HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Tutorial: atomistic simulations for irradiation effects.

Kai Nordlund

Professor, Department of Physics

Adjoint Professor, Helsinki Institute of Physics

University of Helsinki, Finland

UNIVERSITY OF HELSINKI
KUMPULA CAMPUS

-- 1000 STAFF
5000 STUDENTS
600 PhD STUDENTS

The materials simulation groups in Helsinki

Prof. Kai Nordlund
Principal investigator

Doc. Antti Kuronen
Principal investigator

Doc. Krister Henriksson
Nuclear Materials

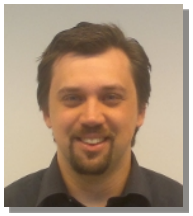
Doc. Flyura Djurabekova
Principal investigator

Dr Carolina Björkas
Fusion reactor mat'ls

Dr Andrea Sand
Fusion reactor mat'ls
Now at CCFE in UK

Dr. Andrey Ilinov
Ion beam processing

M Sc Laura Bukonte
Fusion reactor mat'ls

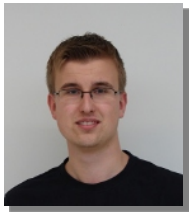


Dr Vahur Zadin*
Particle physics mat'ls
(Univ. of Tartu)

Dr Ville Jansson
Particle physics mat'ls

Dr Andreas Kyritsakis
Particle physics mat'ls

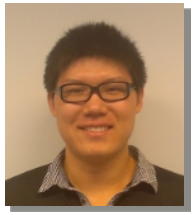
M Sc Wei Ren
Carbon nanostructures



Dr. Fredric Granberg
Dislocations

M Sc Morten Nagel
Nuclear materials

M Sc Elnaz Safi
Fusion reactor mat'ls



M Sc Junlei Zhao
Nanoclusters

M Sc Anders Korsbäck
Particle physics mat'ls

M Sc Ekaterina Baibuz
Particle physics mat'ls

M Sc Mihkel Veske
Particle physics mat'ls

M Sc Alvaro Lopez
Surface ripples

M Sc Shuo Zhang
Ion range calculations

Mr Jesper Byggmästar
Fusion reactor mat'ls

Ms Vitoria Pacela
Nanowires

M Sc Simon Vigonski
Particle physics mat'ls

M Sc Henrique Muinoz
Swift heavy ions

Mr Christoffer Fridlund
Ion beam processing

Ms Jonna Romppainen
Atom probe tomography
(In the army now)

Contents

- Part 1: Brief summary of irradiation physics
  - The rich materials science emerging from ion irradiation
- Part 2: Binary Collison Approximation
- Part 3: Molecular dynamics
  - General approach
  - Features specific to ion irradiation and Irradiation effects
  - Part 3.b: MD of swift heavy ions
  - Part 3.c: MD in recoil interaction approximation
- Part 4: Kinetic Monte Carlo
- Part 5 (time permitting): Some examples of recent applications from our group
  - … of course many other groups also do excellent work …

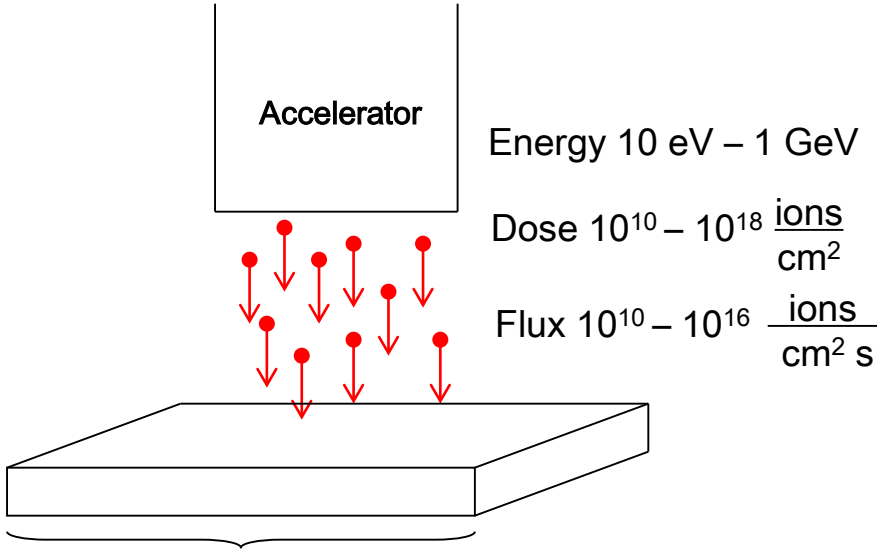
➢ **Similar slides and animations available below my web home page, google for "Kai Nordlund" and click on the "Tutorials…" link**

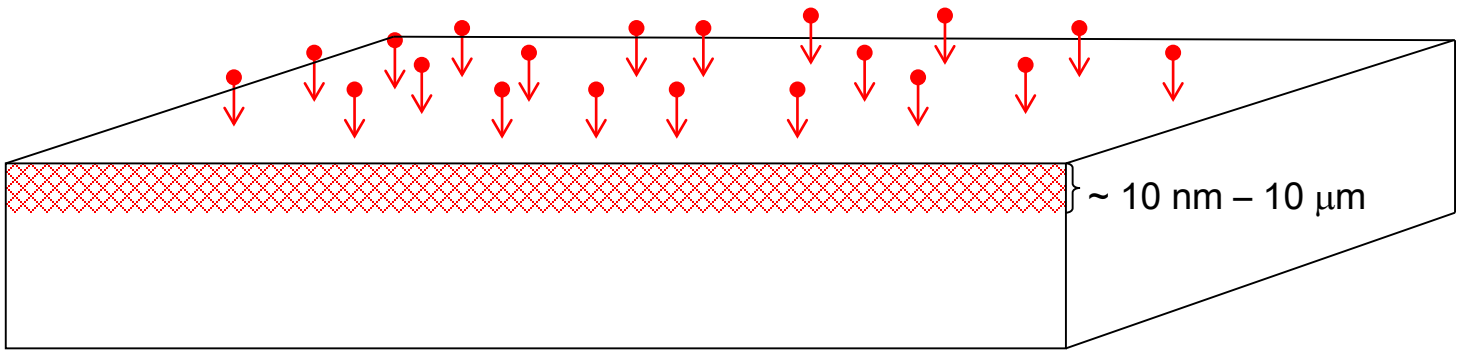
HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Part 1: Brief summary of irradiation physics

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.

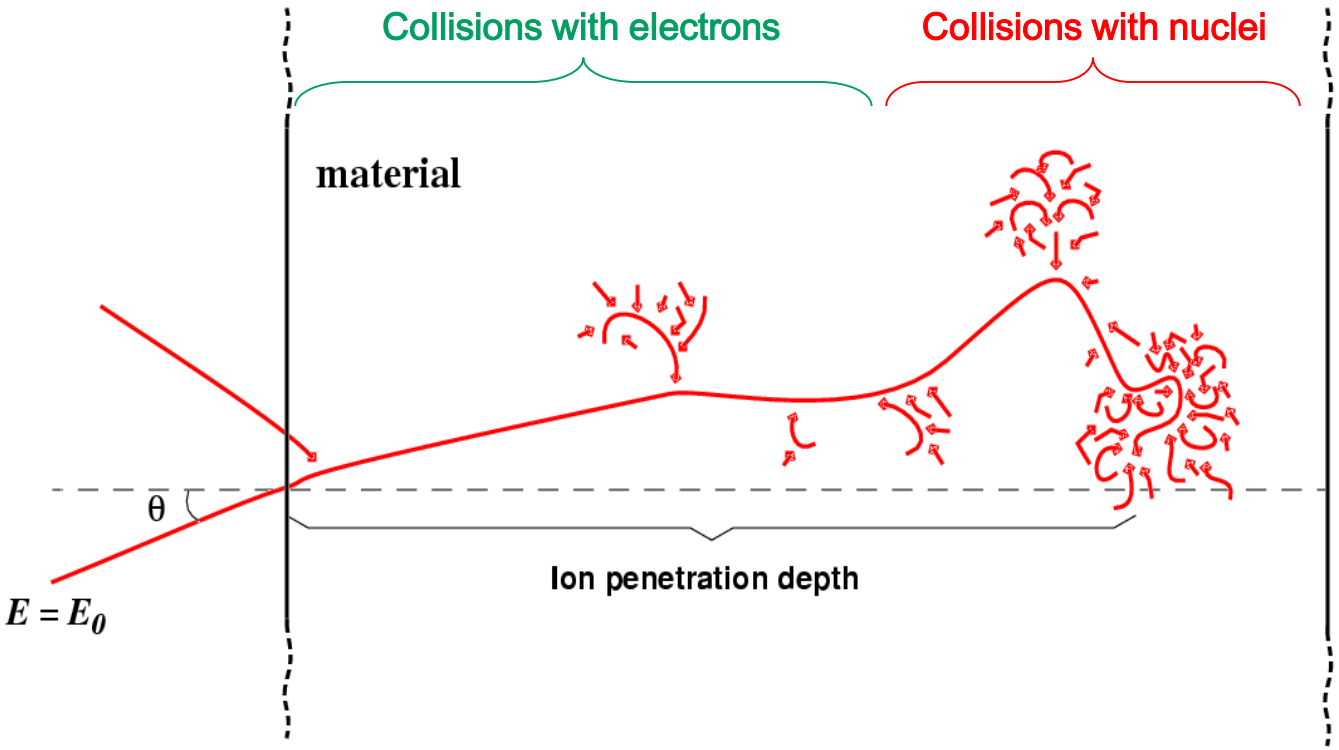


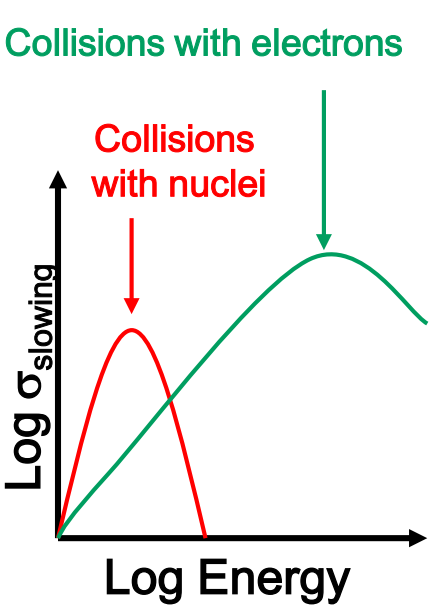


Irradiation effects:

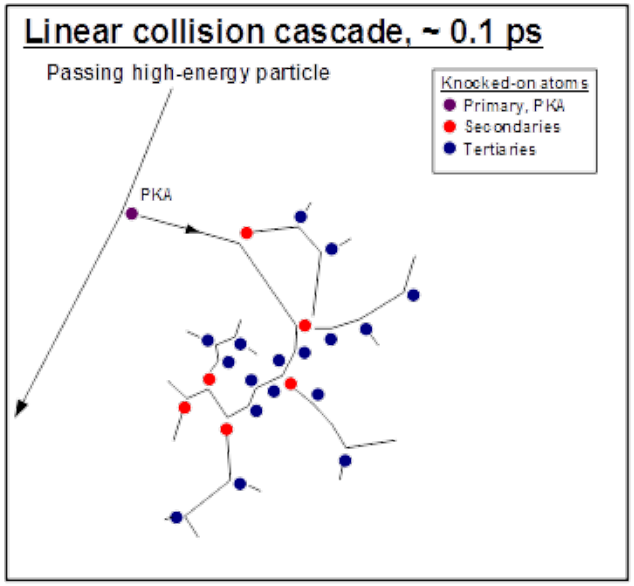
Basic physics

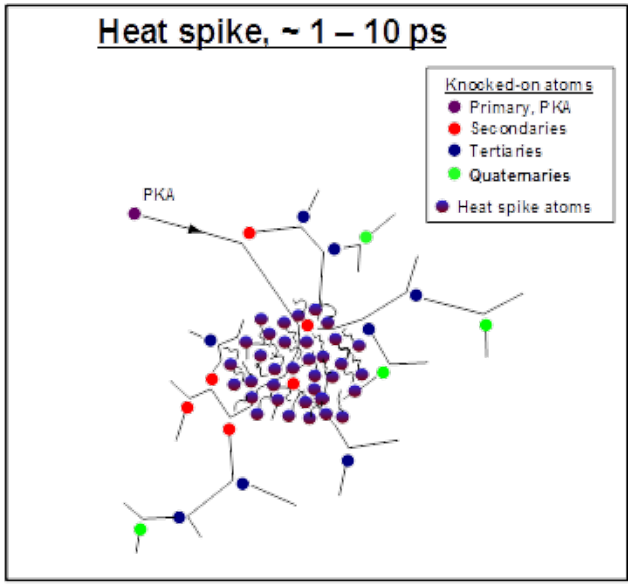
- Schematical illustration of the ion slowing-down process

