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Molecular dynamics method for materials simulations

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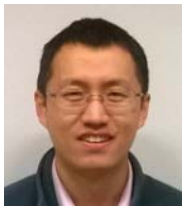

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M Sc Wei Ren
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M Sc Fredric Granberg
Dislocations

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Nuclear materials

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Surface ripples

M Sc Shuo Zhang
Ion range calculations

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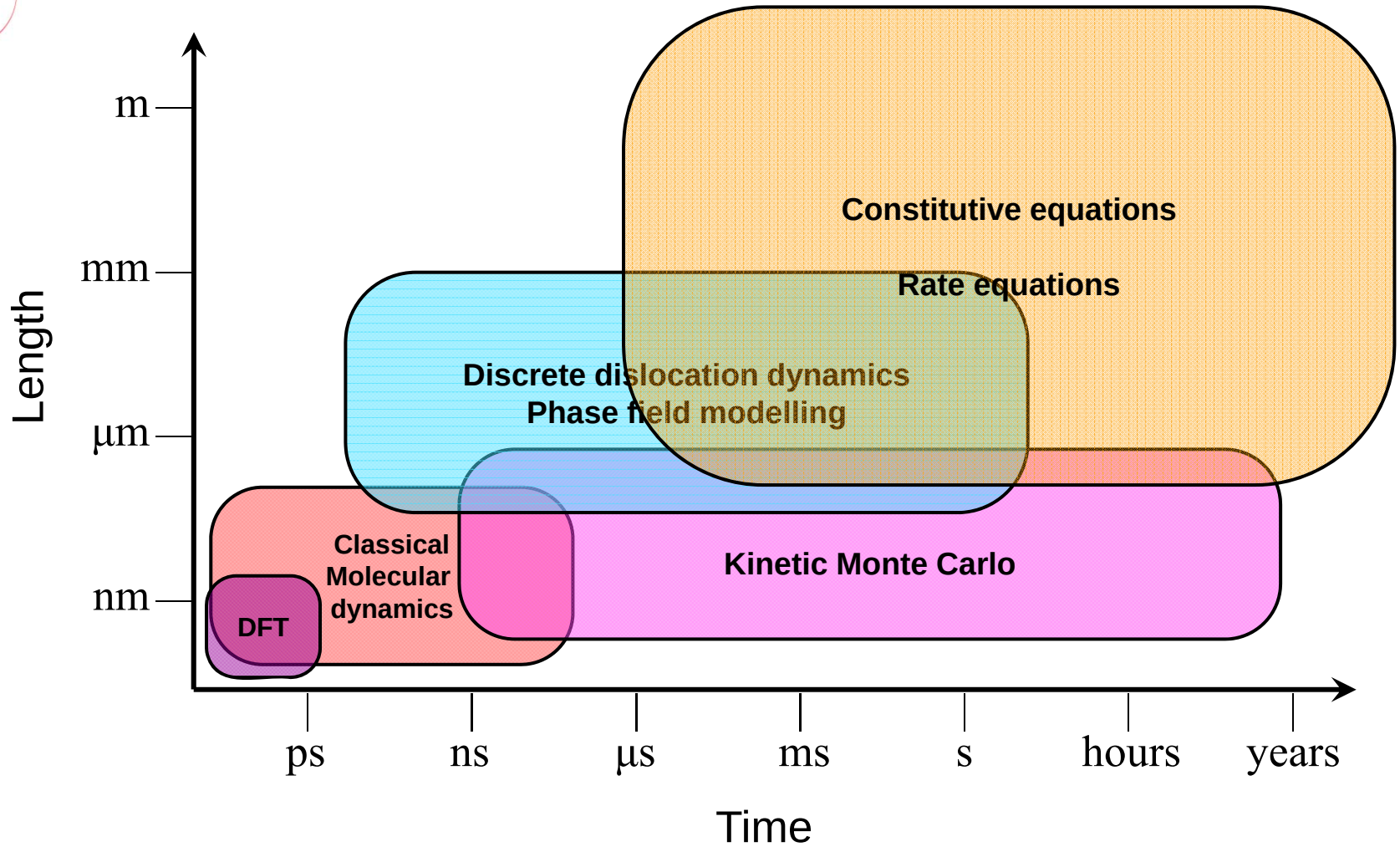
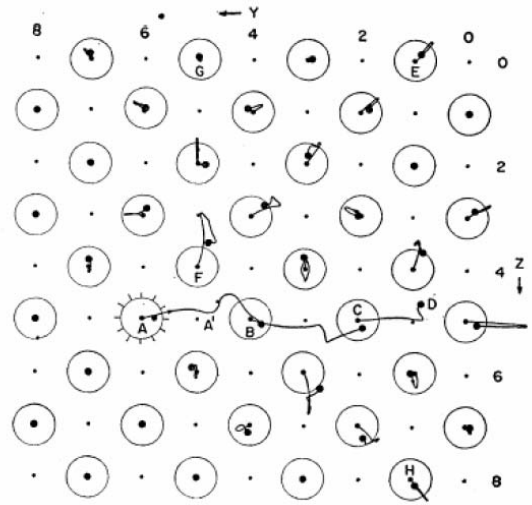
Multiscale modelling of materials

