, and A. E. Sand, *Multiscale modelling of Irradiation effects in fusion reactor conditions*, J. Phys. D: Appl. Phys. **47**, 224018 (2014).
- **Tutorial material including these slides available below my web home page, google for "Kai Nordlund" and click on the "Tutorials…" link**

Contents

- Background
  - Irradiation effects in materials – brief summary of physics
  - The rich materials science emerging from ion irradiation
- Molecular dynamics
  - General approach
  - Features specific to ion irradiation and Irradiation effects
- Some examples of recent applications from our group
  - … of course many other groups also do excellent work …
- Extra slides at end on Binary Collision Approximation and Kinetic Monte Carlo

BCA = Binary collision approximation

- The original way to treat ion irradiation effects on a computer
- Developed by Mark Robinson, ~1955
  - Channeling was predicted by BCA before it was experimentally found!
- In BCA the collisions of an incoming ion are treated as a sequence of independent collisions, where the ion motion is obtained by solving the classical scattering integral
  - Based on the physics insight that at high energies, ion collision cross section with lattice atoms is low => it moves straight much of the time => most interactions can be neglected

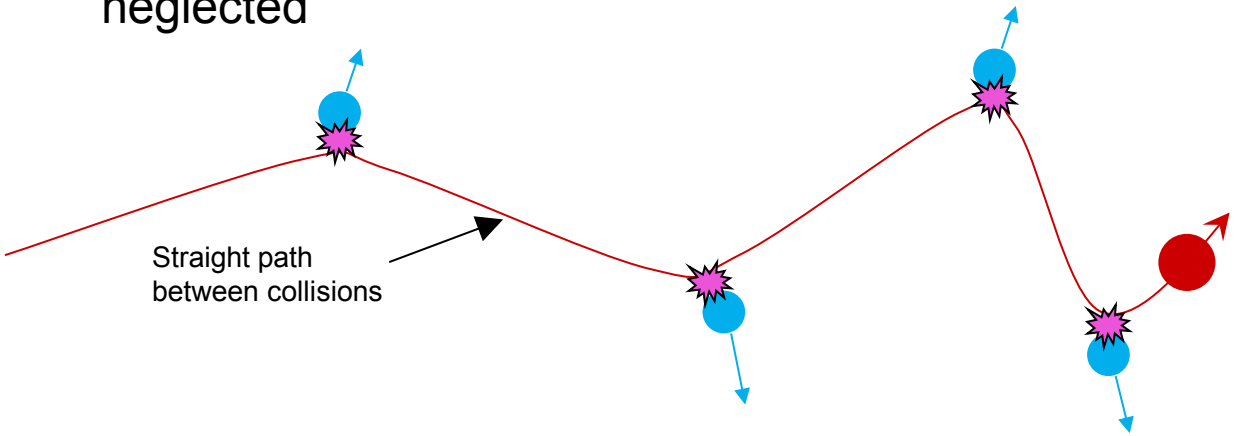
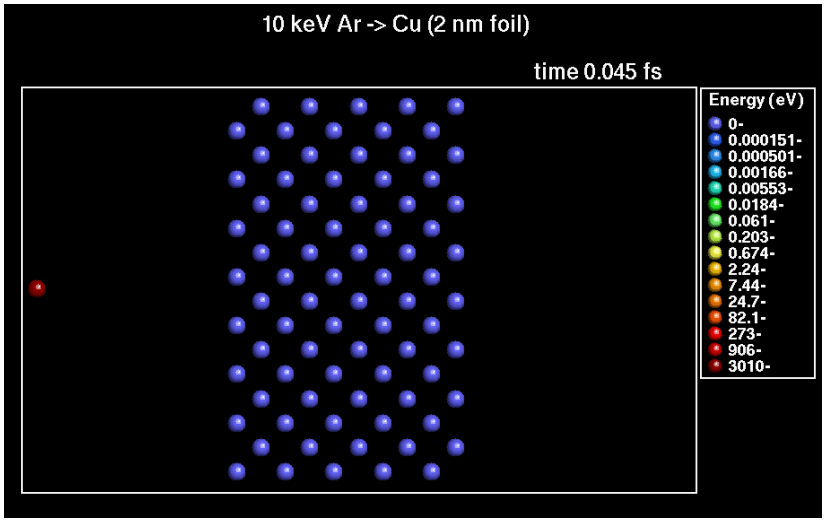


Illustration of BCA vs. MD

- 10 keV Ar -> Cu very thin foil (2 nm)
- Molecular dynamics: as realistic as possible, all atom movements taken into account



- Binary collision approximation (implemented within MD code)