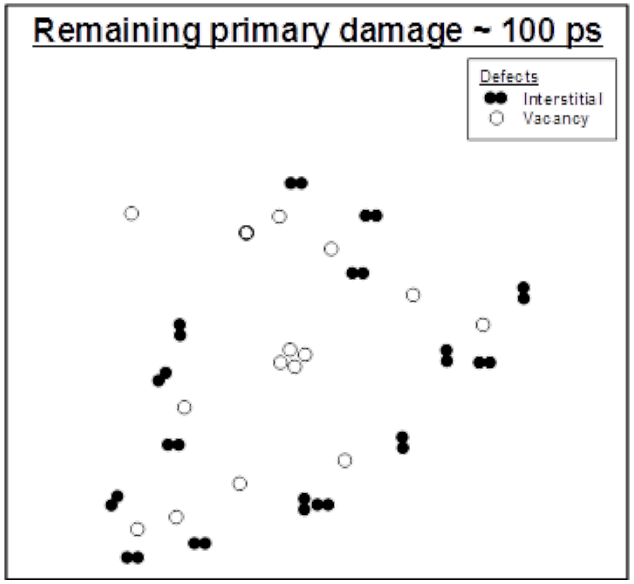


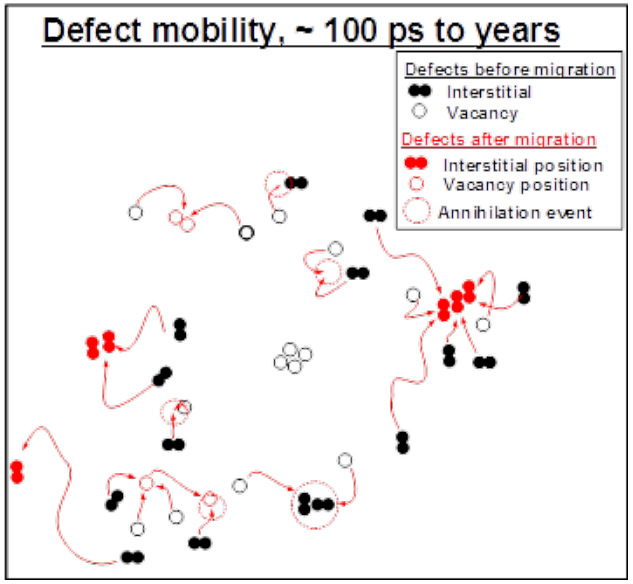


Phases and time scales of events



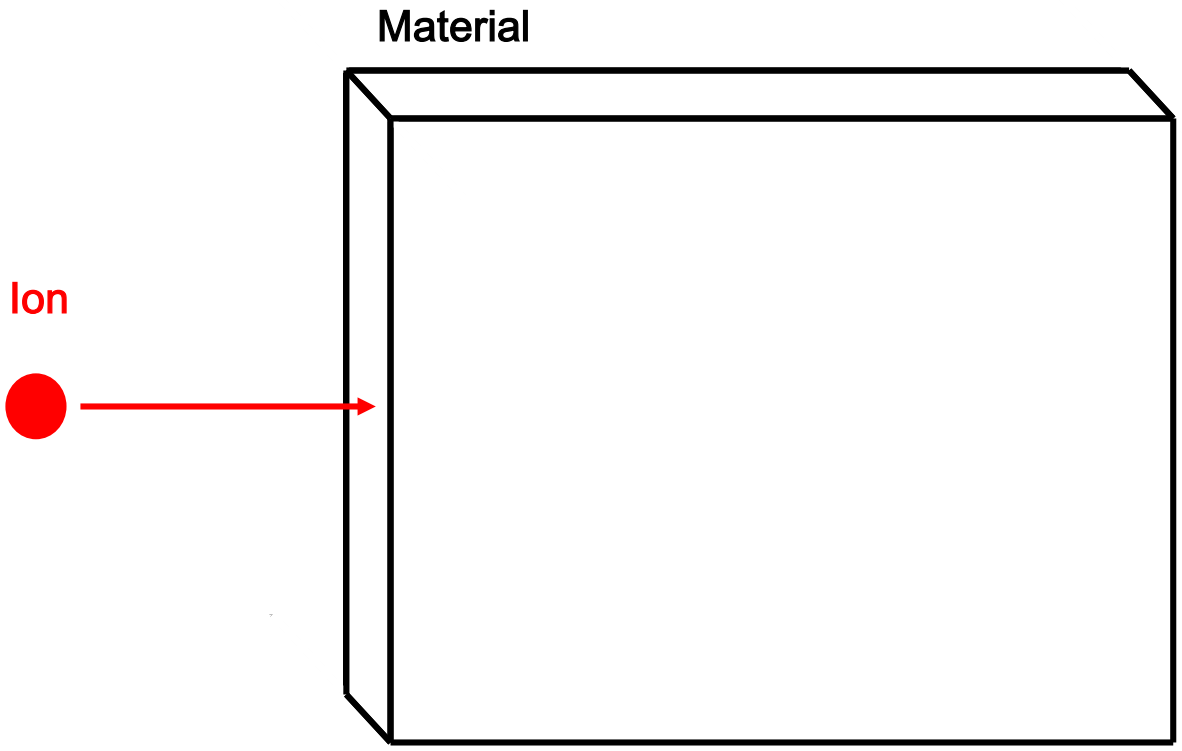






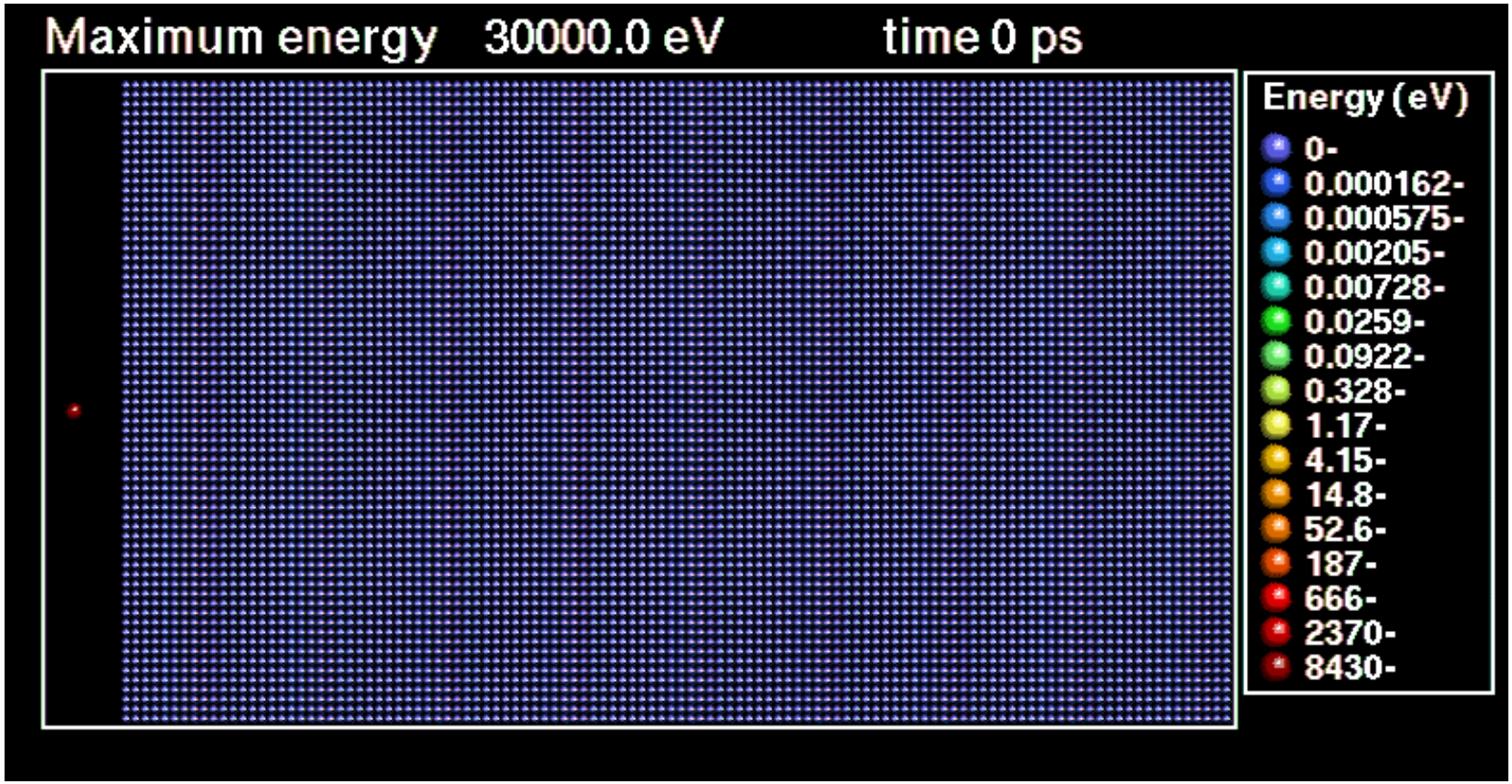
Animation view from MD

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

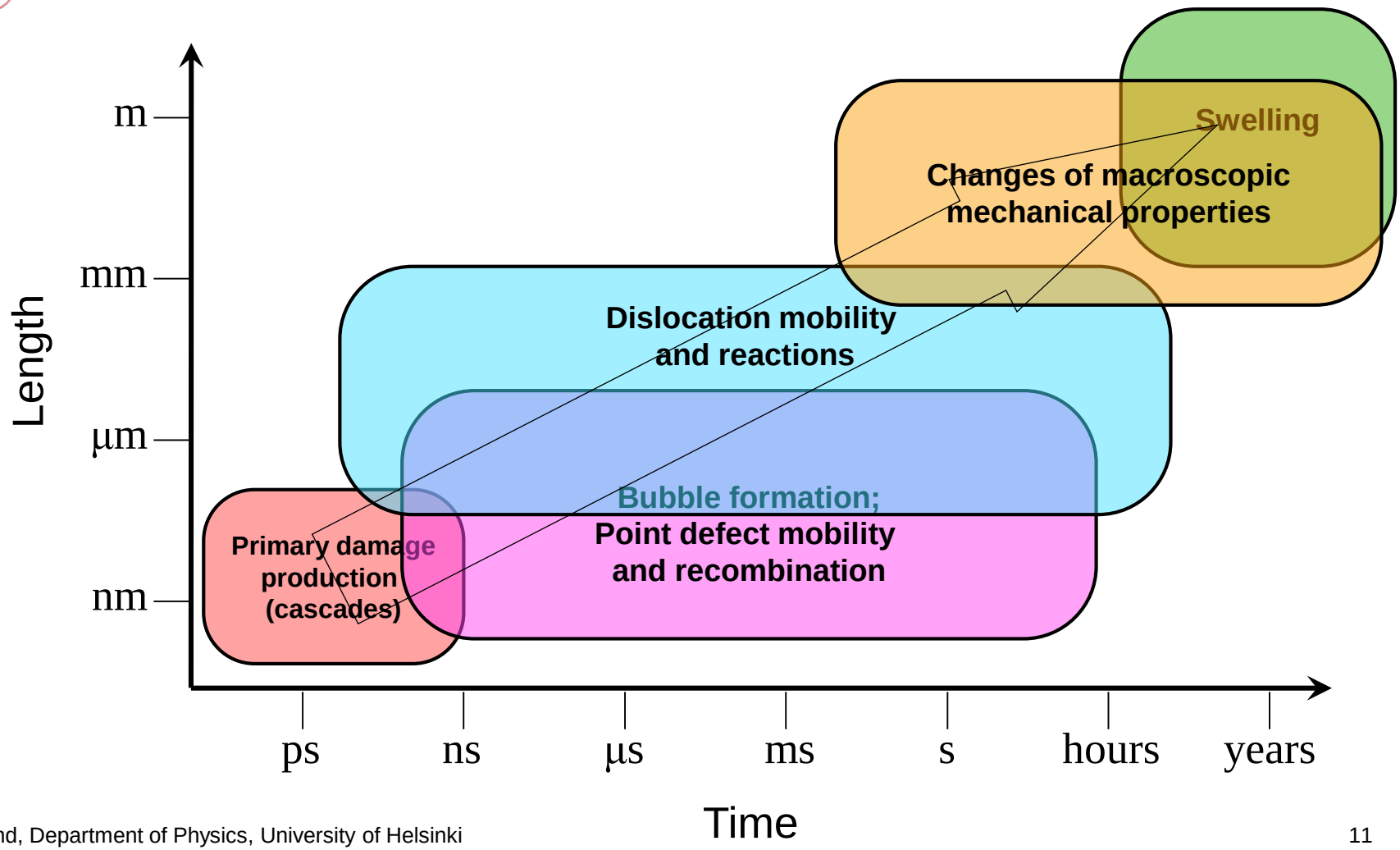


Irradiation effects:

Animation view

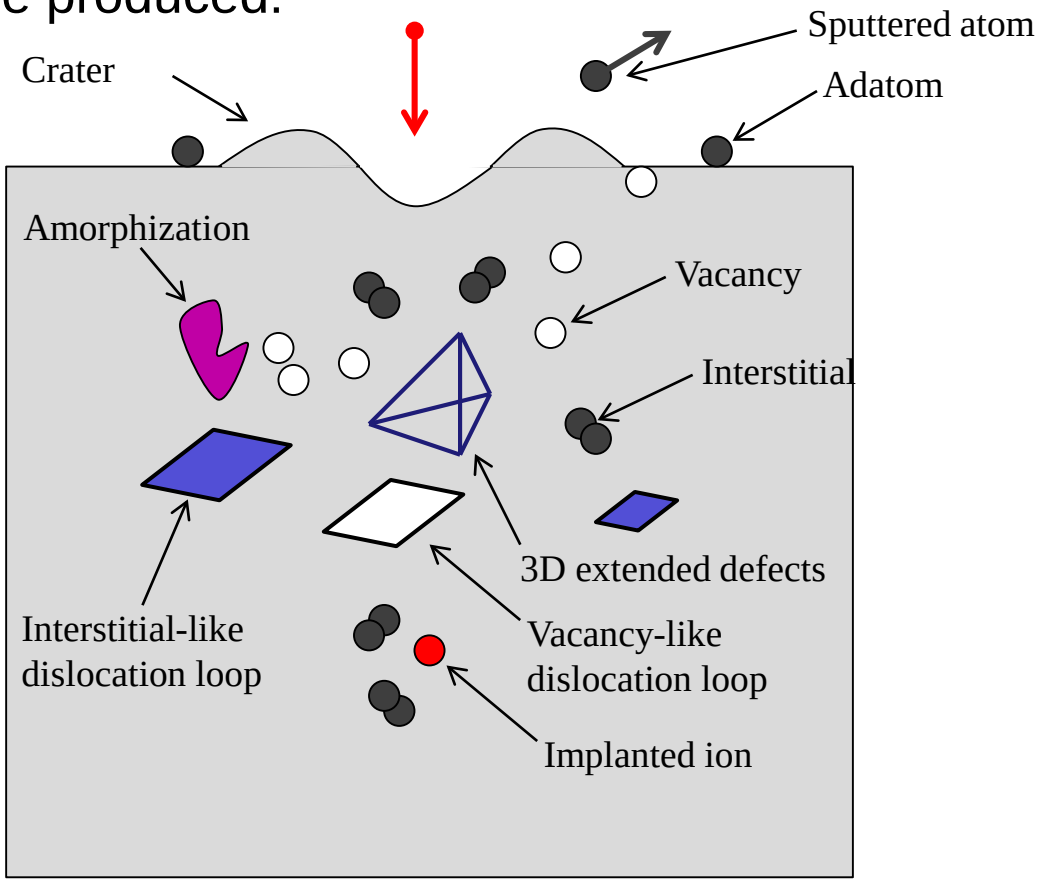


What happens physically in the materials?



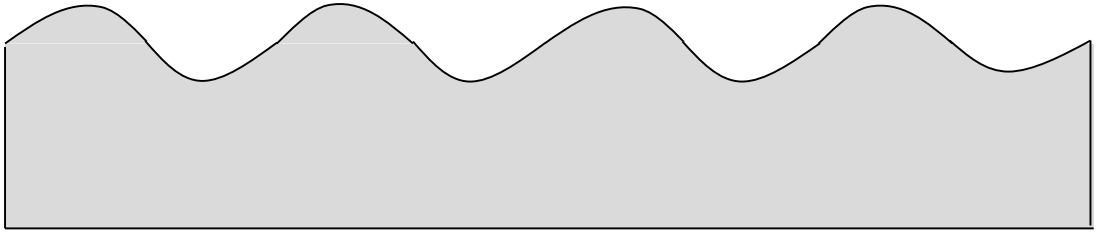
The rich materials science of irradiation effects

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



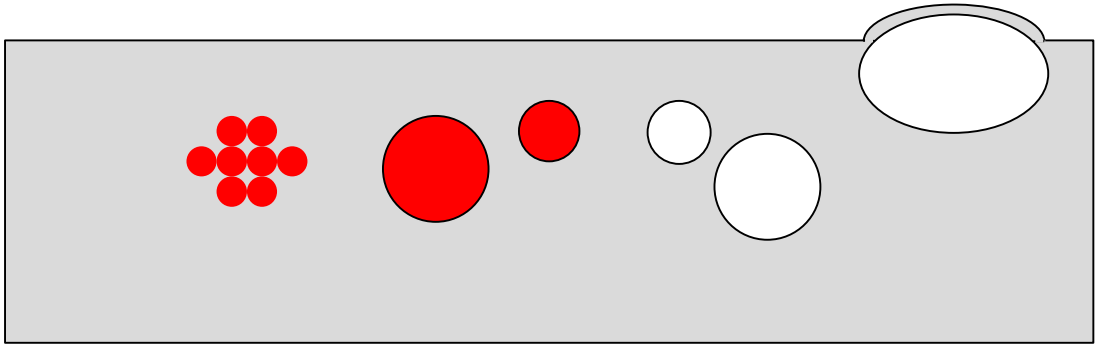
The rich materials science of irradiation effects: high fluences

- In addition, for multiple ions i.e. prolonged irradiation many more things can happen:
  - 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)]

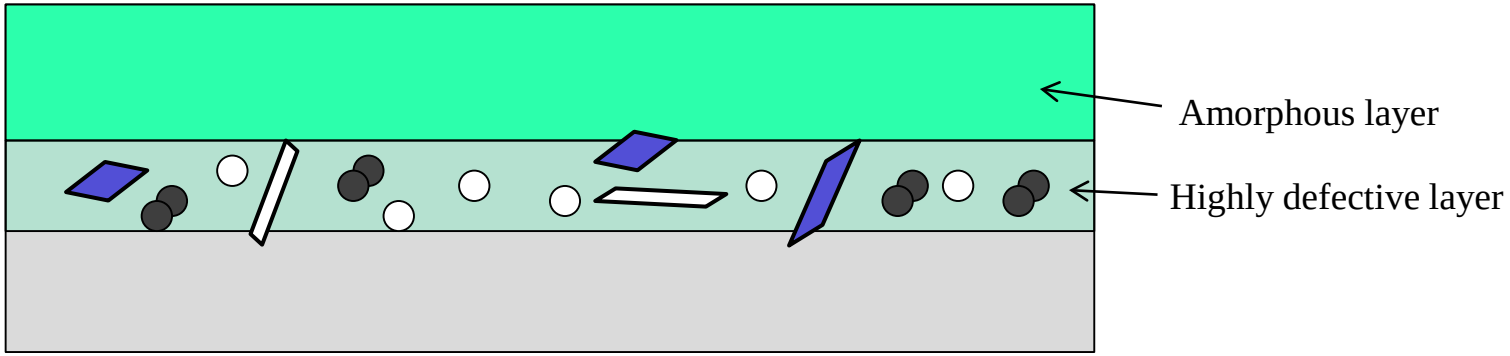
  - Precipitate/nanocluster, bubble, void or blister formation inside solid



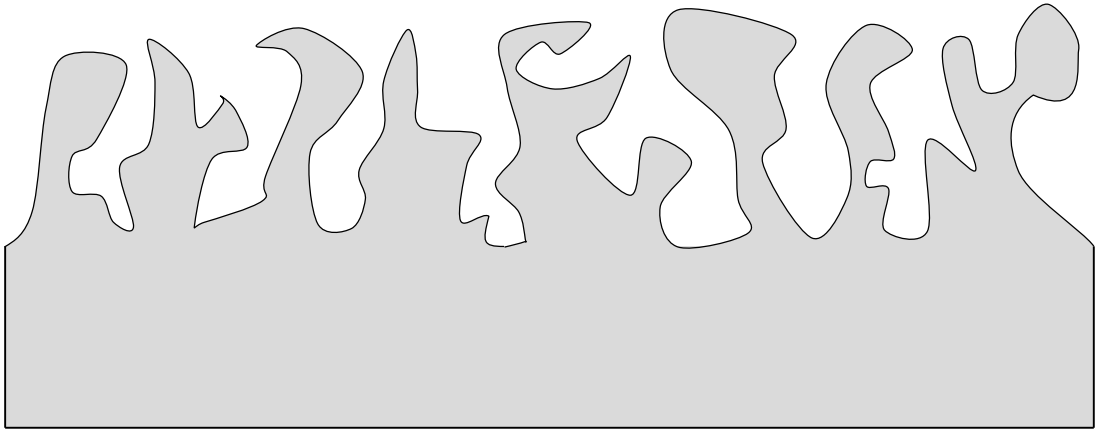
[Bubbles e.g: K. O. E. Henriksson, K. Nordlund, J. Keinonen, D, Physica Scripta T108, 95 (2004); Nanocrystals e.g. 75S. Dhara, Crit. Rev. Solid State Mater. Sci. 32, 1 [2007)]

The rich materials science of irradiation effects: high fluences

- Phase changes, e.g. amorphization:

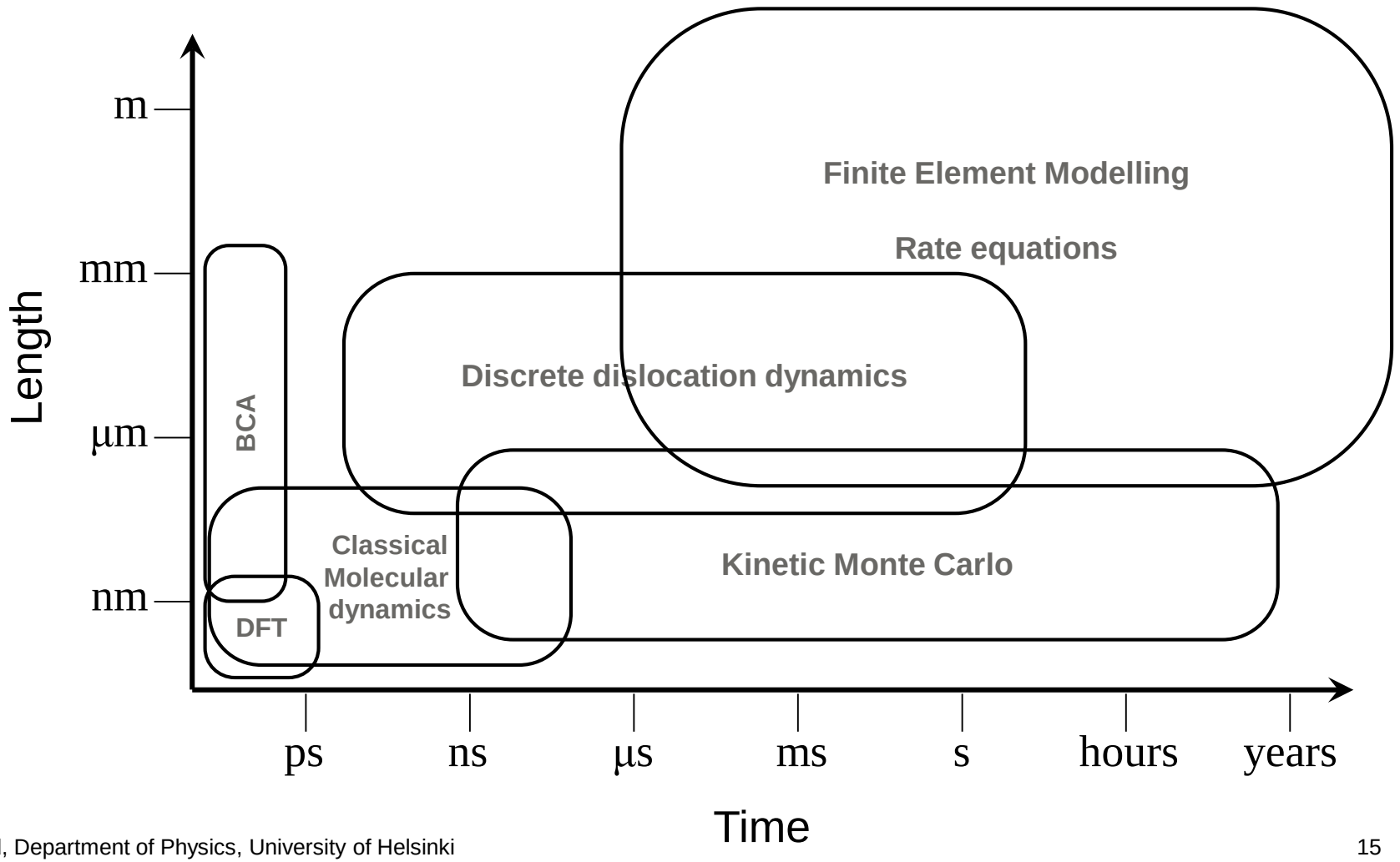


- Spontaneous porousness formation, “fuzz” (e.g. in Ge, W)



What is needed to model all this: the multiscale modelling framework

- Sequential and concurrent multiscale modelling



What is needed to model the atomic level of irradiation effects?