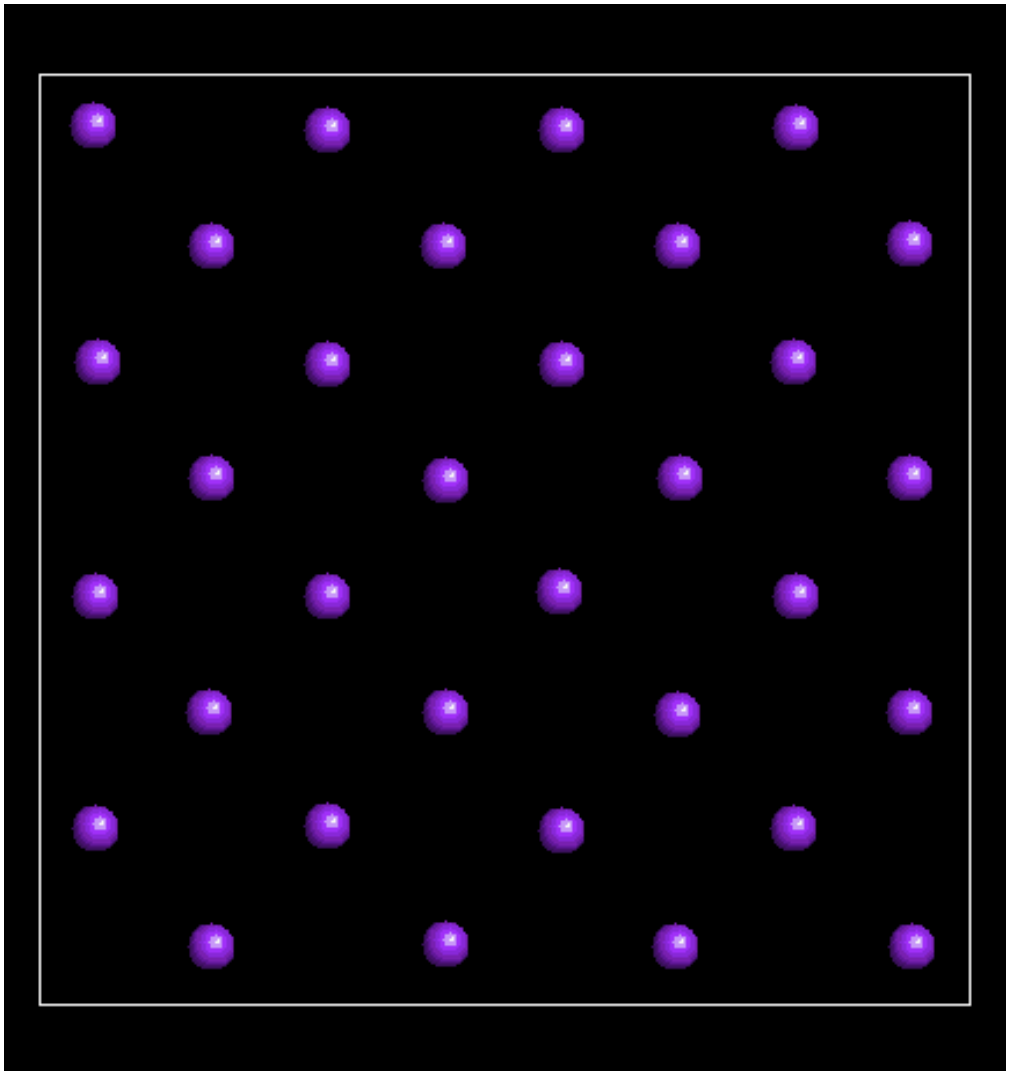


MD = Molecular dynamics

- 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
- First dynamic process simulations: 1960, Gibson simulated radiation effects in solids [Phys. Rev. 120 (1960) 1229)]
  - A few hundred atoms, very primitive pair potentials
  - But atom dynamics clearly visible

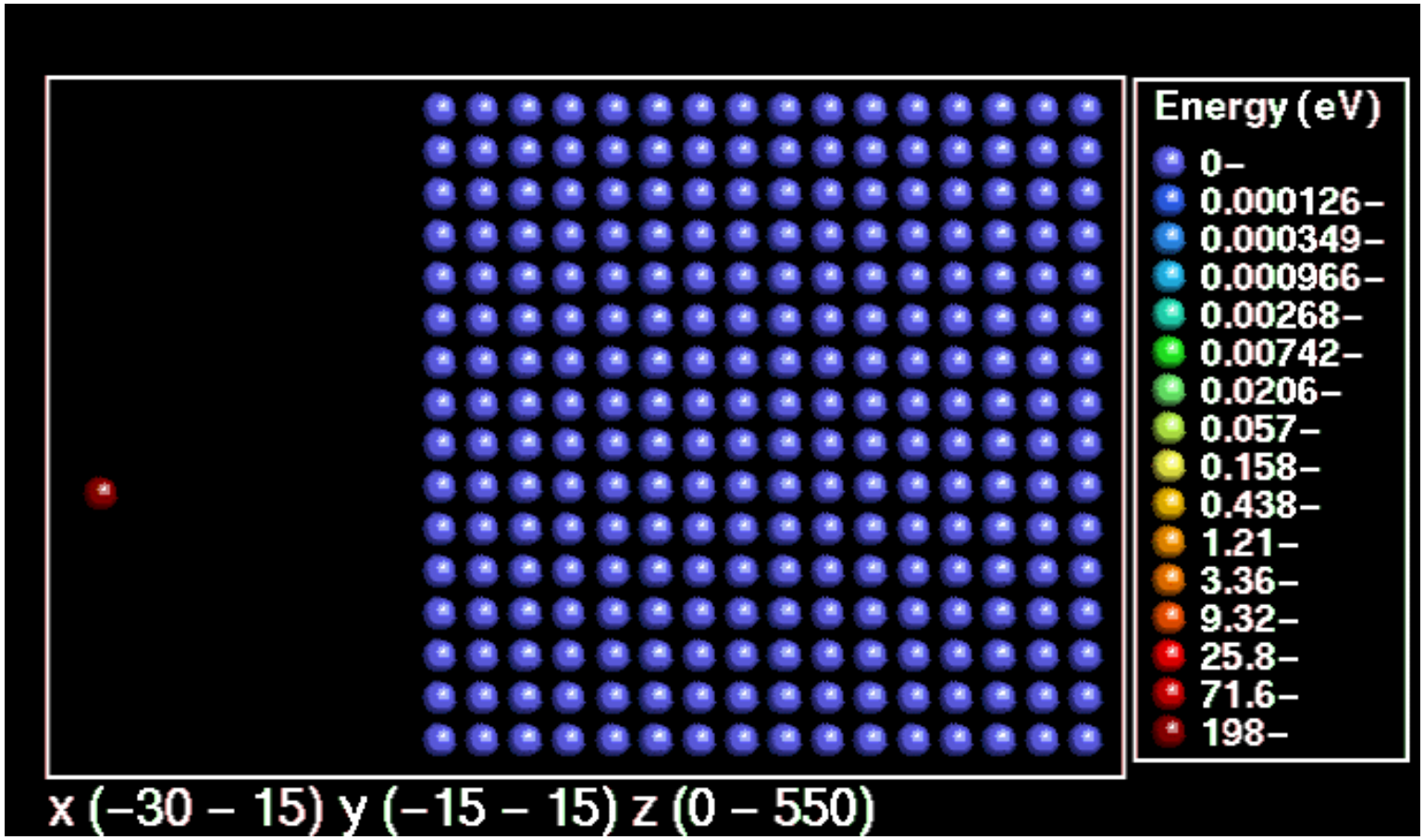


Simple (trivial) example of atom motion by MD: thermal motion in Cu at 600 K, cross section of 2 atom layers