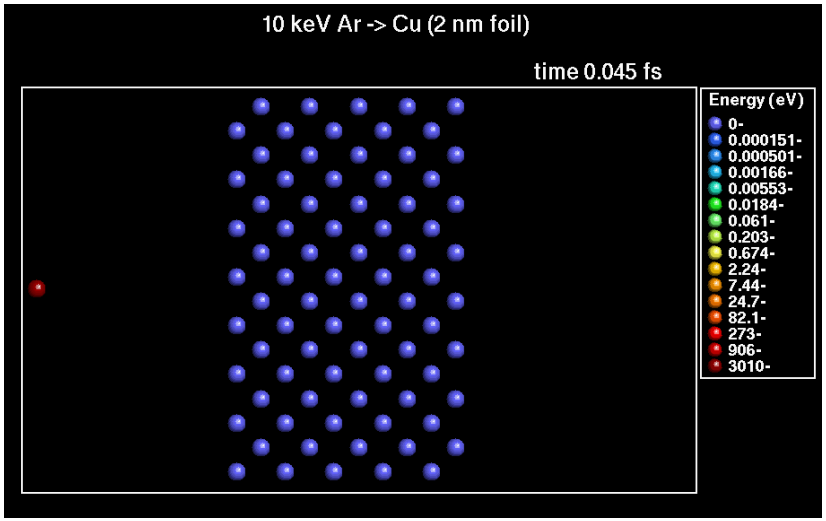
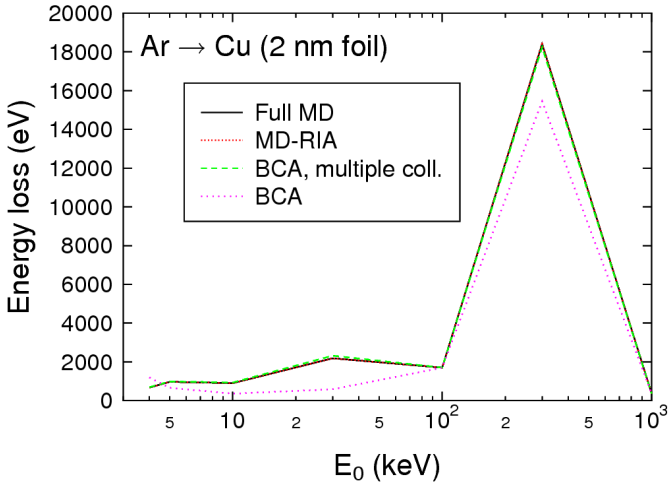
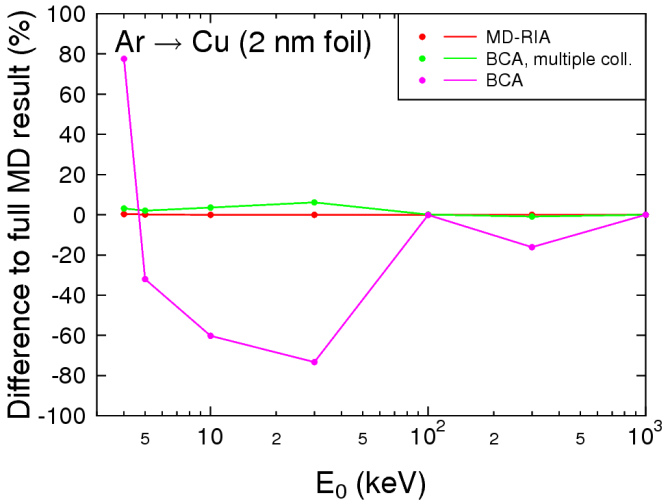


Illustration of BCA vs. MD

- So was there a significant difference?
- In this particular case (5 – 1000 keV Ar -> Cu), yes:
  - Energy loss different even at 500 keV
  - Lower-energy recoils obviously missing from BCA
- But this was single trajectories => in an average the difference certainly would have been much smaller!





[K. Nordlund, NIM B 266 (2008) 1886]

Illustration of BCA vs. MD

- Direct comparison by Gerhards Hobler&Betz [NIMB 180 (2001) 203] on the accuracy of MD vs. BCA in range and reflection:
  - BCA 'breakdown limit' for non-channeling implantation into Si ***at 5 % accuracy in the projected range*** is

$$30M_1^{0.55}\ \mathrm{eV}$$

    where M_1 is the mass of the incoming ion [NIMB 180 (2001) 203]
    - E.g. Si into Si: limit is 190 eV

Different implementations

- BCA can be implemented in many different ways
  - BCA.1. “Plain” BCA : single collision at a time, static target
  - BCA.2. Multiple-collision BCA: ion can collide with many lattice atoms at the same time, static target
    - Needed at low energies
  - BCA.3. Full-cascade BCA: also all recoils are followed, static targets
  - BCA.4. “Dynamic” BCA: sample composition changes dynamically with implantation of incoming ions, ion beam mixing and sputtering
    - full-cascade mode
- Usually ran with amorphous targets (“Monte Carlo” BCA) but can also with some effort be implemented for crystals
- BCA is many many orders of magnitude more efficient than MD

BCA today and in the future?