- One needs to be able to handle:
  1) keV-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

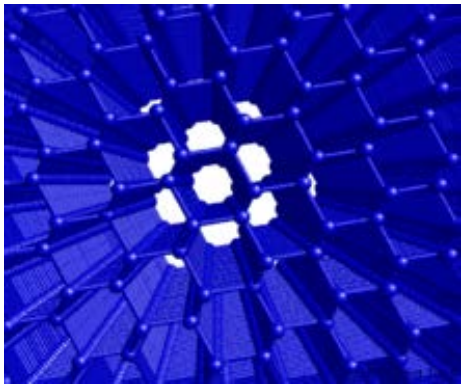
End of Part 1

- Take-home messages:
  - Ion beam processing is an industrially important process
  - Ion, plasma and neutron irradiation of materials modify them in fundamentally similar ways
  - Key mechanisms of energy transfer are loss to electronic excitations (electronic stopping power) and nuclear collisions (nucler stopping power)
  - The materials modification from irradiation can take many different interesting forms

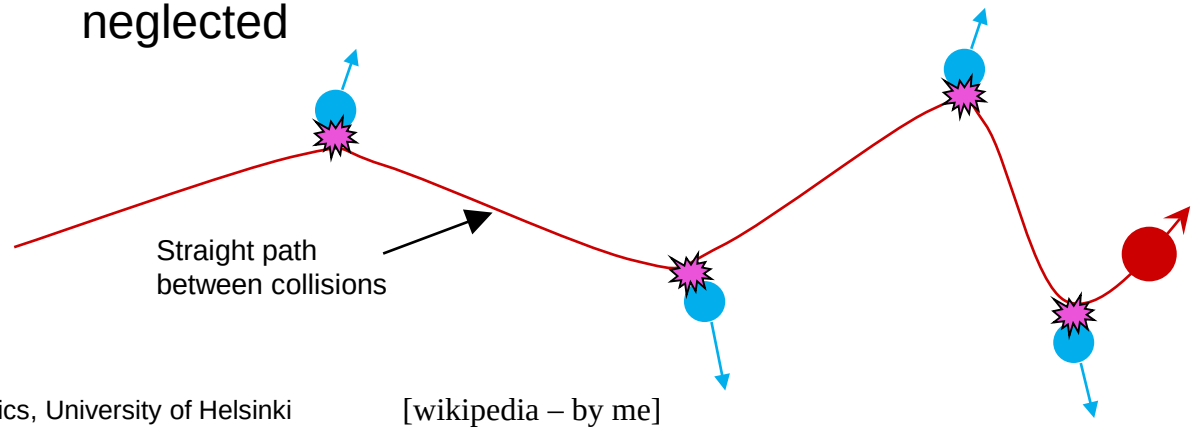
HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Part 2: Binary Collision Approximation

BCA = Binary collision approximation



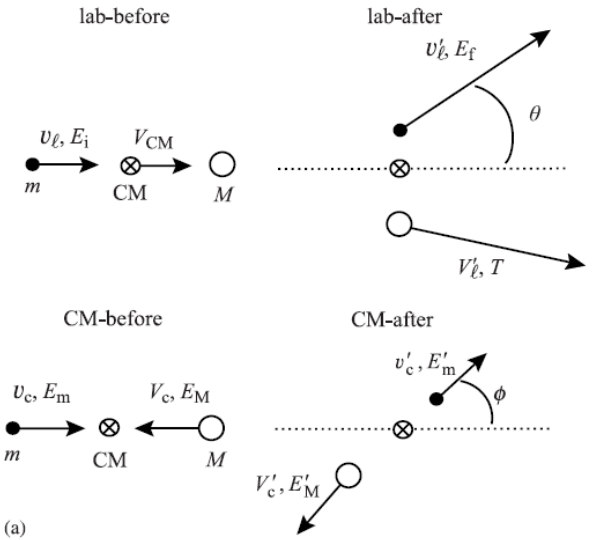
- The original way to treat ion irradiation effects on a computer
- Developed by Mark Robinson, ~1955
  - Channeling was predicted by BCA **before** it was experimentally found!
- In BCA the collisions of an incoming ion are treated as a sequence of independent collisions, where the ion motion is obtained 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



[wikipedia – by me]

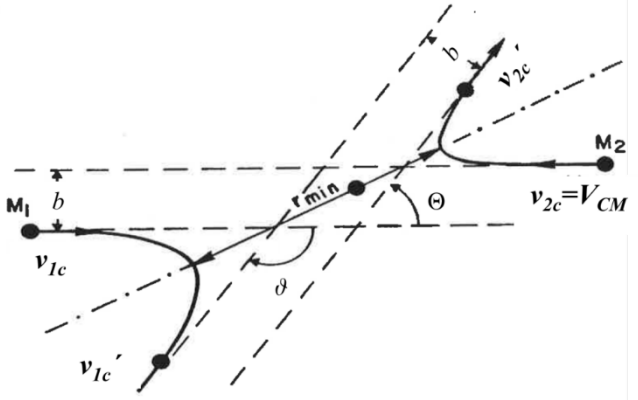
Binary collision approximation: summary of equations

- In BCA, the classical two-body scattering is treated in center-of-mass coordinates, and the repulsive interatomic potential $V(r)$ between atoms is integrated to give the scattering angle Θ for a given impact parameter b.



Interatomic potential

$$\Theta = \pi - \int_{-\infty}^{+\infty} \frac{b\,dr}{r^2\sqrt{1-\frac{b^2}{r^2}-\frac{V(r)}{E_{CM}}}} = \pi - 2\int_{r_{\min}}^{+\infty} \frac{b\,dr}{r^2\sqrt{1-\frac{b^2}{r^2}-\frac{V(r)}{E_{CM}}}}$$



Repulsive interatomic potential: The ZBL potential

- The ZBL screening parameter and function have the form

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{Z_1 Z_2 e^2}{r}\varphi(r/a) \quad a = a_u = \frac{0.8854 a_0}{Z_1^{0.23} + Z_2^{0.23}}$$

$$\varphi(x) = 0.1818e^{-3.2x} + 0.5099e^{-0.9423x} + 0.2802e^{-0.4029x} + 0.02817e^{-0.2016x}$$

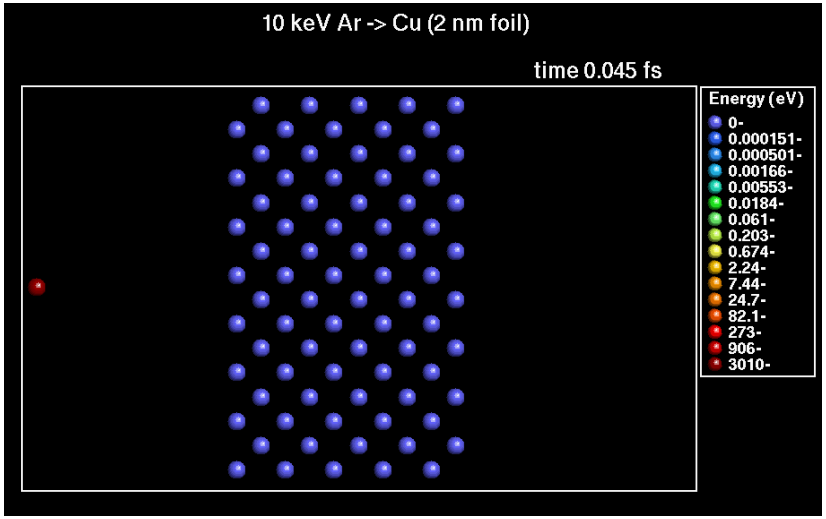
  where $x = r/a_u$, and a_0 is the Bohr atomic radius = 0.529 Å.

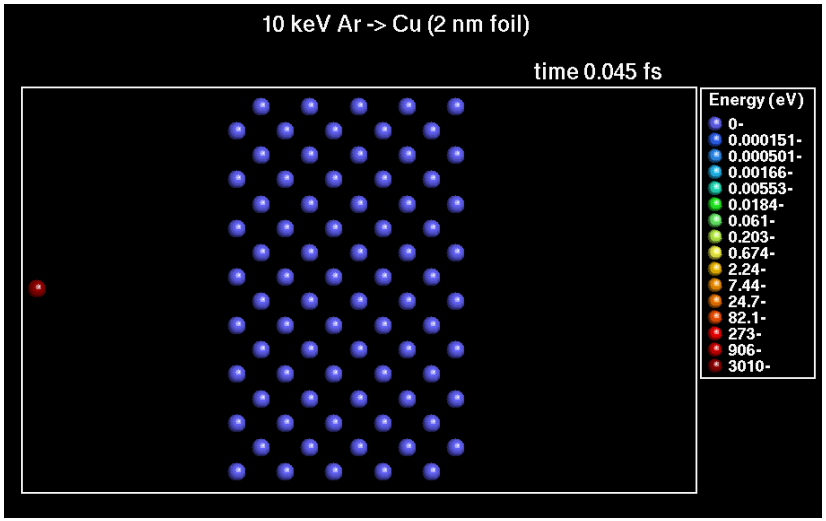
- The standard deviation of the fit of the universal ZBL repulsive potential to the theoretically calculated pair-specific potentials it is fit to is 18% above 2 eV [ZBL book]
- Even more accurate (~1%) repulsive potentials can be obtained from self-consistent total energy calculations using density-functional theory, but much of the time the ZBL potential is 'good enough'

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

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)





Comparison 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

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

    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
  - We have just implemented BCA for arbitrary atom coordinates for up to millions of atoms! [Shuo Zhang et al, Phys. Rev. E (2016) acceptedish]
- BCA is many many orders of magnitude more efficient than MD

Personal gripe on term ”Monte Carlo”

- Some people tend to call BCA just ”Monte Carlo”
- This is **very** misleading
  - … Because other subfields of physics call entirely different methods ”Monte Carlo”: in plasma physics, so called ”Particle-in-Cell” simulations are sometimes called ”Monte Carlo”. In condensed matter physics, Metropolis Monte Carlo is often called just ”Monte Carlo”. Etc.
  - Besides, BCA with a lattice is not even a Monte Carlo method
- Ergo: ***never call any method*** just ”Monte Carlo”, always specify what kind of MC you mean.

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 still a good method for simulating very-high-fluence composition changes
  - As long as chemistry and diffusion does not play a role!
- BCA for arbitrary atom coordinates great for simulating RBS/channeling spectra

End of Part 2

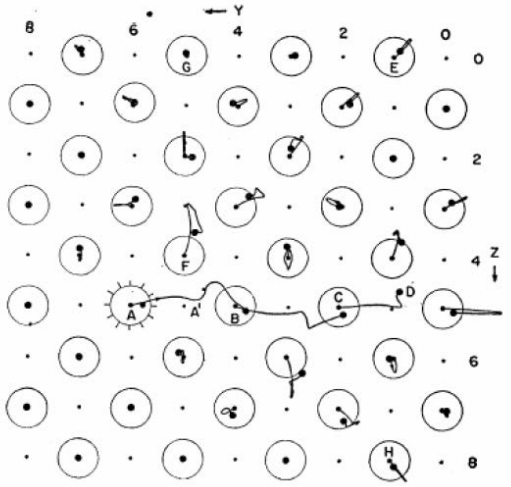
- Take-home messages:
  - The binary collision approximation is a very efficient tool to simulate the collisional part of irradiation effects
  - Some varieties of BCA have been superseded by Molecular dynamics, but others are still relevant
    - At least efficient range calculations, Rutherford backscattering simulation and dynamic composition changes

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

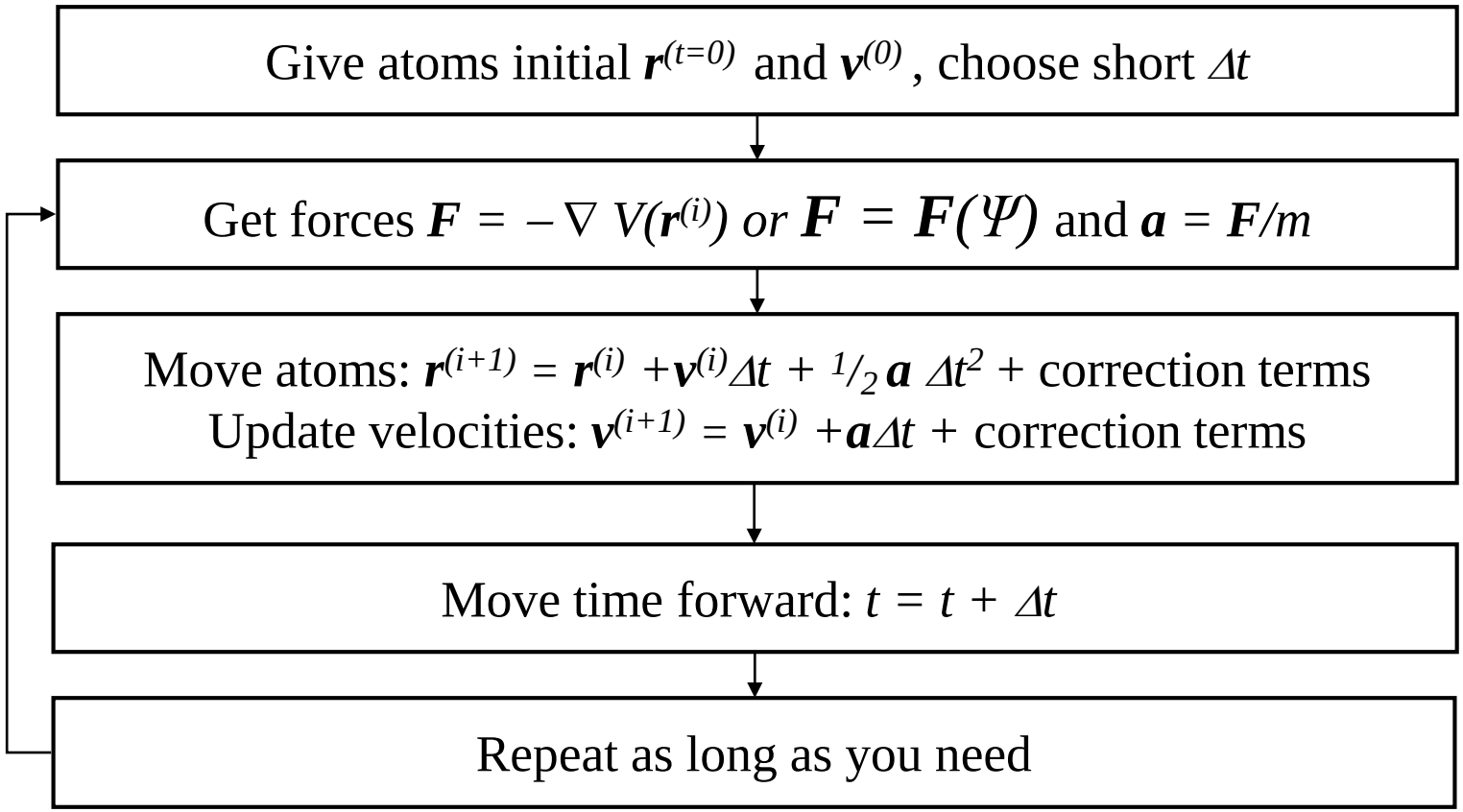
Part 3: Molecular dynamics

MD = Molecular dynamics

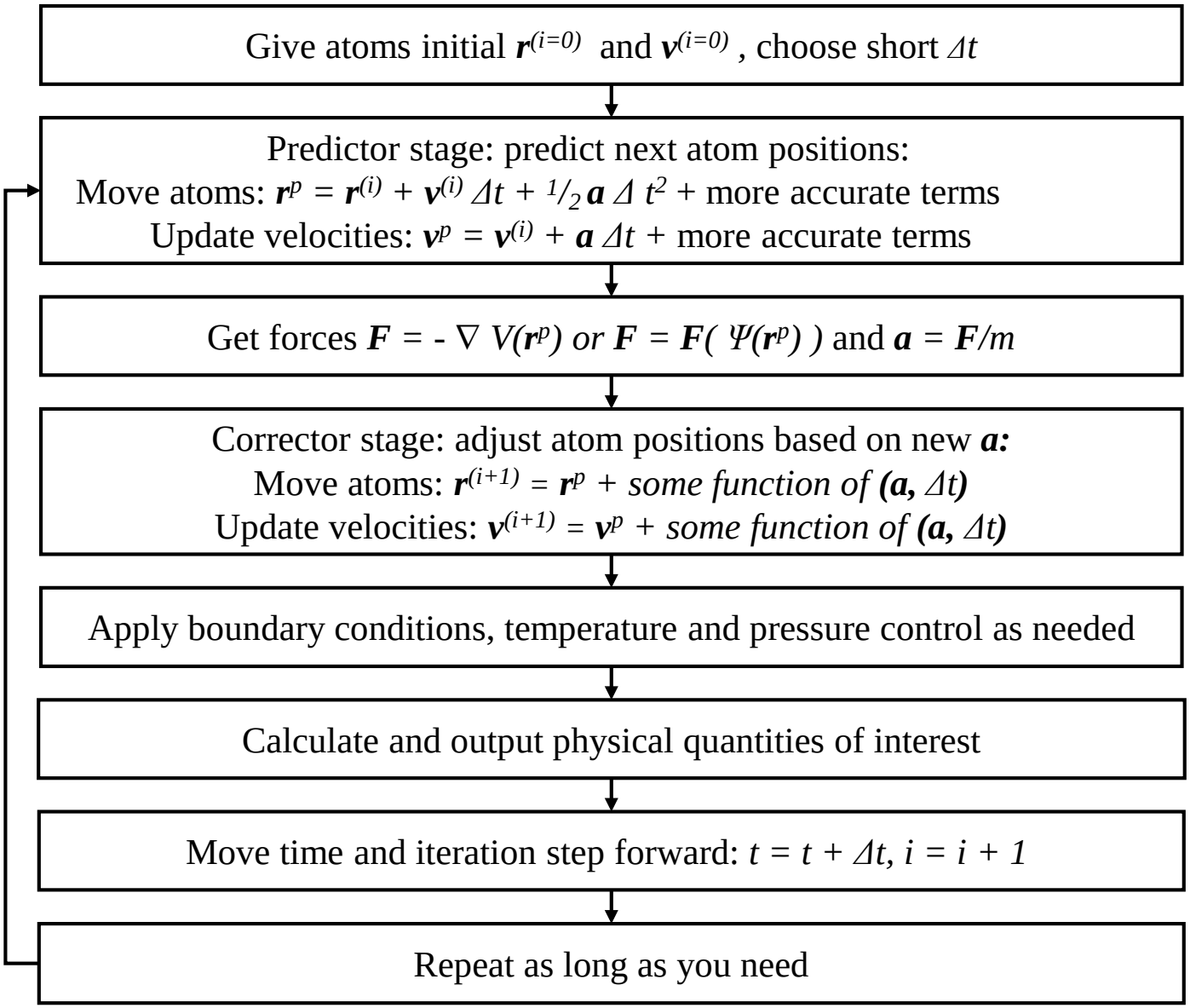
- MD is solving the Newton's (or Lagrange or Hamilton) equations of motion to find the motion of a group of atoms
- Originally developed by Alder and Wainwright in 1957 to simulate atom vibrations in molecules
  - Hence the name "molecular"
  - Name unfortunate, as much of MD done nowadays does not include 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 discovered replacement collision sequences!