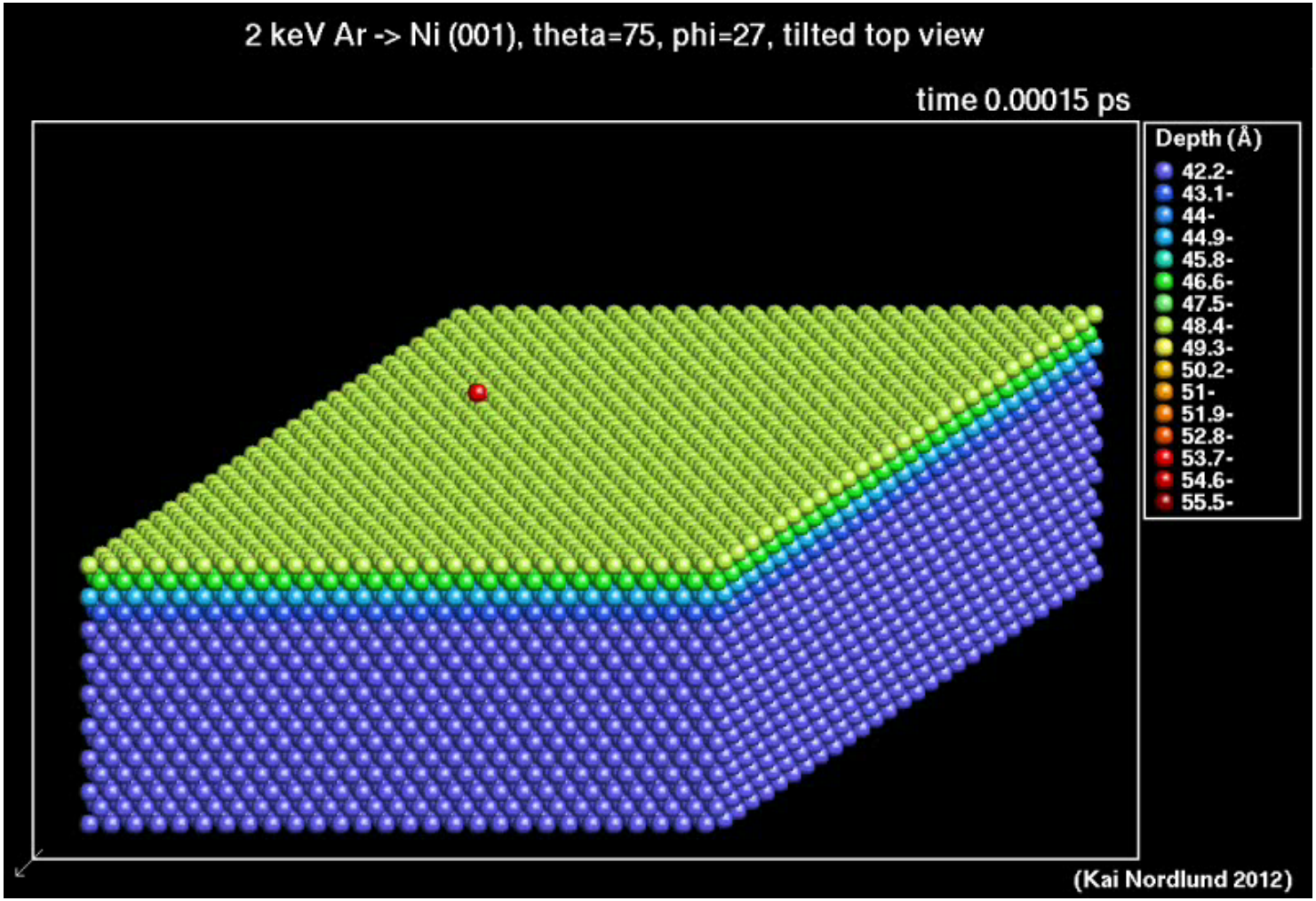


Less trivial example: small atom collision event

- 500 eV kinetic energy Au impacting on Cu
  - Again cross section of 3D cell

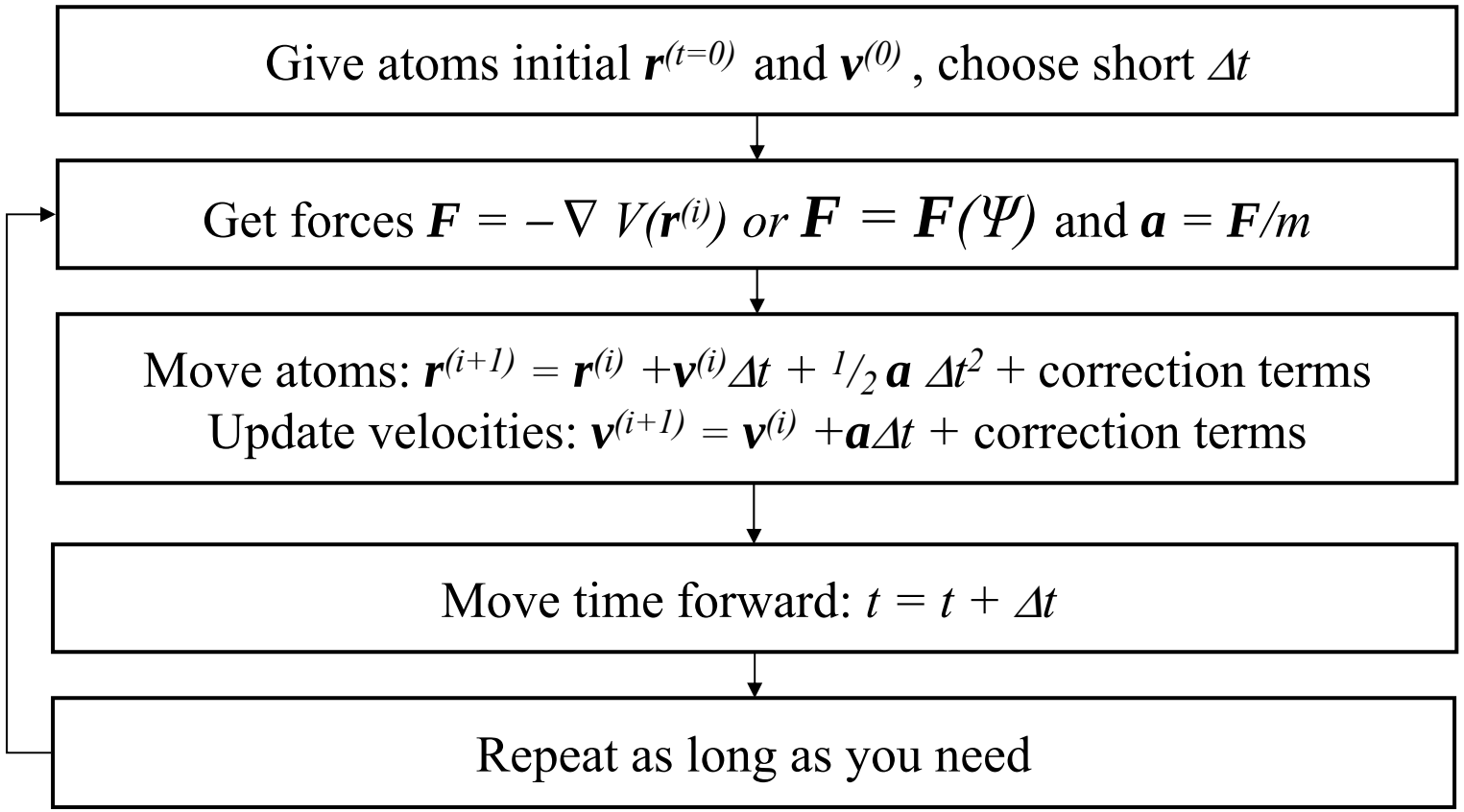


3D view of another bombardment

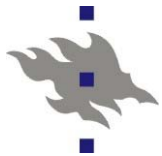


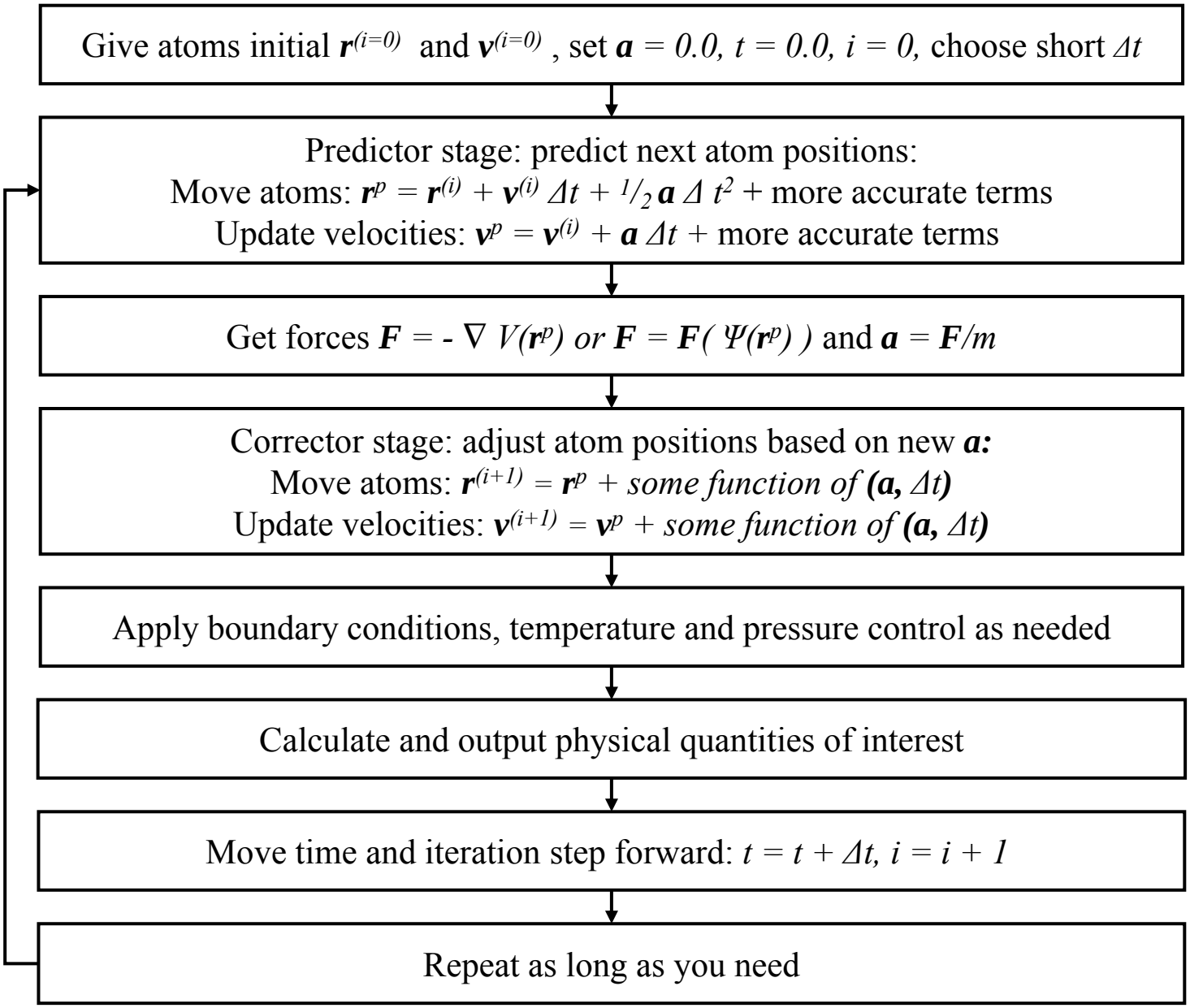
How is this actually achvieved?

The MD algorithm, roughly



The MD algorithm in more detail





[wikipedia by me]

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 predictor-corrector type way to solve differential equations numerically:

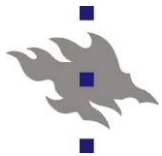
Predictor stage: predict next atom positions:
Move atoms: $\boldsymbol{r}^p = \boldsymbol{r}^{(i)} + \boldsymbol{v}^{(i)}\,\Delta t + {}^1\!/_2\, \boldsymbol{a}\, \Delta\, t^2 +$ more accurate terms