- Historically BCA was extremely important as full MD was too slow for most practical ion irradiation purposes
- But now lots of things can be done with full MD or MD range calculations: BCA starts to get serious troubles in getting physics right below ~ 1 keV
- What is the role of BCA now and in the future?
- It is still ideal method for quick calculations of ion depth profiles, energy deposition, mixing, etc (BCA.1 and BCA.3)
  - SRIM code important and very widely used
- BCA with multiple collisions (BCA.2) is largely useless now
- Dynamic BCA (BCA.4) is and will remain the best method for simulating very-high-fluence composition changes
  - As long as chemistry and diffusion does not play a role!

Kinetic Monte Carlo algorithm

Form a list of all N possible transitions i in the system with rates r_i

↓

Calculate the cumulative function $R_i = \sum_{j=0}^{i} r_j$ for all $i=0,\ldots,N$

↓

Find a random number u_1 in the interval [0,1]
Carry out the event for which $R_{i-1} < uR_N < R_i$

↓

Move time forward: $t = t - \log u_2/R_N$ where u_2 random in [0,1]

↓

Figure out possible changes in r_i and N, then repeat

Comments on KMC algorithm

- The KMC algorithm is actually exactly right for so called Poisson processes, i.e. processes occuring independent of each other at constant rates
  - Stochastic but exact
- Typical use: atom diffusion: rates are simply atom jumps
- But the big issue is how to know the input rates r_i ??
  - The algorithm itself can't do anything to predict them
  - I.e. they have to be known in advance somehow
- From experiments, DFT simulations, …
- Also knowing reactions may be difficult
- Many varieties of KMC exist: object KMC, lattice object KMC, lattice all-atom KMC, …
  - For more info, see wikipedia page on KMC (written by me ☺)

Principles of object KMC for defects

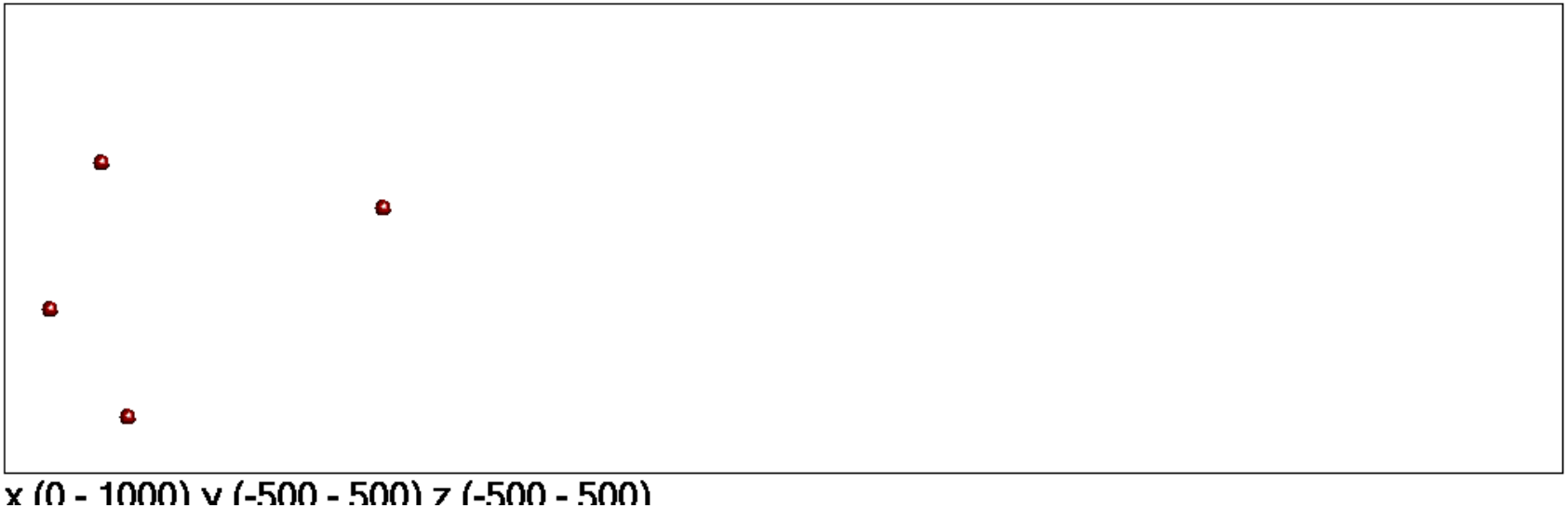
- Basic object is an impurity or intrinsic defect in lattice
- Non-defect lattice atoms are not described at all!
- Basic process is a diffusive jump, occurring at Arrhenius rate

$$r_i = r_0 e^{-E_A / k_B T}$$

- But also reactions are important: for example formation of divacancy from two monovacancies, or a pair of impurities
- Reactions typically dealt with using a simple recombination radius: if species A and B are closer than some recombination radius r_{AB}, they instantly combine to form defect complex

Example animation

- Simple fusion-relevant example: He mobility and bubble formation in W
  - Inputs: experimental He migration rate, experimental flux, recombination radius of 3 Å, clusters assumed immobile



[K. O. E. Henriksson, **K. Nordlund**, A. Krasheninnikov, and J. Keinonen, Fusion Science & Technology **50**, 43 (2006).]