MD algorithm, simple version



MD algorithm, detailed version



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

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

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

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

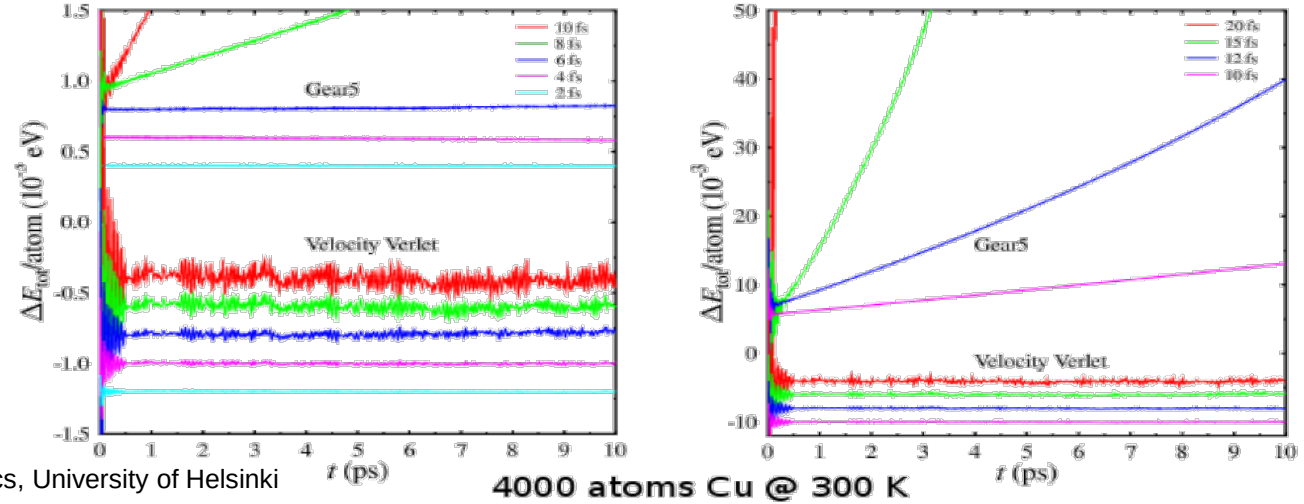
[L. Verlet, Phys. Rev. 159 (1967) 98]

- 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]

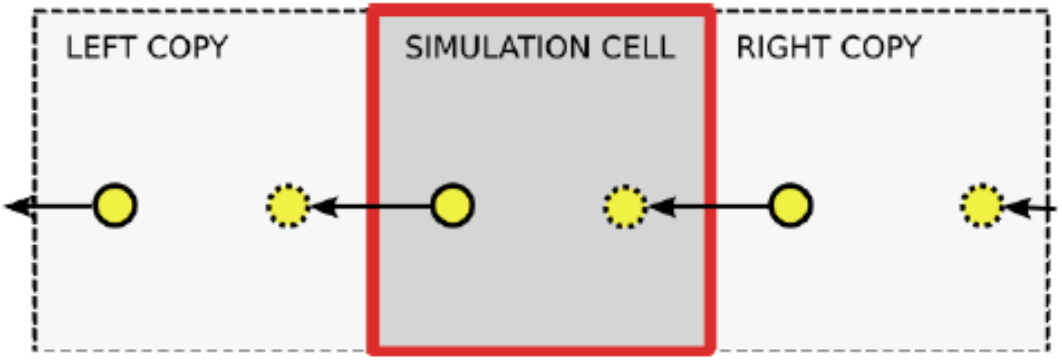
MD – time step selection

- 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



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.

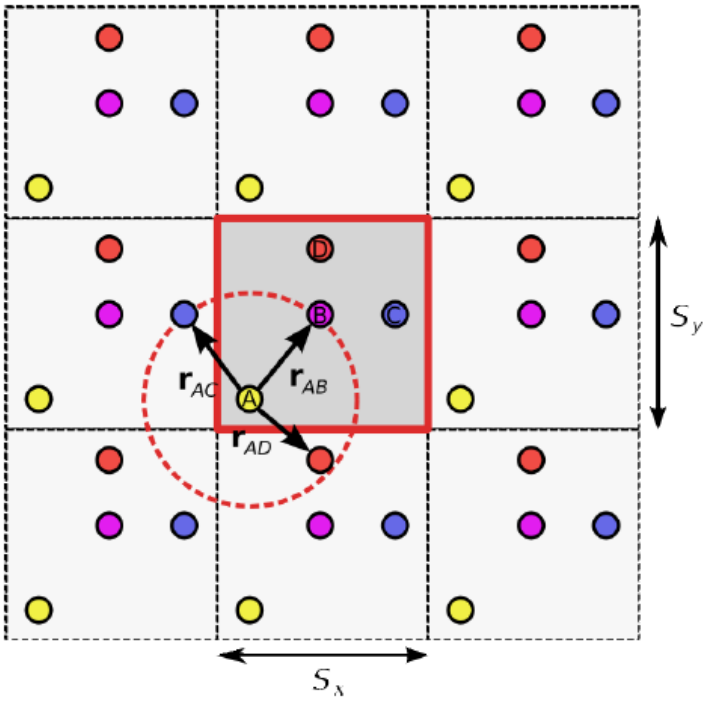


MD: periodics continued

- 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 – 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

Notes on pressure control

- ***Never use pressure control if there is an open boundary in the system!!***
- Why??
- Think about it...
- Hint: surface tension and Young's modulus

- ***Never ever ever use them during an irradiation simulation!!***

  - Why??

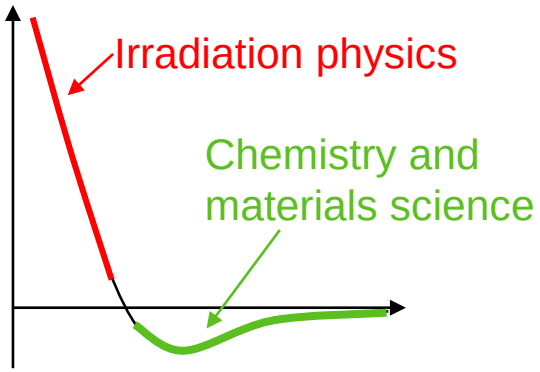
    - Hint: strong collisions...

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

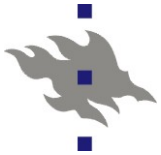
- The basic MD algorithm is not suitable for high-energy interactions, and does not describe electronic stopping at all
- But over the last ~25 years augmentations of MD to be able to handle this have been developed by us and others

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!

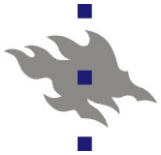


[K. Nordlund, N. Runeberg, and D. Sundholm, Nucl. Instr. Meth. Phys. Res. B 132, 45 (1997)].



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)

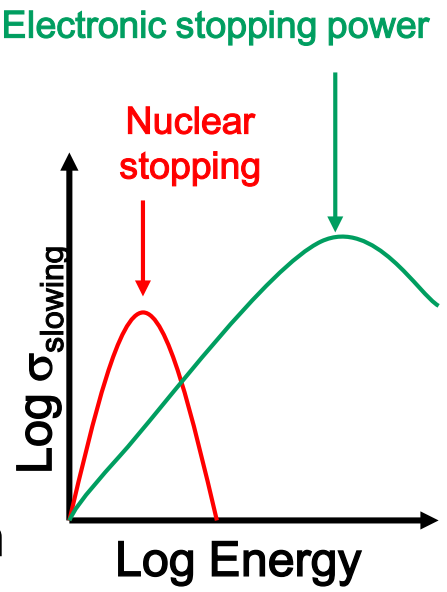
[K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)].

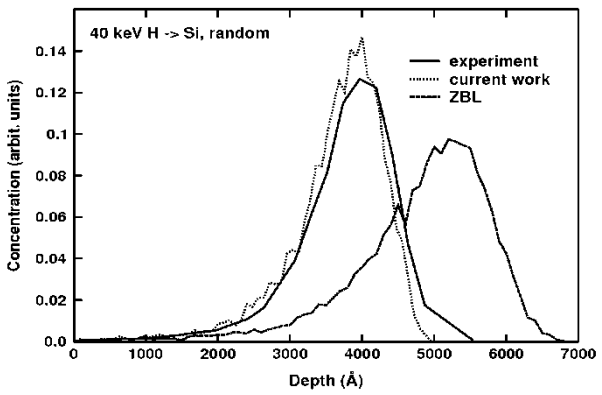
2) Energy loss to electronic excitations

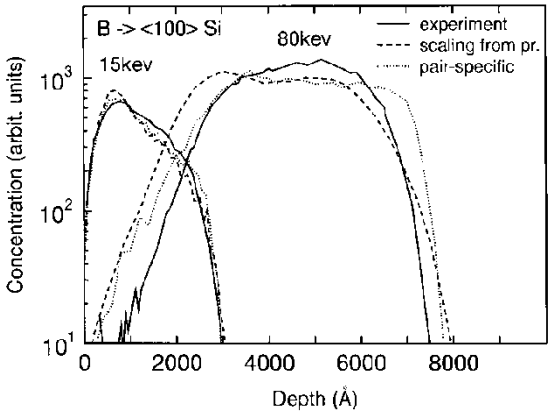
- The energy loss to electronic excitations = electronic stopping S can be included as a frictional force in MD simply as:

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

- 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:





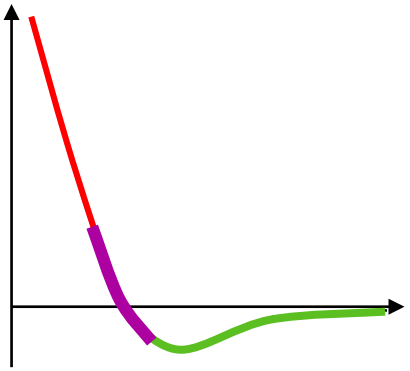


[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen,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

What is needed to model irradiation effects?

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

- Requires realistic **intermediate part** in potential



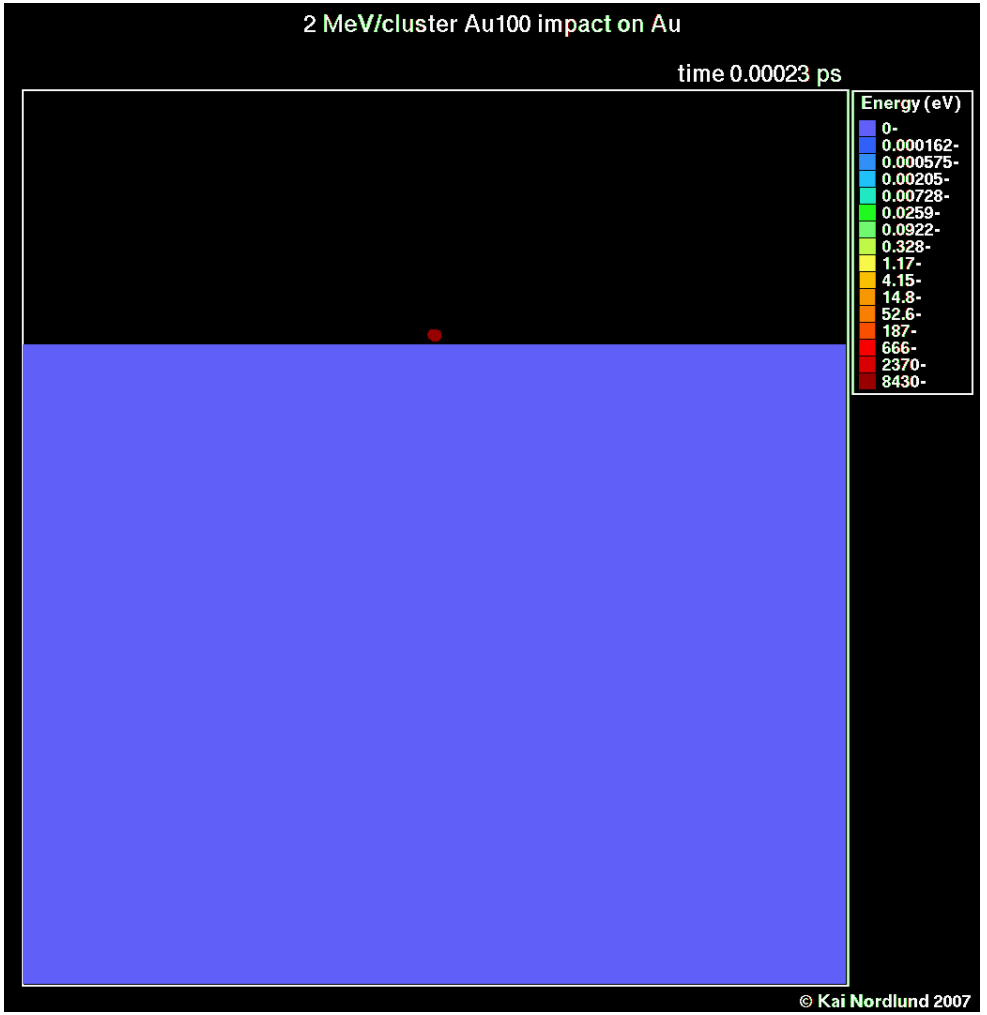
  - Can be adjusted to experimental high-pressure data and threshold displacement energies
    - Somewhat tedious ‘manual’ fitting but doable
  - Could also be fit to DFT database in this length range, done recently e.g. by Tamm, Stoller et al.

[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

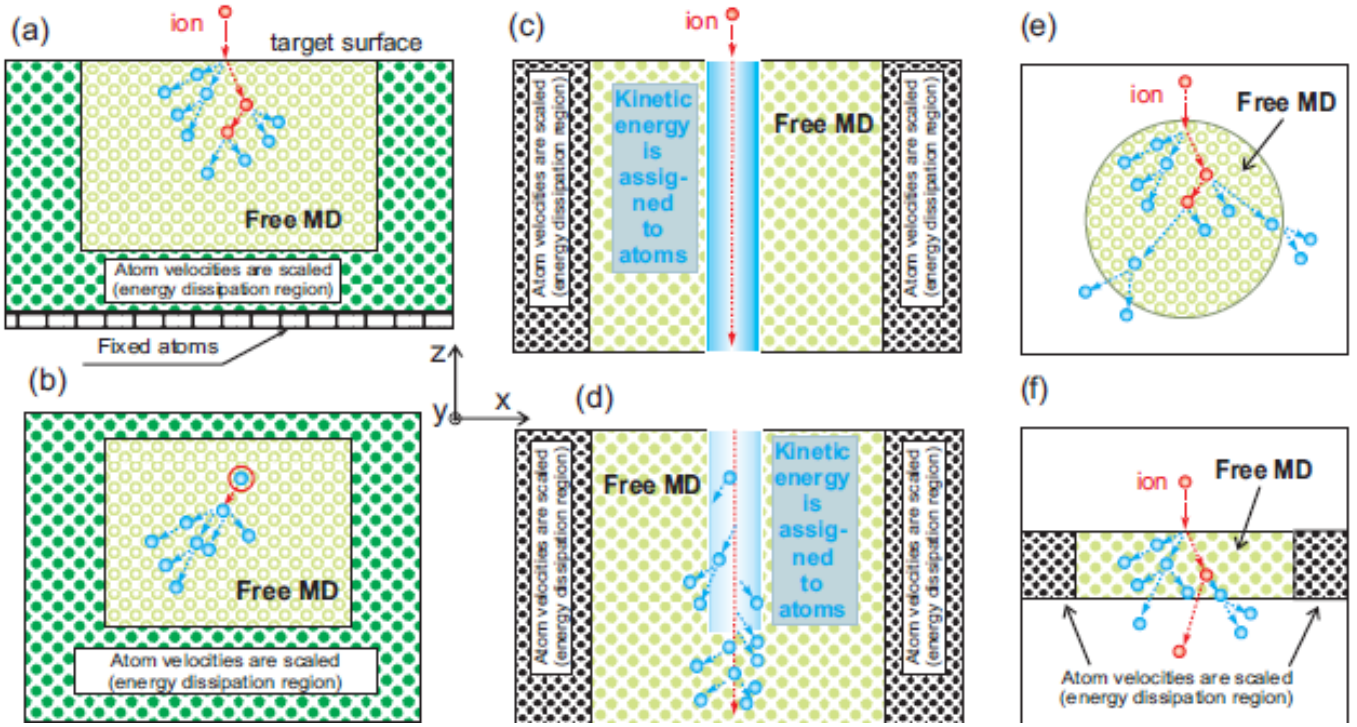
- The transition to thermodynamics occurs naturally in MD
- But boundary conditions a challenge due to heat and pressure wave emanating from a cascade



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:

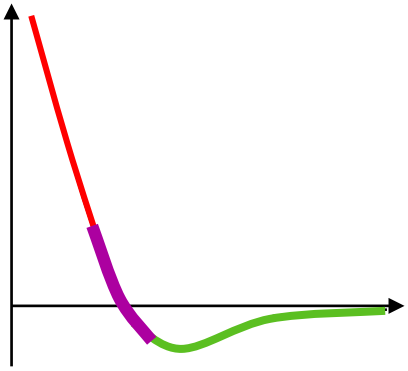
a) surface, b) bulk recoil, c-d) swift heavy ion, e) nanocluster, f) nanowire



[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



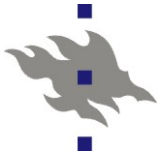
- Since we start out with the extremely non-equilibrium collisional part, all chemical bonds in system can break and reform and atoms switch places
  - **Conventional Molecular Mechanics force fields are no good at all!**

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



Potentials developed: one-slide overview of thousands of publications…

- 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

End of Part 3

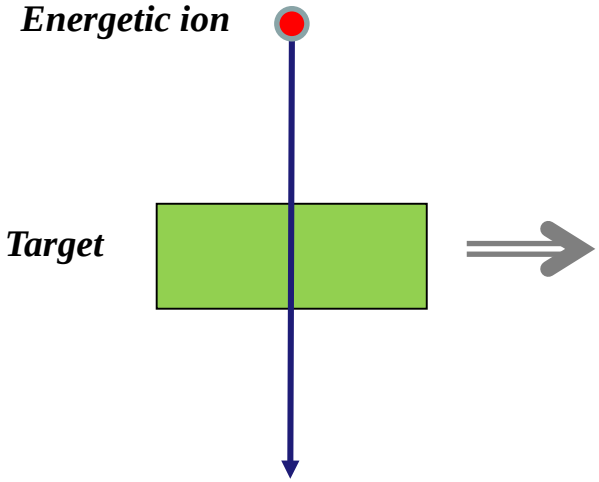
- Take-home messages:
  - Molecular dynamics is very well suited to model all aspects of primary damage formation
  - With classical potentials and modern supercomputers, ion or recoil energies up to ~1 MeV can be treated
  - Irradiation effects MD needs special algorithms not part of normal MD codes or textbooks!
  - Interatomic potential selection is crucial for reliability, and can be a limiting factor