Update velocities: $\boldsymbol{v}^p = \boldsymbol{v}^{(i)} + \boldsymbol{a}\,\Delta t +$ more accurate terms

↓

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

↓

Corrector stage: adjust atom positions based on new ***a:***
Move atoms: $\boldsymbol{r}^{(i+1)} = \boldsymbol{r}^p +$ *some function of* $(\boldsymbol{a}, \Delta t)$
Update velocities: $\boldsymbol{v}^{(i+1)} = \boldsymbol{v}^p +$ *some function of* $(\boldsymbol{a}, \Delta t)$



MD – Solving equations of motion

- Simplest possible somewhat decent algorithm: velocity Verlet

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

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

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

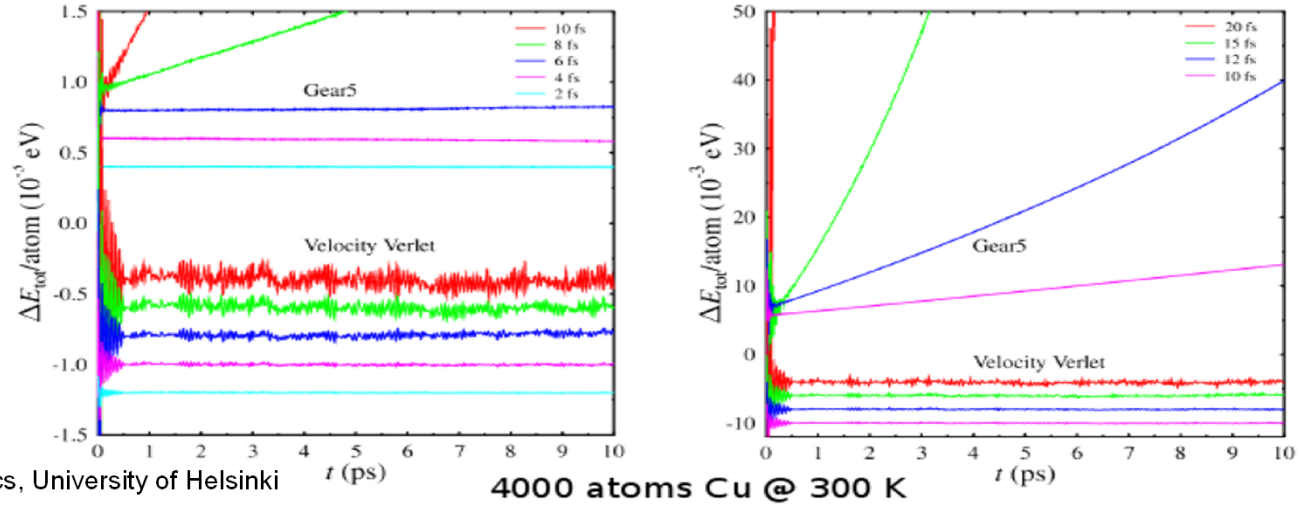
[L. Verlet, Phys. Rev. 159 (1967) 98]

- Another, much more accurate: Gear5, Martyna
  - I recommend Gear5, Martyna-Tuckerman or other methods more accurate than Verlet,

[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

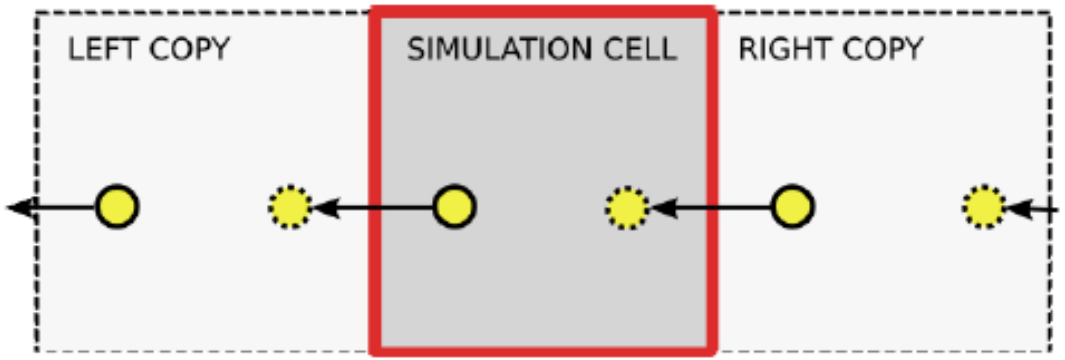
- Time step selection is a crucial part of MD
  - Choice of algorithm for solving equations of motion and time step are related
- Way too long time step: system completely unstable, “explodes”
- Too short time step: waste of computer time
- Too long time step: total energy in system not conserved
  -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

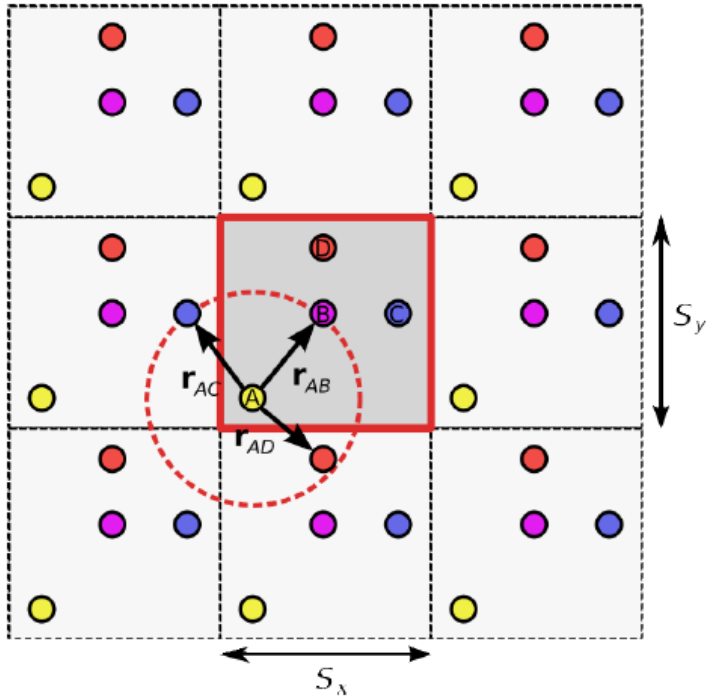
- A real lattice can be extremely big
  - E.g. 1 cm^3 of Cu: 2.1e22 atoms => too much even for present-day computers
  - Hence desirable to have MD cell as segment of bigger real system
- Standard solution**: periodic boundary conditions**
  - This approach involves “copying” the simulation cell to each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



MD: periodics continued

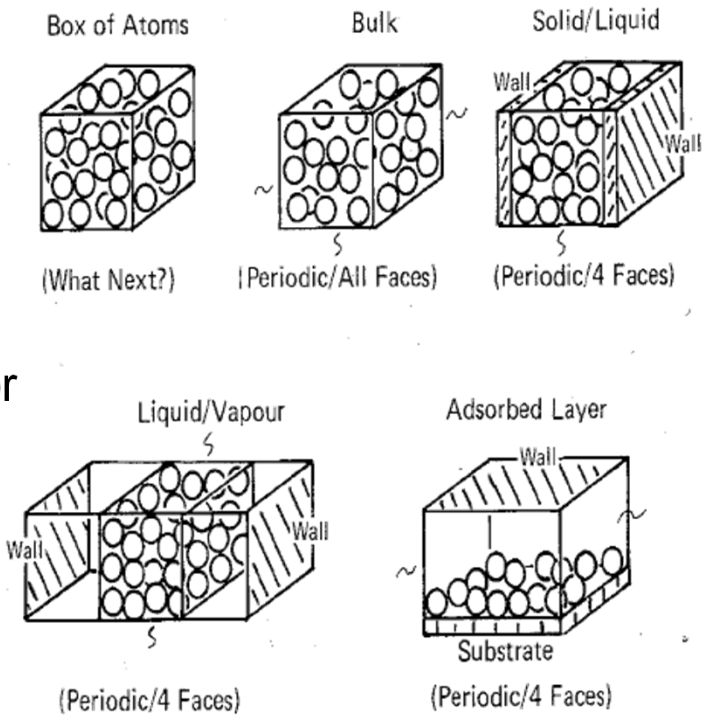
- This has to also be accounted for in calculating distances for interactions
- “Minimum image condition”: select the nearest neighbour of an atom considering all possible 27 nearest cells
- Sounds tedious, but can in practice be implemented with a simple comparison:

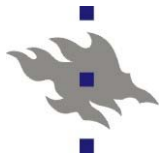
```
if (rijx > box(1)/2.0)   rijx=rijx-box(1)
if (rijy > box(2)/2.0)   rijy=rijy-box(2)
if (rijz > box(3)/2.0)   rijz=rijz-box(3)

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

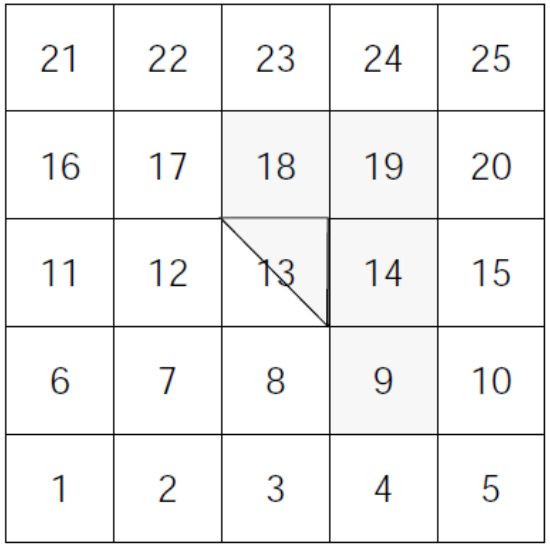
- Controlling temperature and pressure is often a crucial part of MD
- "Plain MD" without any T or P control is same as simulating NVE thermodynamic ensemble
  - **In irradiation simulations NVE only correct approach to deal with the collisional phase !!**
- NVT ensemble simulation: temperature is controlled
  - Many algorithms exist, Nosé, Berendsen, …
  - Berendsen does not strictly speaking simulate thermodynamic NVT ensemble – but is often good enough
- NPT ensemble simulation: both temperature and pressure is controlled
  - Many algorithms exist: Andersen, Nosé-Hoover, Berendsen, Berendsen does not strictly speaking simulate thermodynamic NPT ensemble – but is often good enough

Note 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

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

- The basic MD algorithm is not suitable for many nonequilibrium simulations
- But over the last ~30 years augmentations of MD for nonequilibrium simulations have been developed
  - Our group has specialized in irradiation effects
  - Slides on these are left at the end for interested readers, here just a few aspects described

Variable time step schemes

- In case the velocities of atoms are varying during the simulation, it is worth using a variable time step
- Example for irradiation simulations

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

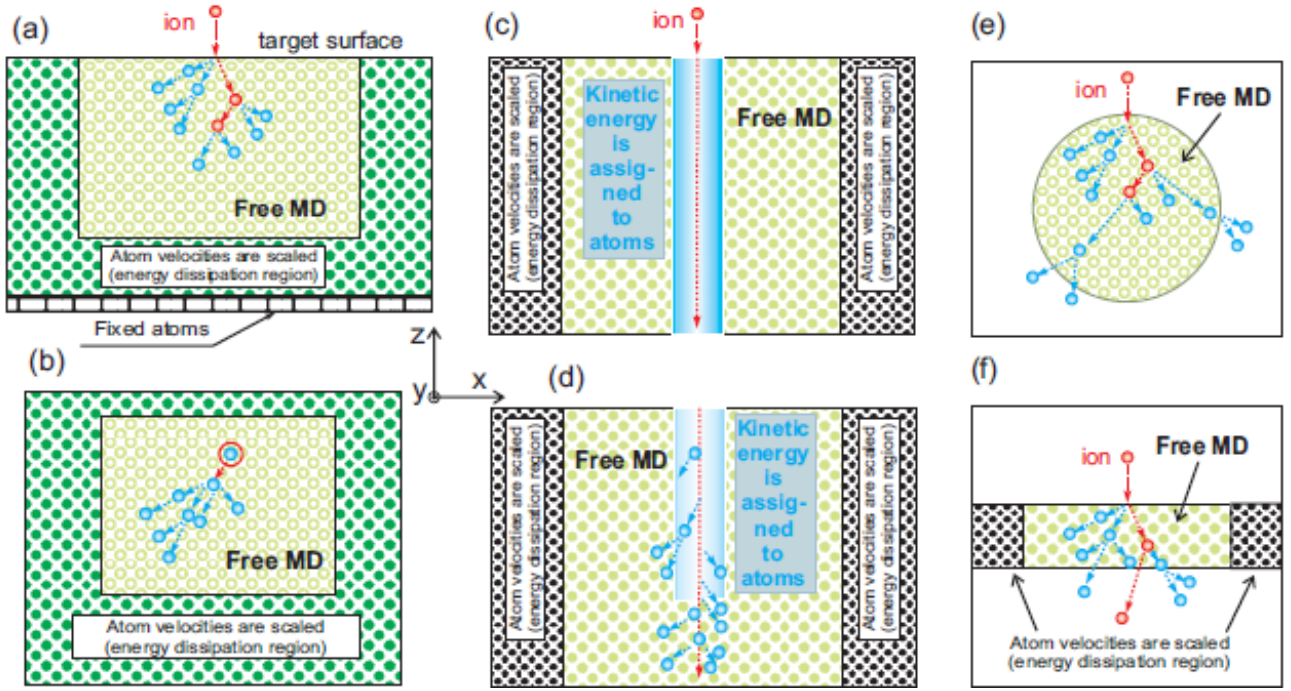
Here Δx_{max} *is the maximum allowed distance moved* during any *t (e.g. 0.1 Å),* ΔE_{max} *is the maximum allowed* change in energy (e.g. 300 eV), v_{max} *and* F_{max} *are the* highest speed and maximum force acting on any particle at *t*, respectively, $c_{\Delta t}$ prevents sudden large changes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

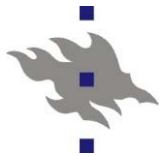
- This relatively simple algorithm has been demonstrated to be able to handle collisions with energies up to 1 GeV

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

Special boundary conditions

- In a zone which is far from thermodynamic equilibrium, one cannot and should not use any thermodynamic ensemble simulation method!
- Only use NVE = direct solution of Newton's equation of motion, "Free MD"
- Example for various irradiation cases:





Interatomic potentials

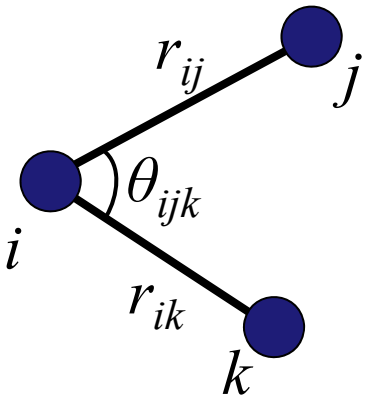
- The key (and often only) physics input to the MD algorithm are the interatomic forces
  - Either from classical interatomic potentials or quantum mechanical methods (typically DFT)
  - Reliability of results depends entirely on this!
- Efficiency of MD for practical purposes:
  - Classical (analytical) potentials: 100 million atoms
  - DFT: 100 atoms
- Classical interatomic potentials are hence very desirable to have, and their development is a long-going iterative process
- By now, good potentials exist for almost all pure elements and most binary alloys of practical interest

Interatomic potentials

- In general, total energy of a system of N atoms can be written:

$$V_{TOT} = \sum_{i}^{N} V_1(\vec{r}_i) + \sum_{i,j}^{N} V_2(\vec{r}_i, \vec{r}_j) + \sum_{i,j,k}^{N} V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \cdots$$

- Because the energy of a bond should not depend on the explicit atom coordinates, and if there are no external forces V1, this can be simplified to:

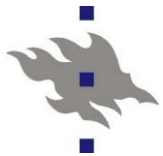


$$V_{TOT} = \sum_{i,j}^{N} V_2(r_{ij}) + \sum_{i,j,k}^{N} V_3(r_{ij}, r_{ik}, \theta_{ijk}) + \cdots$$

- From these the forces can be obtained in principle simply using

$$\vec{F}_i = \nabla_{\vec{r}_i} V_{TOT}$$

  - In reality, doing and coding this derivative for already a 3-body potentials is incredibly tedious: it has to be **perfect** for energy conservation in the MD simulation



Interatomic potentials

- Interatomic potentials can in general be divided in 2 classes:
- **Molecular mechanics force fields**
  - Used in chemistry and biophysics and biology, with a few exceptions non-reactive, i.e. covalent chemical bonds cannot break
    - Also same element can have different interactions depending on place in molecular: Carbon-1, Carbon-2, …
  - Useless in most materials science applications, since these typically involve phase changes, bond breaking etc.
- **(Reactive) Interatomic potentials**
  - Chemical bonds can break and reform
  - Only one atom type per element

Equilibrium potentials

- In modern materials science potentials used are almost always many-body in nature (i.e. beyond pair potentials)
  - 3-body potentials, and sometimes more
- 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)
  - 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!

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 of these potentials in our group done in systematic approach introduced by Prof. Karsten Albe (TU Darmstadt)