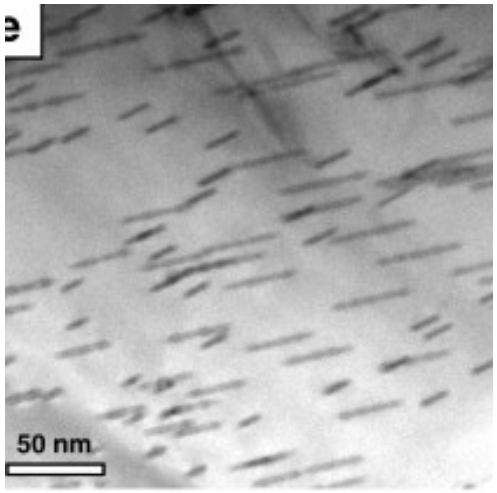
HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Part 3b: Molecular dynamics of swift heavy ions

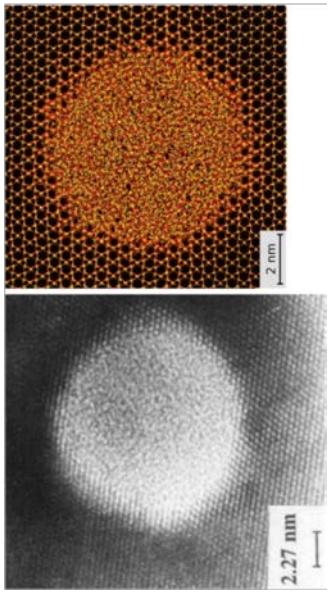
Swift heavy ions by MD

- 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]



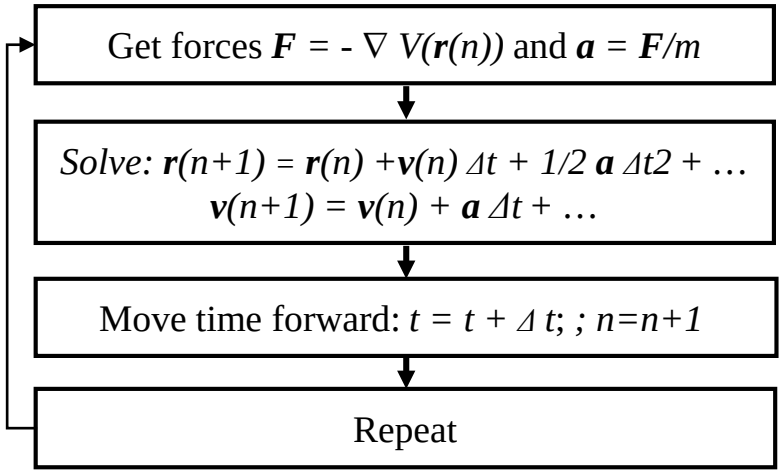
What happens physically: excitation models

- 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, …

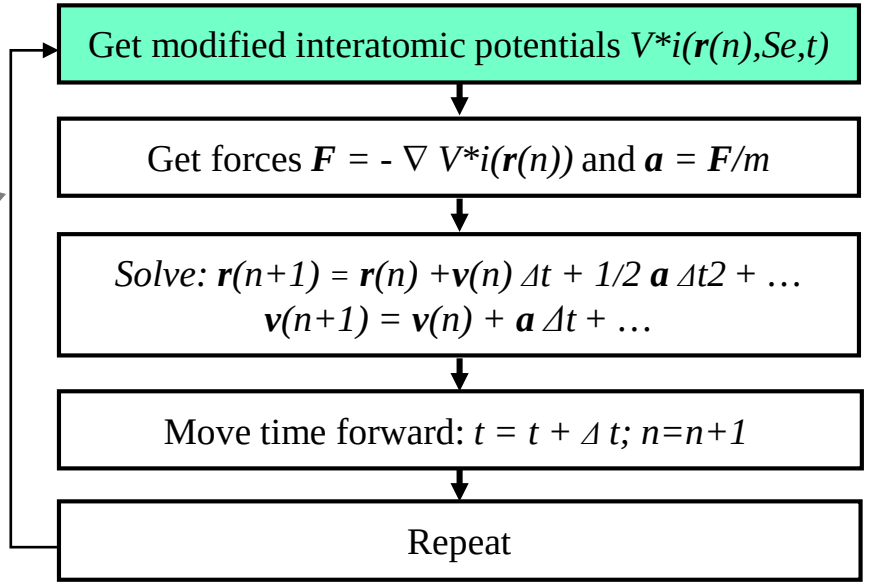
How to model it

- 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



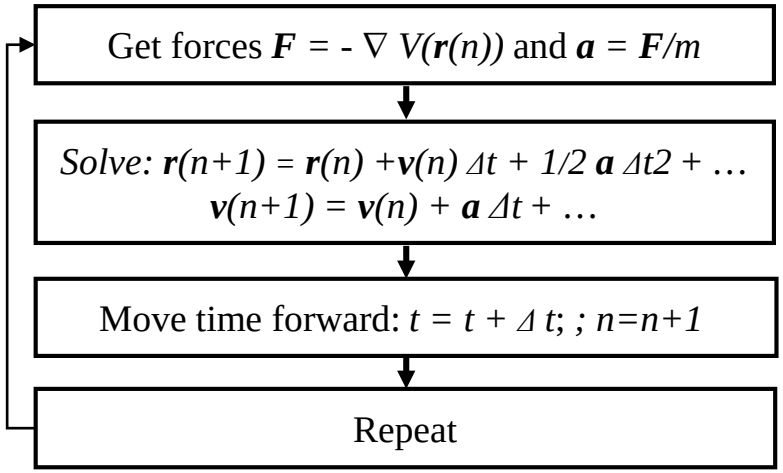
MD + antibonding or Coulomb



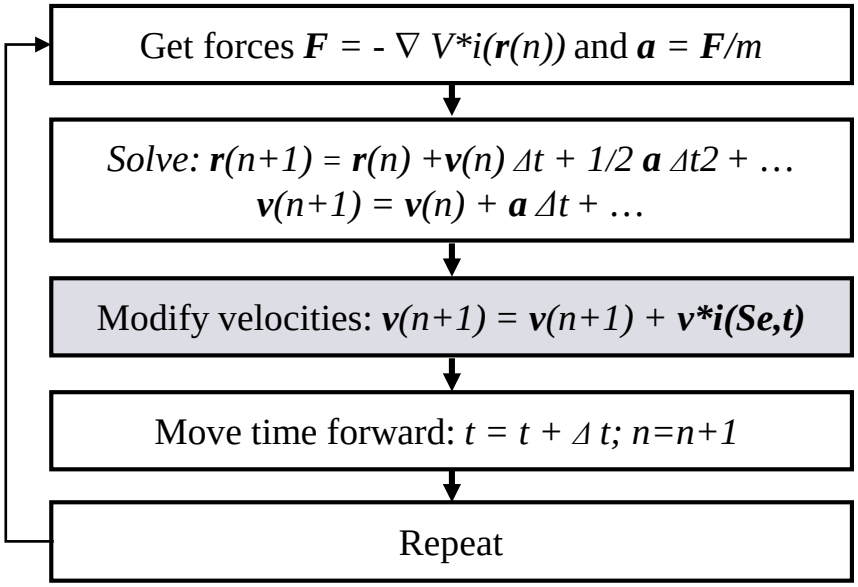
How to model it

- 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

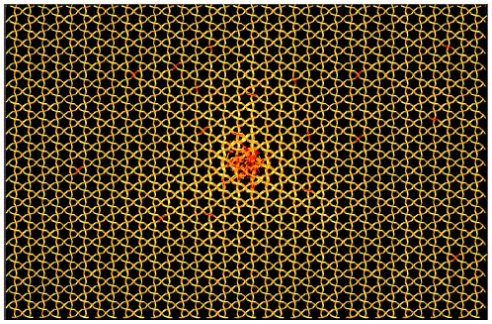


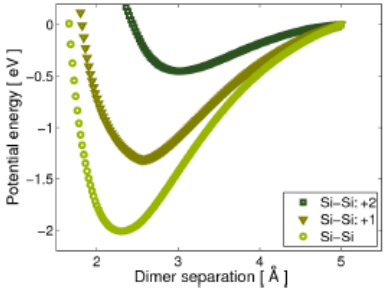
MD + heat spike model



How to model it

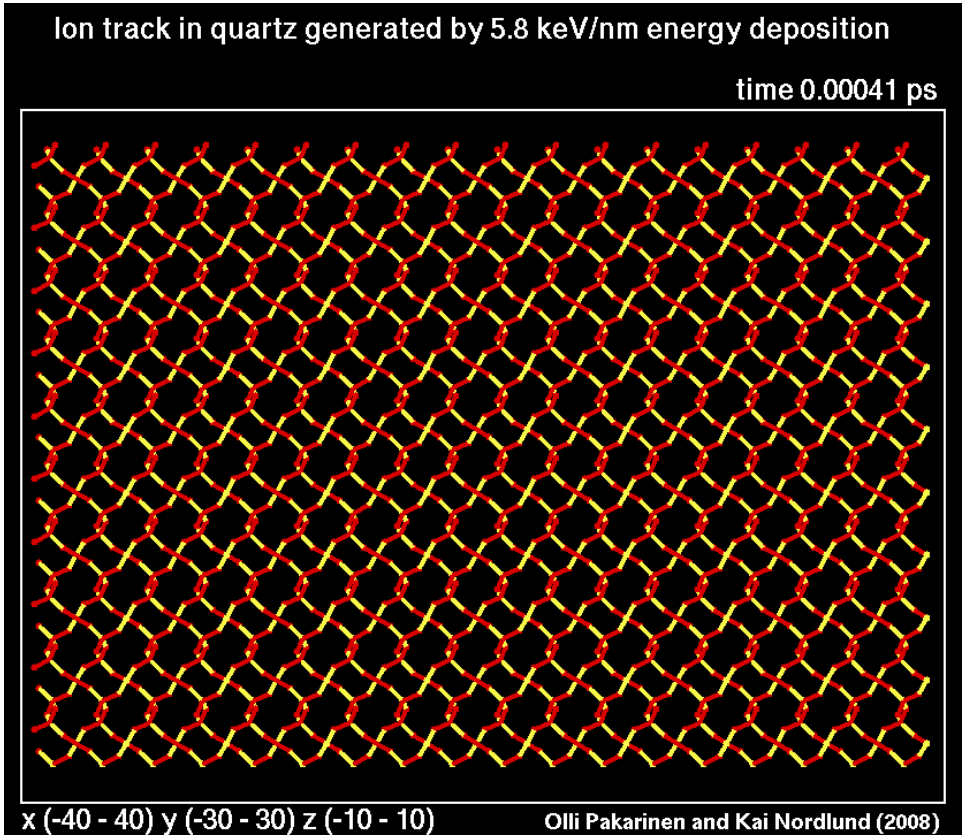
- The concurrent multiscale models give a way to test the excitation models against experiments
- We have implemented the heat-spike model and variations of cold melting models into our MD code
- Basic result is that both heat-spike (Toulemonde) models and cold melting models give tracks in SiO_2
  -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

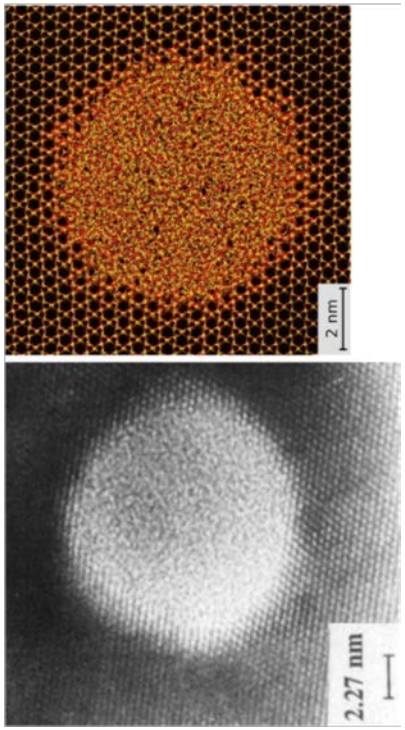




Sample result

- 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)]

End of Part 3b

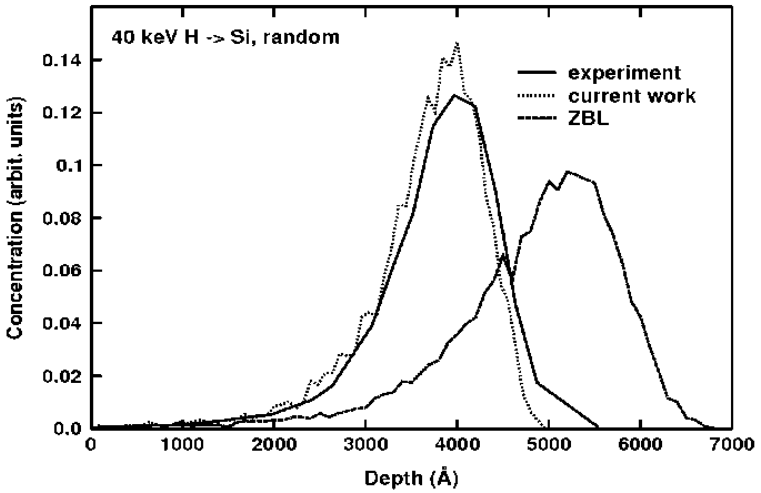
- Take-home messages:
  - Molecular dynamics can be extended to deal with swift heavy ions
  - Direct energy deposition corresponding to nuclear stopping from simple two-temperature models gives pretty good (within ~50% or so) agreement with experimental track sizes
  - However, how exactly the electronic energy deposition should be treated is not all clear

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Part 3c: Efficient MD for ions: the recoil interaction approximation (RIA)

MD for ion range calculations

- Consider the ion range profiles shown earlier:

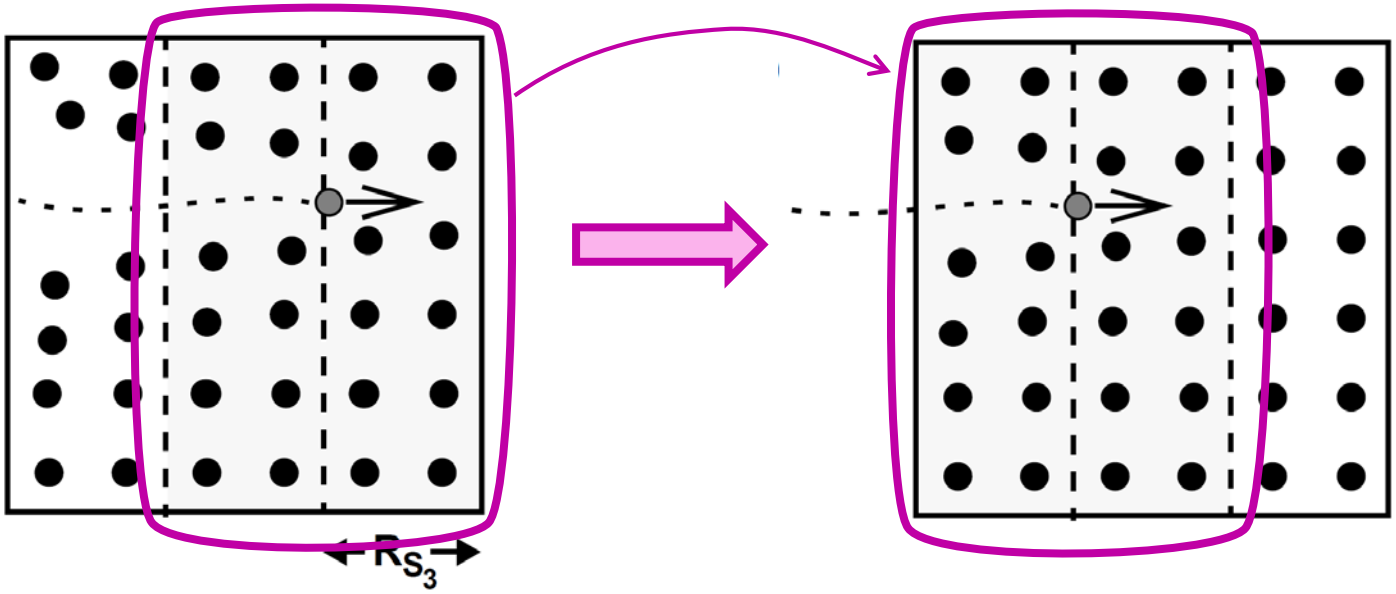


- To get a profile like this requires simulating ~ 10 000 ions. Very slow with MD even for modern supercomputers
- These were actually obtained with a speeded-up MD algorithm: the recoil interaction approximation (RIA)

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

MD-RIA algorithm

- The basic idea of the RIA is to use an MD algorithm, but only calculate the **interactions** between the **recoil** and sample atoms.
  - Enormous saving of computer time as N^2 sample-atom interactions not simulated
- Another speedup trick: use a small simulation cell, keep shifting it in front of the ion (from initial perfect positions)



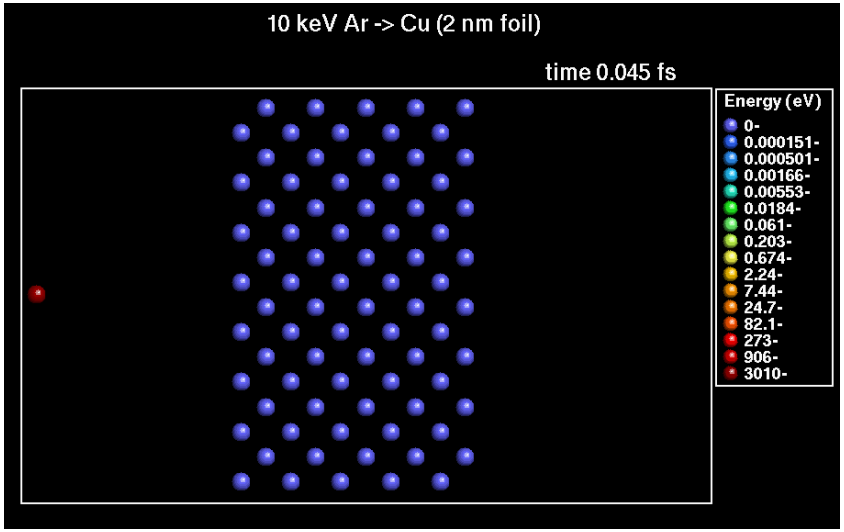
[K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)].

MD-RIA vs. BCA

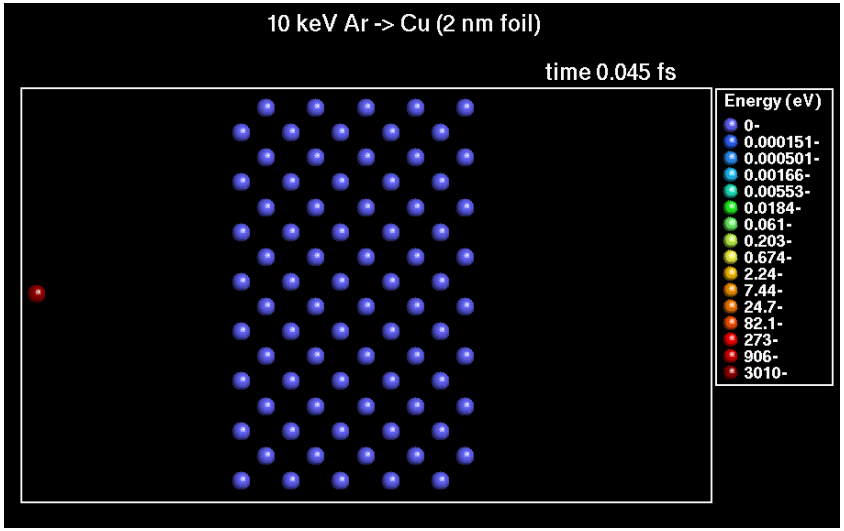
- The basic idea of the RIA is to use an MD algorithm, but only calculate the **interactions** between the **recoil** and sample atoms.
  - Enormous saving of computer time as N^2 sample-atom interactions not simulated
- Another speedup trick: use a small simulation cell, keep shifting it in front of the ion (from initial perfect positions)

Illustration of MD-RIA vs. Full MD

- 10 keV Ar -> Cu very thin foil (2 nm)
- MD-RIA



- Full MD

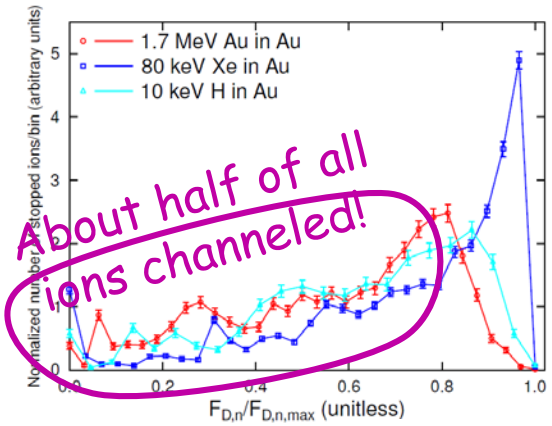


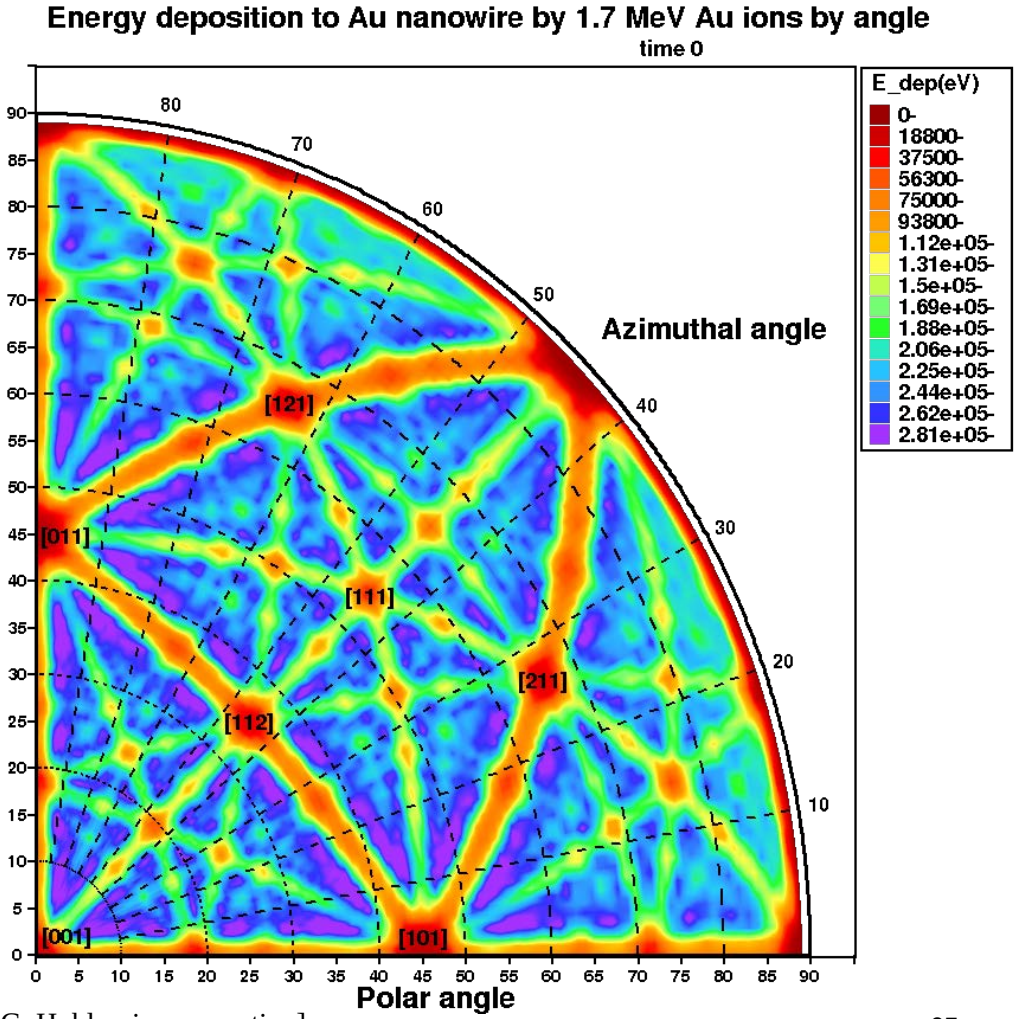
Advantages of MD-RIA

- MD-RIA inherently includes multiple simultaneous collisions
- There is no ambiguity in how to select the next colliding atom (which at low energies becomes a problem in BCA)
- Ion channeling effects come out naturally
- Both local and non-local electronic stoppings can be implemented, including ones with a 3D electron density of the solid
- It can also be used with attractive potentials!
  - Most recently we implemented it for antiprotons (purely attractive screened potential)

Recent usage example: systematic ion channeling calculations

- We have recently used MD-RIA to estimate channeling effects in nanostructures
- Example: 1.7 MeV Au in Au 20 nm thin film energy deposition
- Huge fraction of all incoming ion directions are channeling





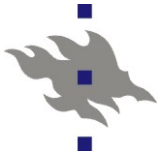
[K. Nordlund and G. Hobler, in preparation]

End of Part 3c

- Take-home messages:
  - If you want fast ion range or penetration calculations without the complexities of BCA, use MD-RIA
    - My MD-RIA code available to anybody, just ask for it.

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

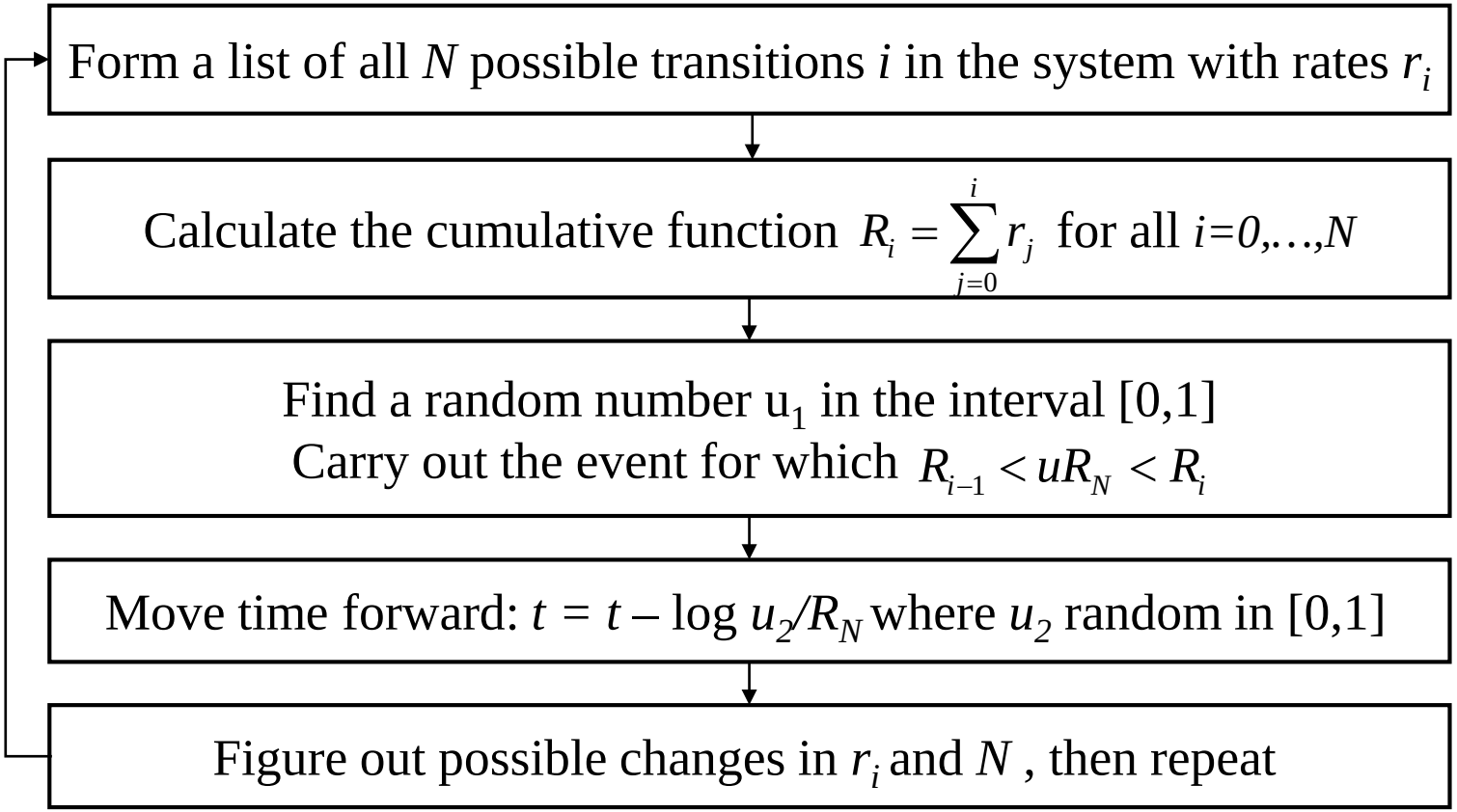
Part 4: Kinetic Monte Carlo

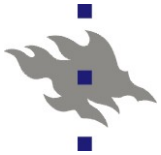


5) Long-term relaxation of defects

- 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, including us, 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

Kinetic Monte Carlo algorithm






Comments on KMC algorithm

- The KMC algorithm is actually exactly right for so called Poisson processes, i.e. processes occurring 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

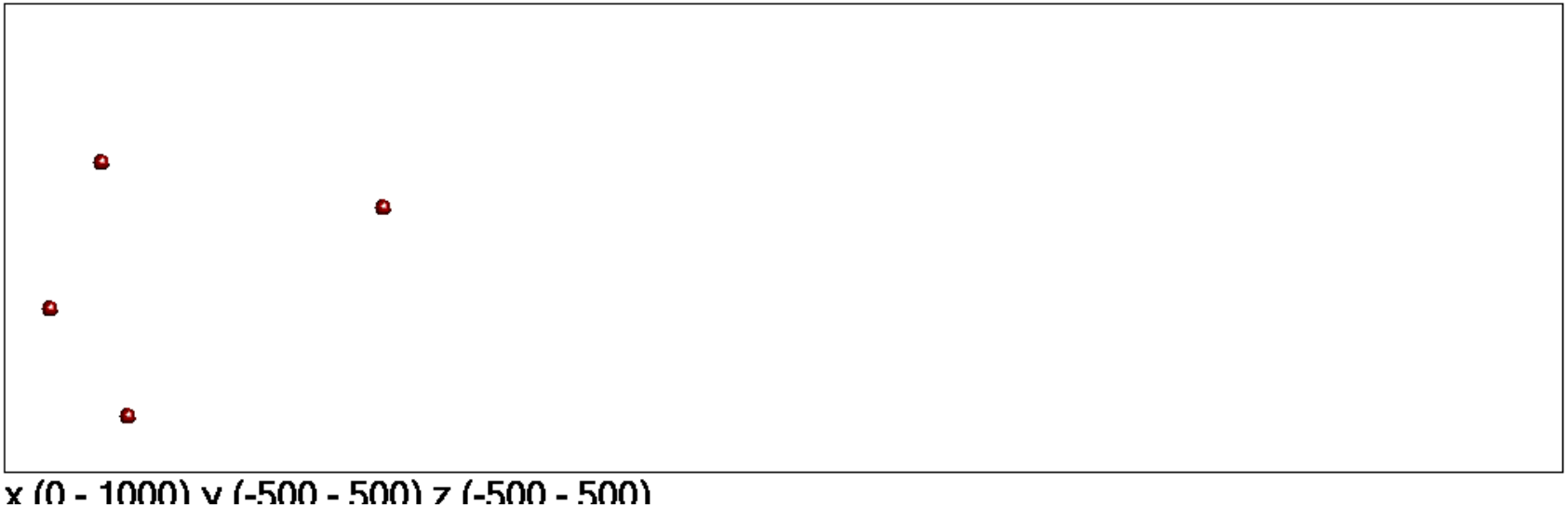
- Basic object is an impurity or intrinsic defect in lattice
- Non-defect lattice atoms are not described at all!
- Basic process is a diffusive jump, occurring at Arrhenius rate

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

- Incoming ion flux can be easily recalculated to a rate!
- 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).]

End of Part 4

- Take-home messages:
  - Kinetic Monte Carlo is a beautiful tool in that the basic algorithm does not involve any approximations
  - It can treat any process with known rates (diffusion jumps, incoming ion flux, …) as well as defect reactions
  - Can be implemented both for defects neglecting lattice atoms (Object KMC) or for all atoms in a system (Atomic KMC)
  - KMC needs as inputs knowledge of all the relevant rates: if some of these are missing, the results may be misleading or even complete rubbish

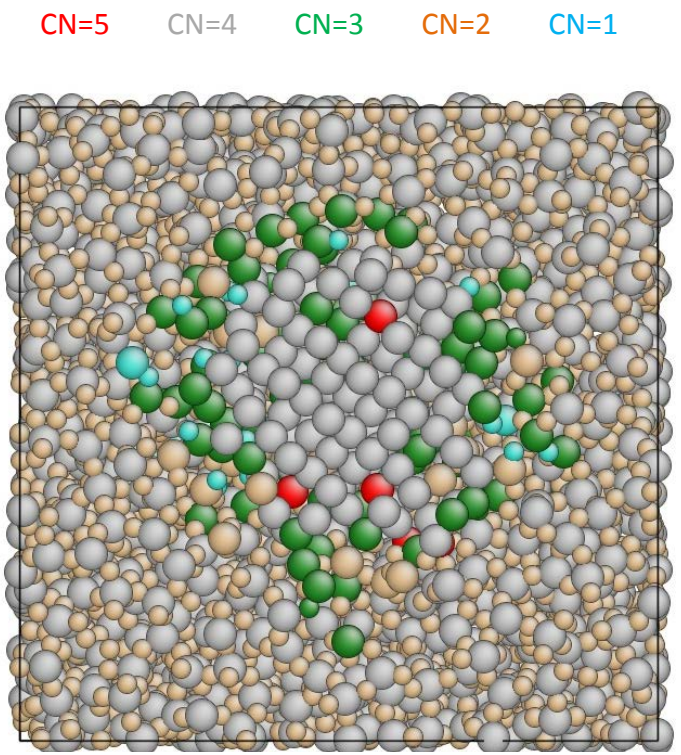
HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Part 5: Examples of recent use (time permitting)

Highlights:
1. Nanoclusters

- We have extensively studying nanocrystals embedded in silica (amorphous SiO_2) to understand their atomic-level-structure and modification by ion irradiation
  - **We have shown that the atomic-level structure of a Si nc – silica interface contains many coordination defects**
  - **Together with experiments, we have shown that the core of a swift heavy ion track in SiO_2 is underdense**

[P. Kluth et al, Phys. Rev. Lett. 101, 175503 (2008)]

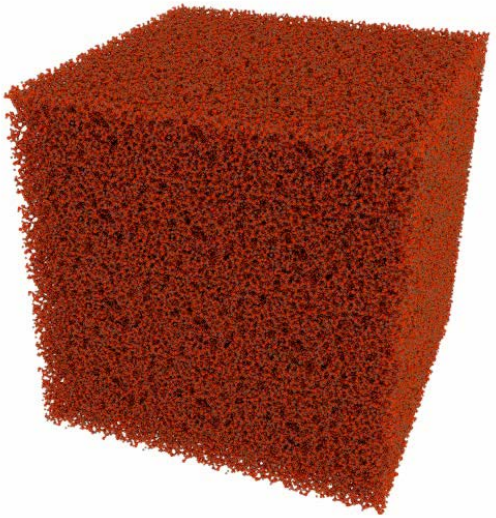


[F. Djurabekova et al, Phys. Rev. B 77, 115325 (2008)]

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

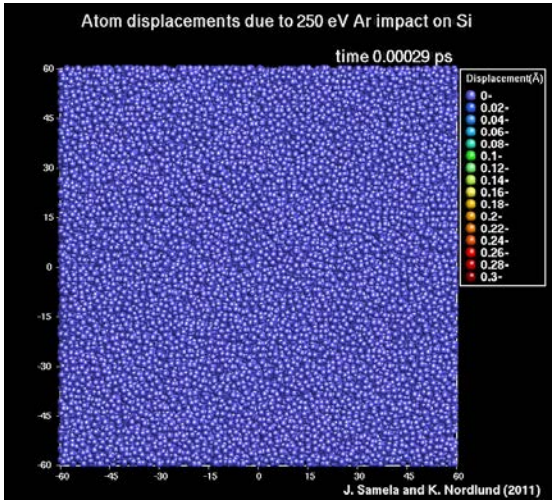
➢ **We have explained the mechanism by which swift heavy ions create nanostructures in silicon, silica and germanium and change nanocrystal shapes**

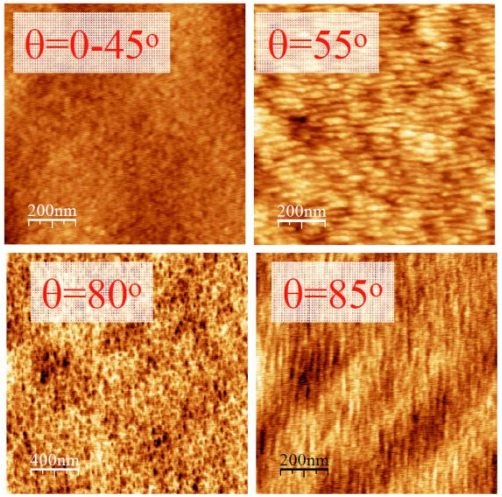


[Ridgway et al, Phys. Rev. Lett. 110, 245502 (2013); Leino et al, Mater. Res. Lett. (2013)]

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**



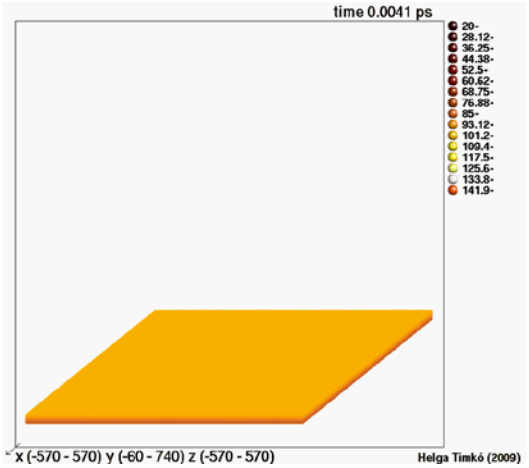


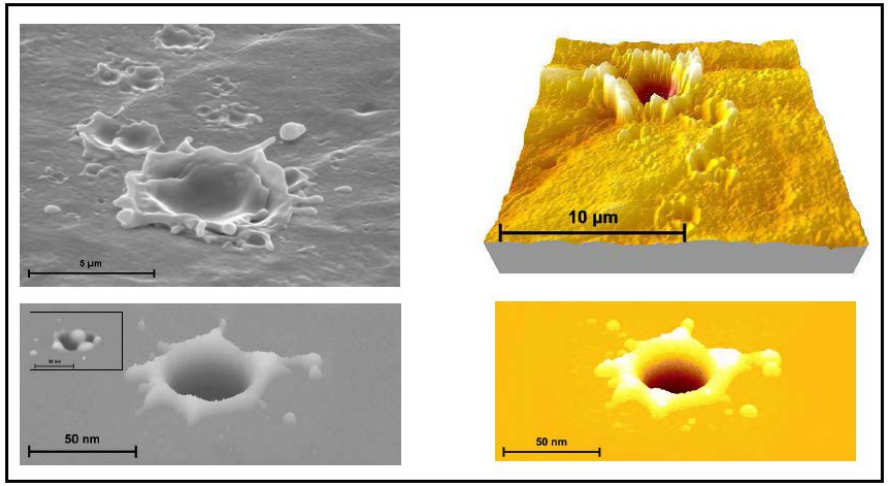
[Norris et al, Nature commun. 2 (2011) 276]

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

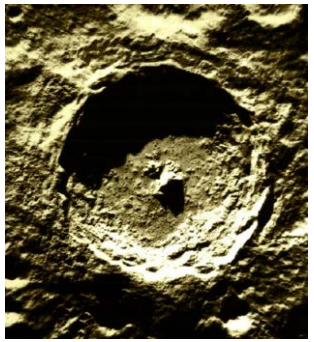
  - **We have shown that the complex crater shapes observed in experiments can be explained as a plasma ion irradiation effect – multiple overlapping heat spikes**



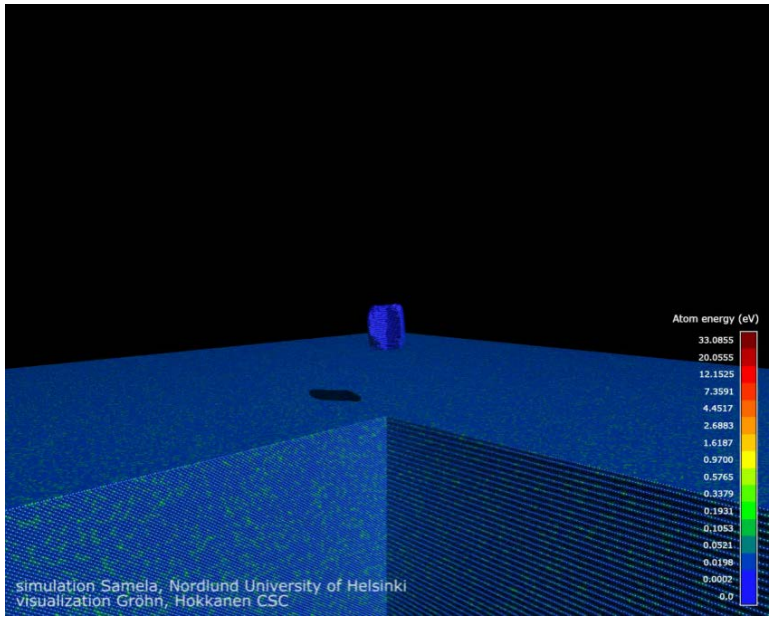


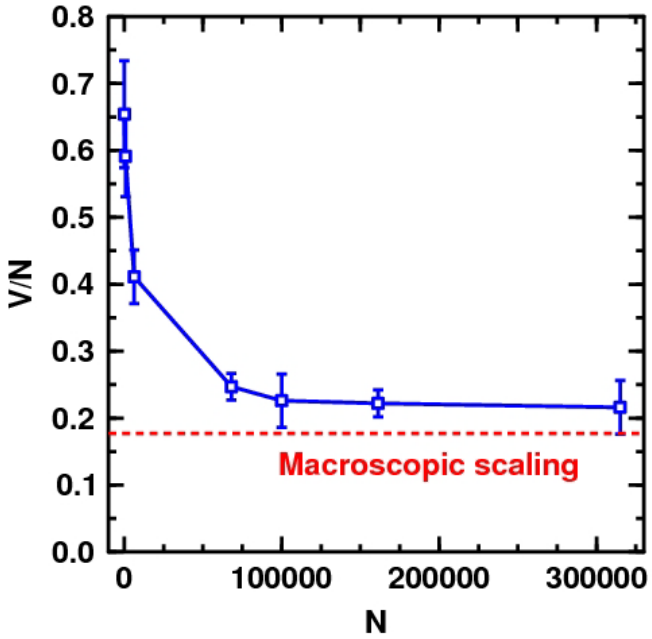
[H. Timko et al, Phys. Rev. B 81 (2010), 184109]

5. Cluster cratering over 40 orders of magnitude



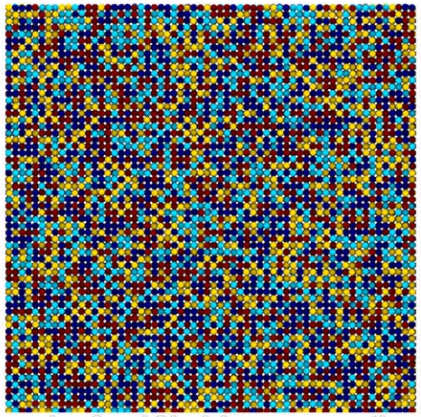
- Using classical MD, we demonstrated that at a size ~ 10000 atoms, cluster bombardment starts producing craters with the same mechanism as meteorites on planets
  - 100 million atom simulations with statistics



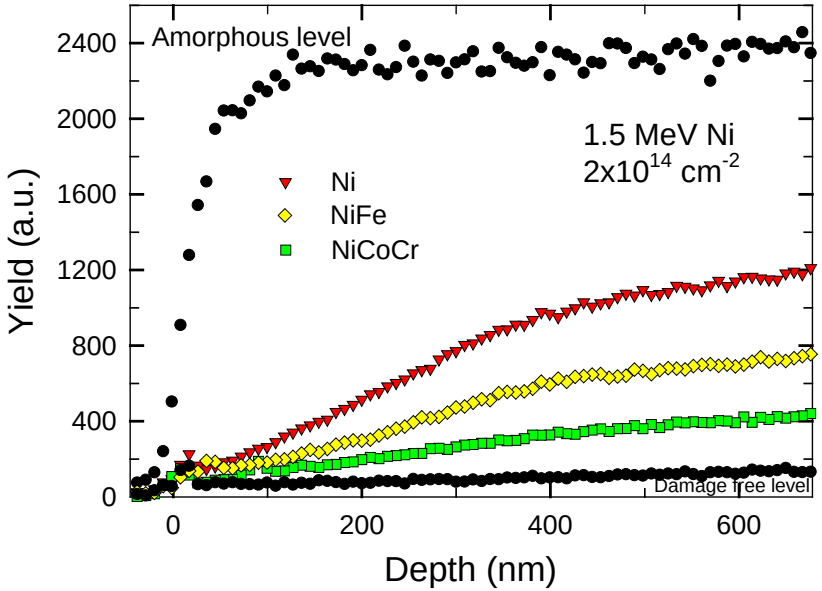


[J. Samela and K. Nordlund, Phys. Rev. Lett. 101 (2008) 27601, and cover of issue 2]

Highlights 6:
Damage reduction in high-entropy alloys



- So called equiatomic or high-entropy alloys (alloys with multiple elements at equal or roughly equal concentrations in a single simple crystal) are subject to a rapidly rising interest due to promising mechanical, corrosion-resistant and radiation hardness properties
- Experiments by Yanwen Zhang *et al* (ORNL) show that damage in some FCC high-entropy alloys can be lower than in the corresponding pure elements

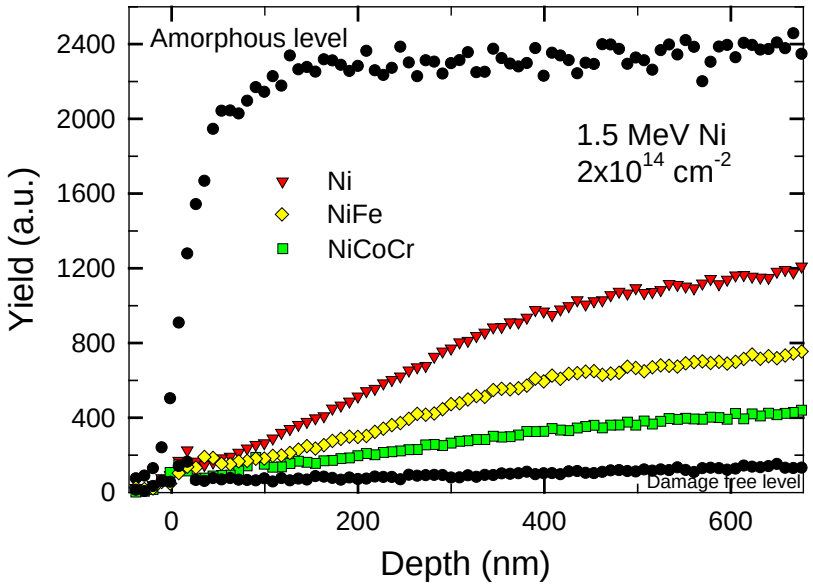


 [Granberg, Nordlund, Zhang, Djurabekova et al, Phys. Rev. Lett 116, 135504 (2016)]

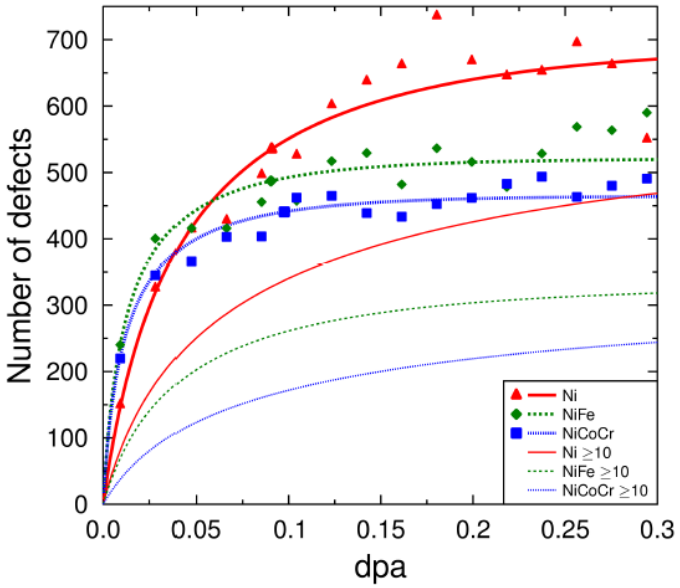
Highlights 6:
Damage in clusters in HEA's

- The clustered damage shows a similar damage reduction effect as the experiments!
  - Explanation: alloying reduces dislocation mobility and hence growth of dislocations

Experiment



Simulation



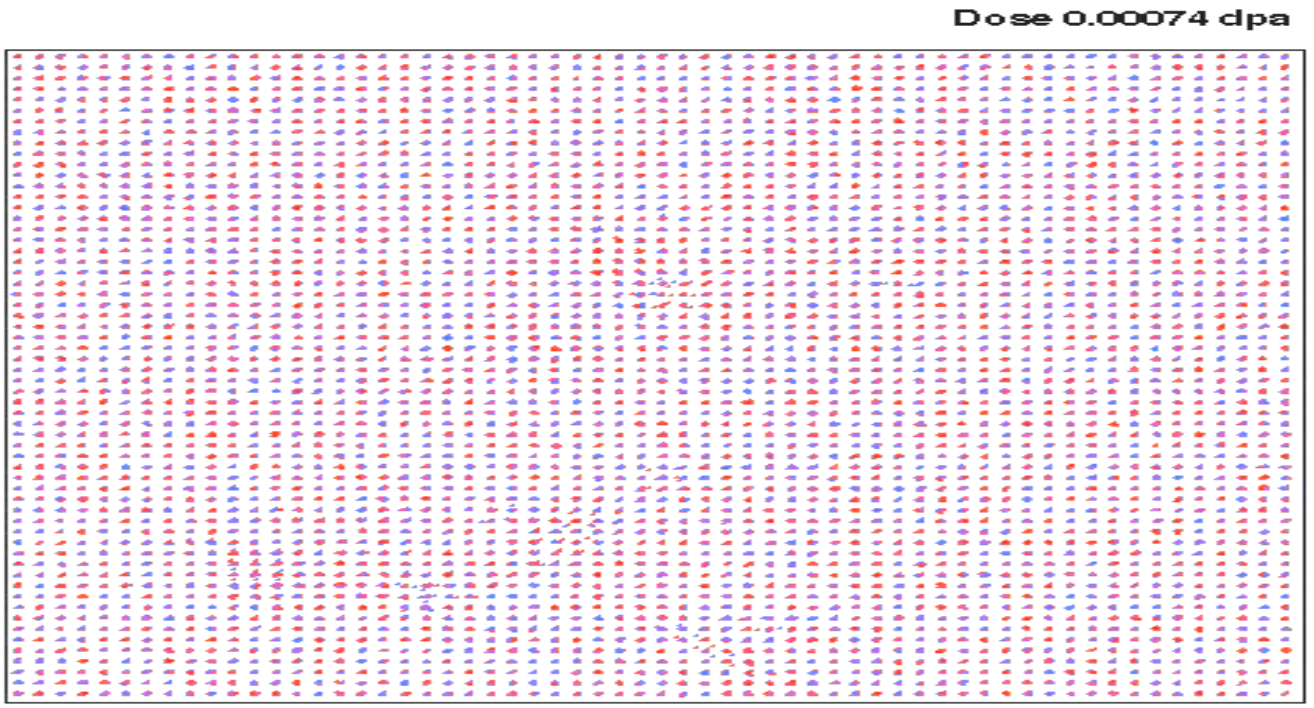
[Granberg, Nordlund, Zhang, Djurabekova et al, Phys. Rev. Lett 2016]

Further reading

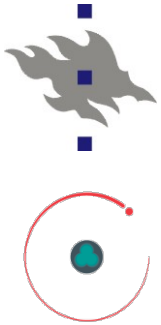
- General:
  - Classic book: Allen-Tildesley, Molecular dynamics simulations of liquids, Oxford University Press, 1989.
  - Newer book: Daan Frenkel and Berend Smit. Understanding molecular simulation: from algoritms to applications. Academic Press, San Diego, second edition, 2002
- Ion irradiation-specific 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**

- Take-home messages:
  - ***Atomistic simulations are a powerful tool for modelling irradiation effects – when you know what you are doing!***

And a lot of fun! ☺



Granberg et al. (2015)



Extra and backup slides

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Part X: Interatomic potential development in Tersoff formalism

Kai Nordlund

Professor, Department of Physics

Adjoint Professor, Helsinki Institute of Physics

University of Helsinki, Finland

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

- Achieving all this starts to sound prohibitively difficult
- But there is one common factor for the main requirements:
  - Melting, defects and different phases all involve unusual atom coordination states
  - Hence if we use a framework to fit as many coordination states of the system as possible, we have some hope of getting many of the properties right

- A Tersoff (Abell / Brenner)-like formalism can do this!
  - This is our favourite formalism for mixed materials, and hence I will now describe it in detail

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)

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

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

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

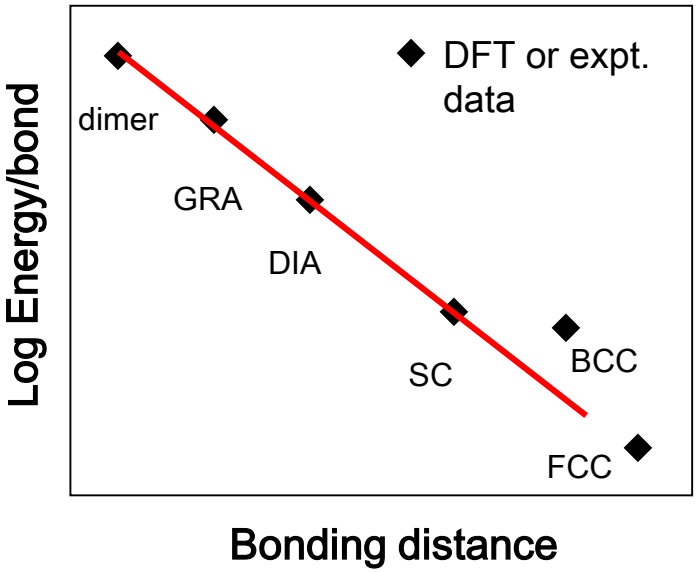
  - The 3 parameters r_0, D_0 and β can be set directly from the experimental dimer interatomic distance, energy and vibration frequency!

"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

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

No power of 3

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

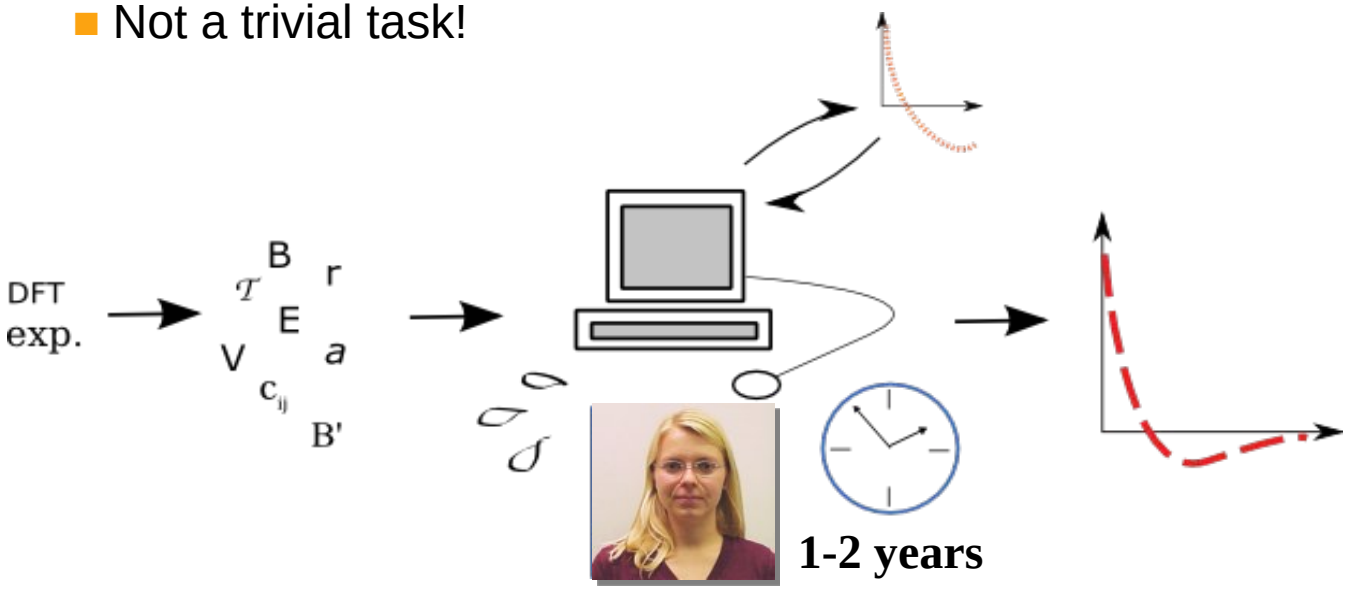
ik-dependent angular term

- 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

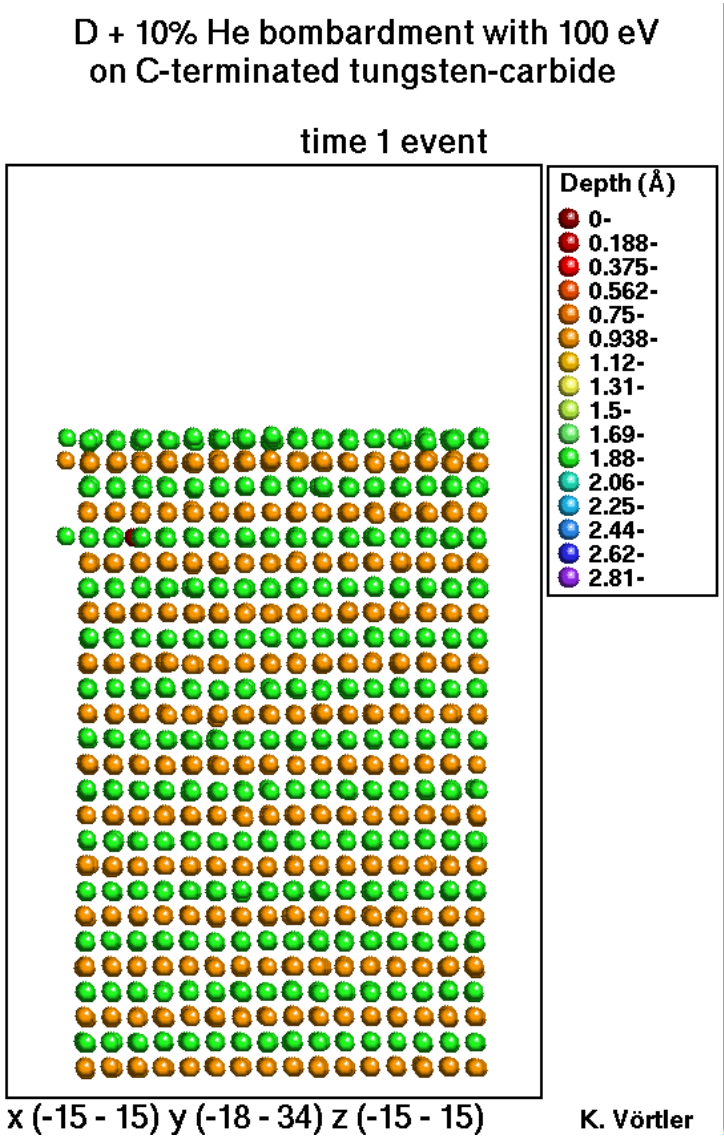
- There are all in all 11 parameters that must be specified
- Constructing a good potential means finding suitable values for these
  - This is done by fitting to different experimental or density-functional theory values of ground state and hypothetical phases – also for other functional forms than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

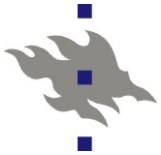


[Schematic courtesy of Dr. Carolina Björkas]

Potentials developed by us

- We, and/or the Albe group, have so far developed potentials for:
  - BN, PtC, GaAs, **GaN**, SiC, **ZnO,** FePt, BeWCH, FeCrC, FeCH, WN …
    + 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

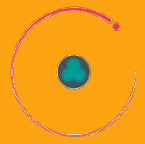




Potentials developed in general

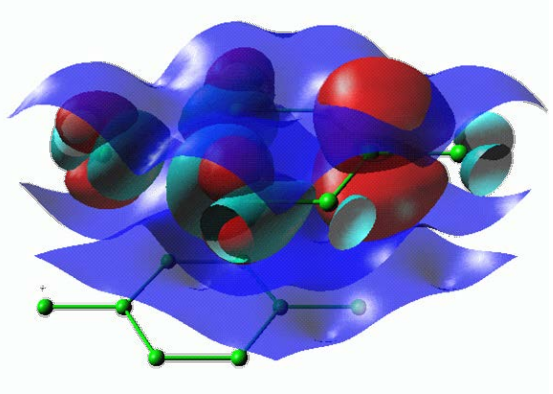
- In general, potentials suitable for irradiation effects exist:
  - For almost all pure elements
  - For the stoichiometric state of a wide range of ionic materials
    - But these do not always treat the constituent elements sensibly, e.g. in many oxide potentials O-O interactions purely repulsive => 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

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI



Random backup slides

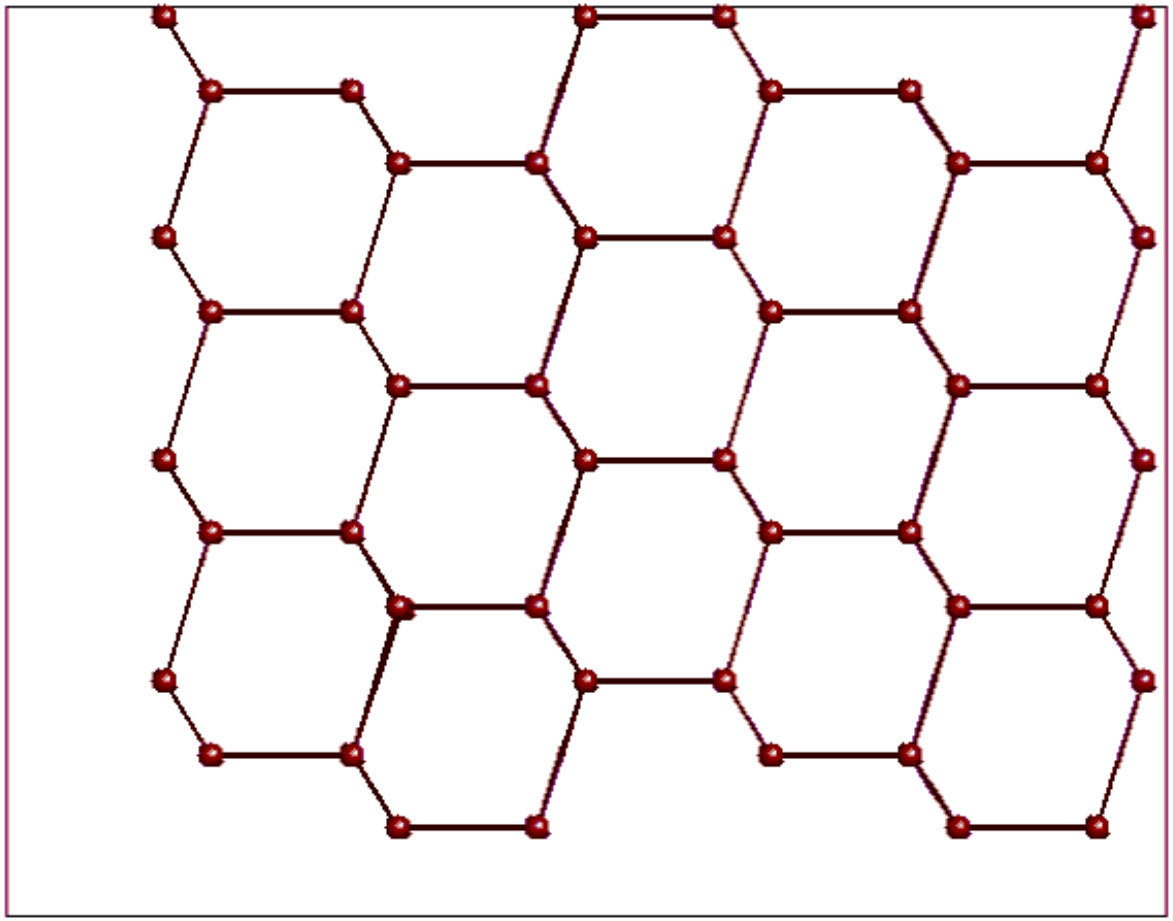
Methods: Density Functional Theory



- DFT is a way to calculate the ground state electron density in a system of atoms
  - Achieved by iteratively solving a Schrödinger-like equation
- Most fundamental method that can give results of practical value in materials physics systems
  - But it is not exact, it has inherent and dubious assumptions
  - “Works surprisingly well”
- Extremely widely used method, “DFT is an industry”
- Nowadays efficient enough for DFT-based atom dynamics = DFT MD

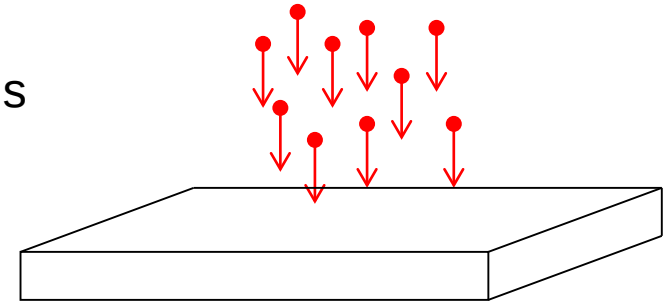
Example of DFT MD

- Si threshold displacement energy



Ion beam and plasma energies and fluxes

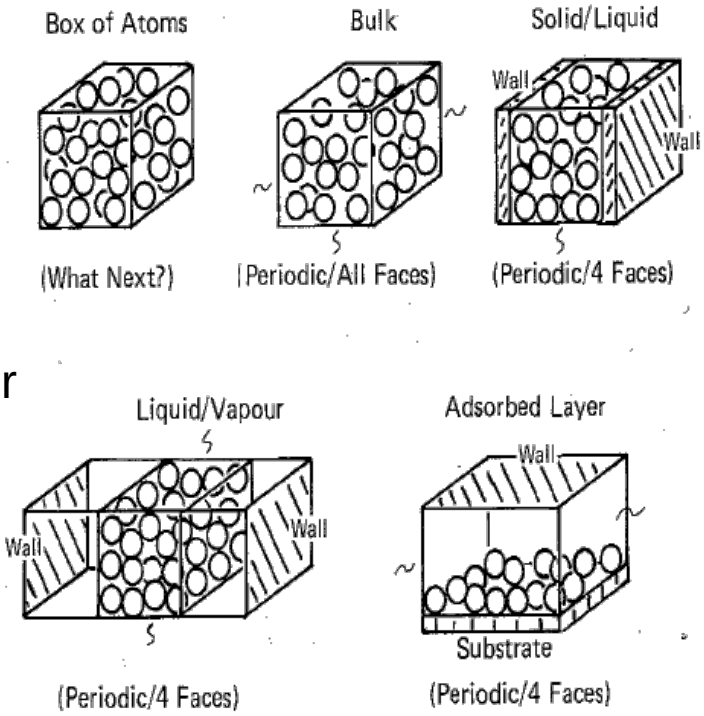
- How do ions hit a material?
- From an **accelerator**, with a well-defined single energy E_0 with very little energy spread
  - Time between impacts ~ μs – s on a nanometer scale => **each impact independent of each other**



- 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!

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 – 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

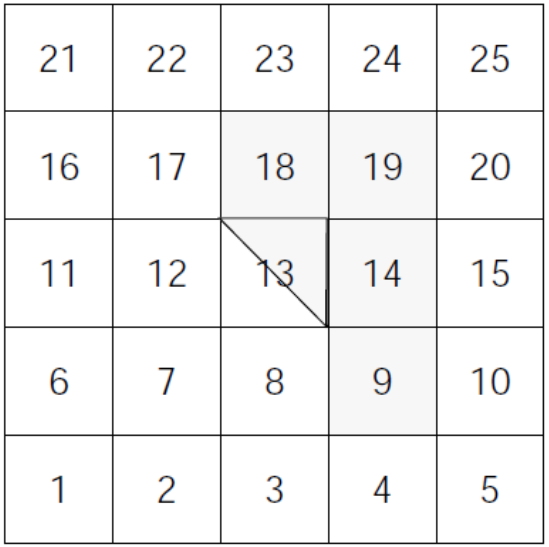
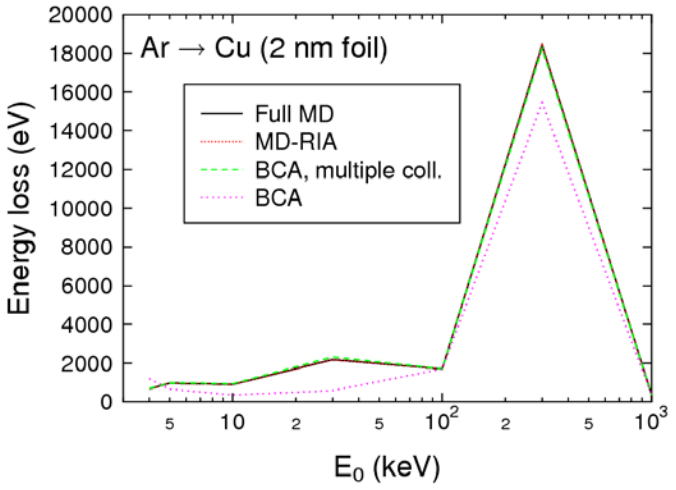
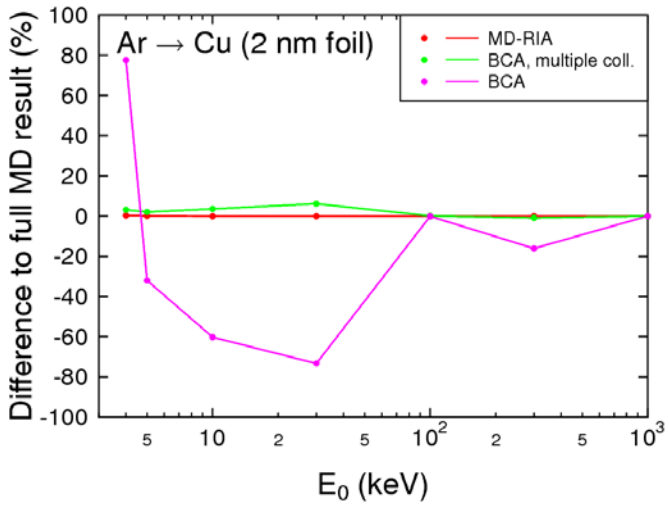


Illustration of BCA vs. MD

- 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]

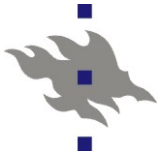
MD – atom representations

- 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)
```




Initializing atom positions

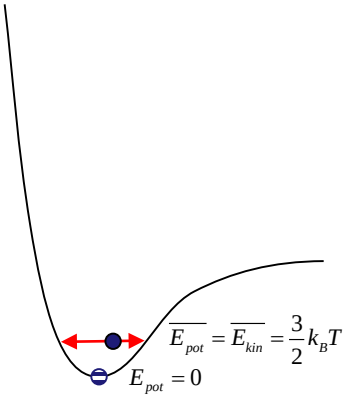
- Atom coordinates can (should) be initialized to the structure of interest
- Simplest: single crystal: just make atom coordinates according to basis vectors. Simple 4D loop over (x,y,z,basis vectors)
  - Some codes like LAMMPS have built-in construction routines
- Other possible cases are numerous
  - Biomolecules: use databases of coordinates
  - Amorphous material: very tricky to get something similar to experiments. Simplest: start from random atom coordinates, simulate at high T and cool down slowly. But this gives often too much coordination defects. Other approach: Wooten-Weaire-Winer Monte Carlo, can generate coordination-defect free materials
  - Quasicrystals: not known how to do it!

Initializing velocities

- How to set initial velocities depends on the physical case to be simulated
- Simplest case: thermal equilibrium: give initial Gaussian velocities to the atom (=Maxwell-Boltzmann distribution)
- Code snippet:

```
! Gaussian distributed velocities
  x(i) = vmean*gaussianrand(0)
  y(i) = vmean*gaussianrand(0)
  z(i) = vmean*gaussianrand(0)
```

- Mean velocity obtained from $\frac{1}{2}mv_{mean}{}^2 = \frac{3}{2}k_BT$
- Basic physics note: if you start from perfect crystal positions, atoms initially have $E_{pot} = 0$, whereas by the equipartition theorem, at a given temperature T, each degree of freedom has $\frac{1}{2}k_BT$ of energy in both E_{pot} and E_{kin}
- Hence in this case to get desired temperature T, you need to give initial velocities for $2T$ and simulate about 1 ps to get correct equipartitioning of E_{pot} and E_{kin}

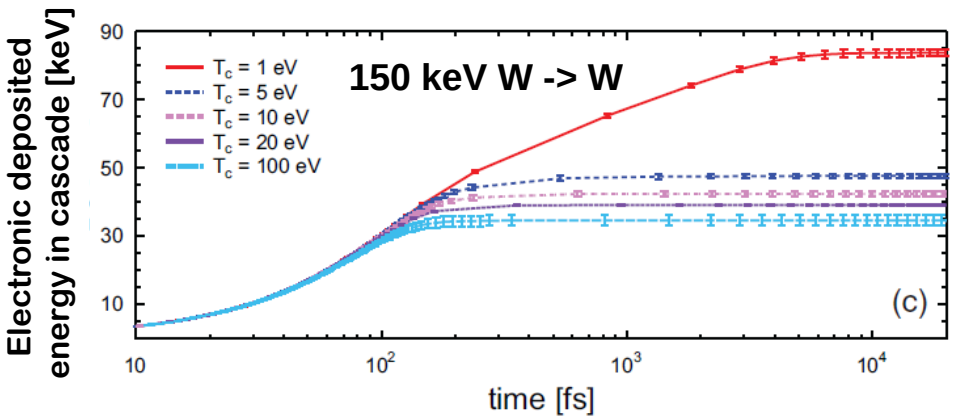


2) Energy loss to electronic excitations

- 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)]