“Albe” fitting formalism

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

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

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

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

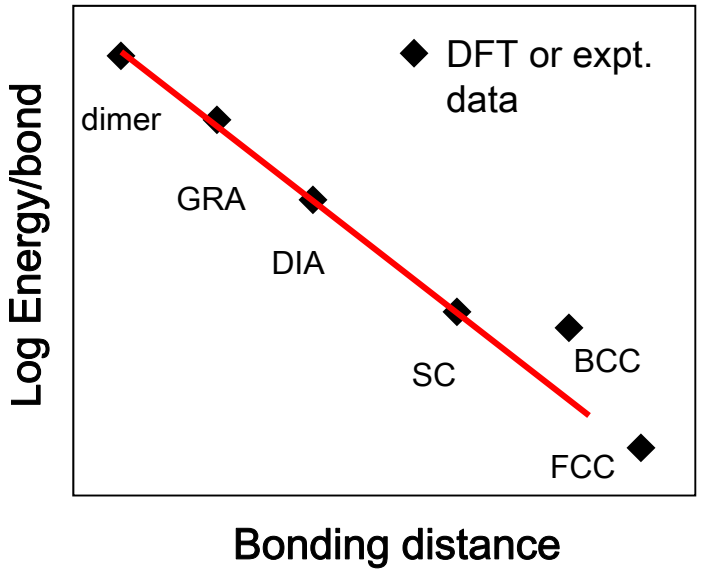
  - The 3 parameters r_0, D_0 and β can be set directly from the experimental dimer interatomic distance, energy and vibration frequency!

"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:

Second-moment approximation exponential

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

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

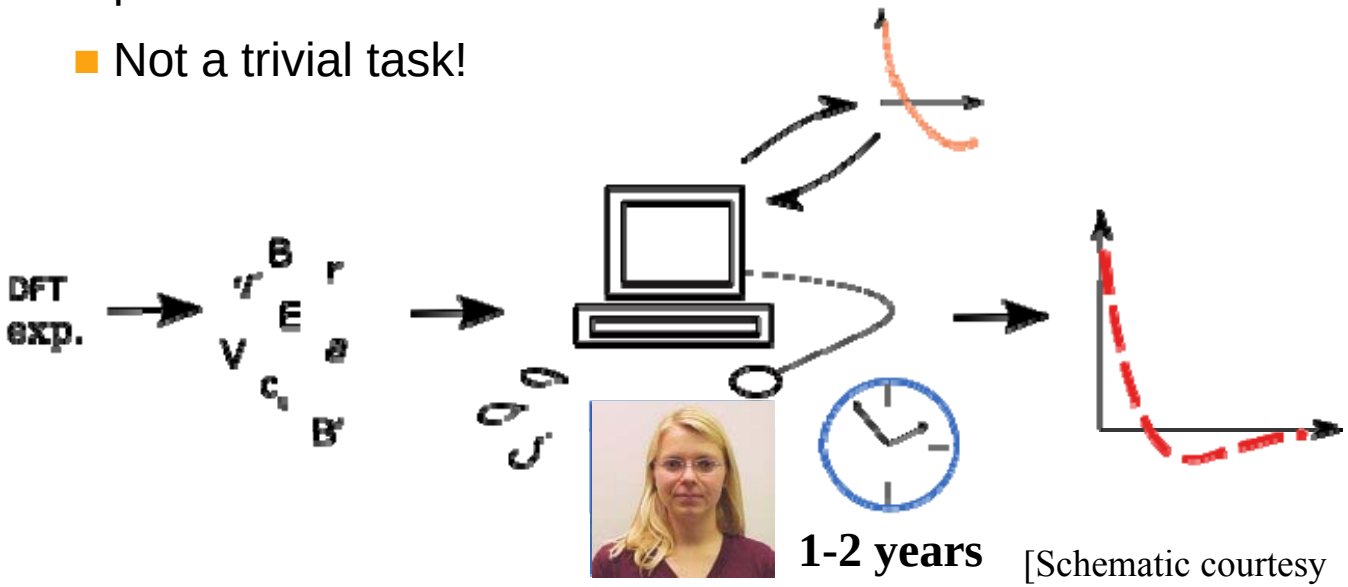
ik-dependent angular term modifying strength of ij bond

- This form for b_{ij} conforms to $b_{ijk} \propto \frac{1}{\sqrt{\text{coordination of } i}}$ consistent with Pauling's theory of chemical bond

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

The “blood, sweat and tears” part

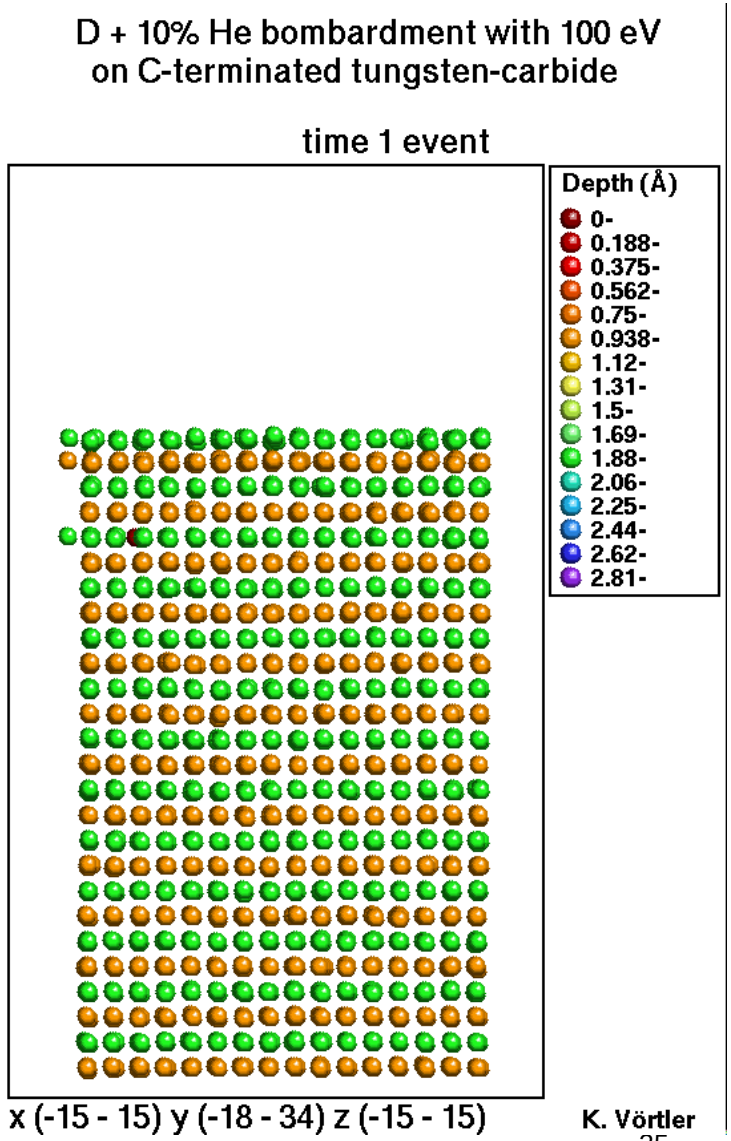
- There are all in all 11 parameters that must be specified
- Constructing a good potential means finding suitable values for these
  - This is done by fitting to different experimental or density-functional theory values of ground state and hypothetical phases
  - Not a trivial task!



[Schematic courtesy of Carolina Björkas]

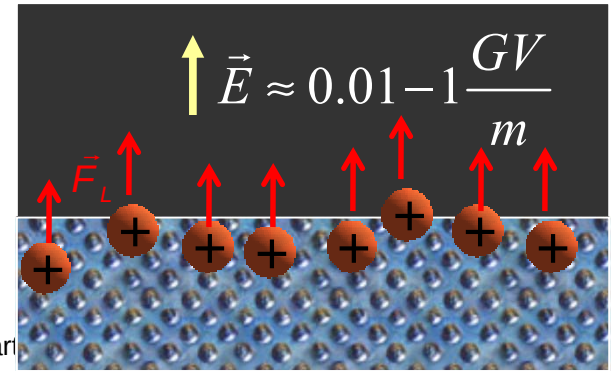
Potentials developed in our group

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



Hybrid ED&MD (HELMOD) by Djurabekova *et al*

- A new kind of molecular dynamics was developed by us to enable simulation of metal surfaces under electric field
- Atomic interactions obtained from EAM-like potentials as in usual metal MD
- But in ED&MD hybrid code $\vec{F} = -\nabla V(\vec{r}_i) + \vec{F}_q + \vec{F}_{Coul}$ for surface atoms as due to the excess or depletion of electron density (atomic charge)
- E_{loc} is obtained by solution of the Laplace equation $\nabla^2 \varphi = 0$ in the vacuum above the metal surface
- Gauss law implemented on a surface $\sigma = \varepsilon_0 E_{loc}$ is applied to calculate the charges q_i on surface atoms

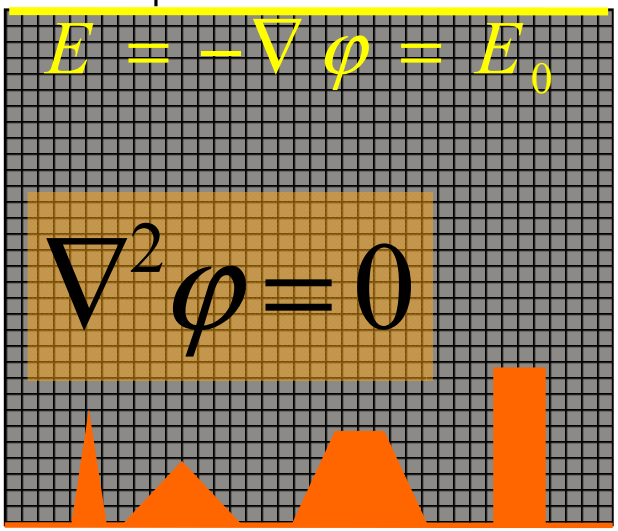


Thus, the motion of surface atoms is corrected due to the pulling effect of the electric field as a 1-body force $F_q = E_{loc} q_i$

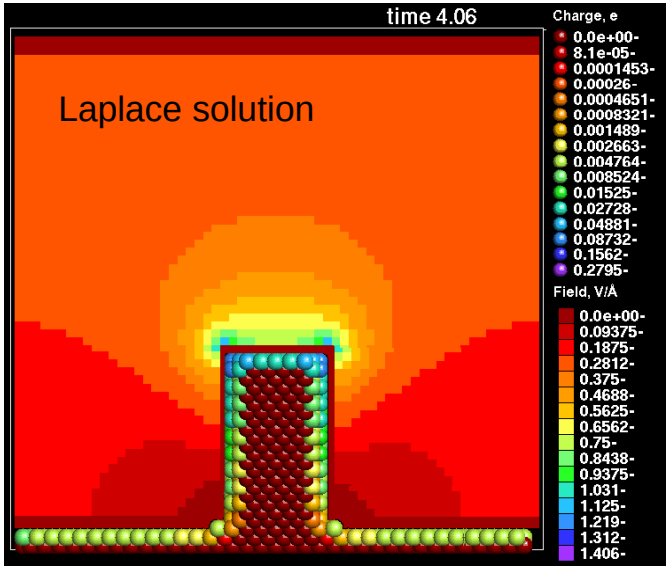
Special case for CLIC simulations: HELMOD

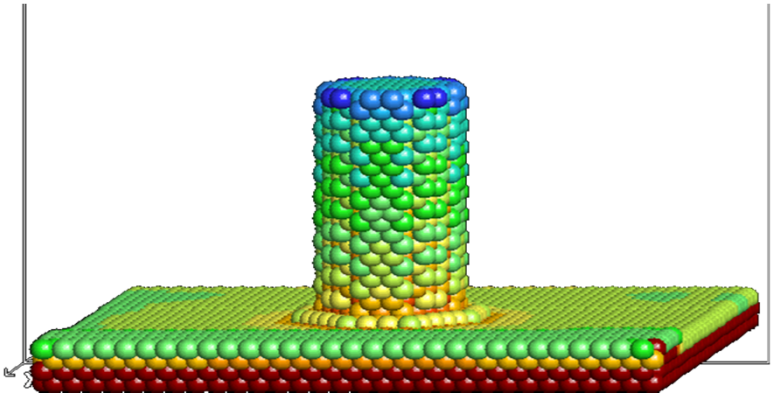
Hybrid ED&MD (HELMOD) by Djurabekova *et al*

Laplace solver



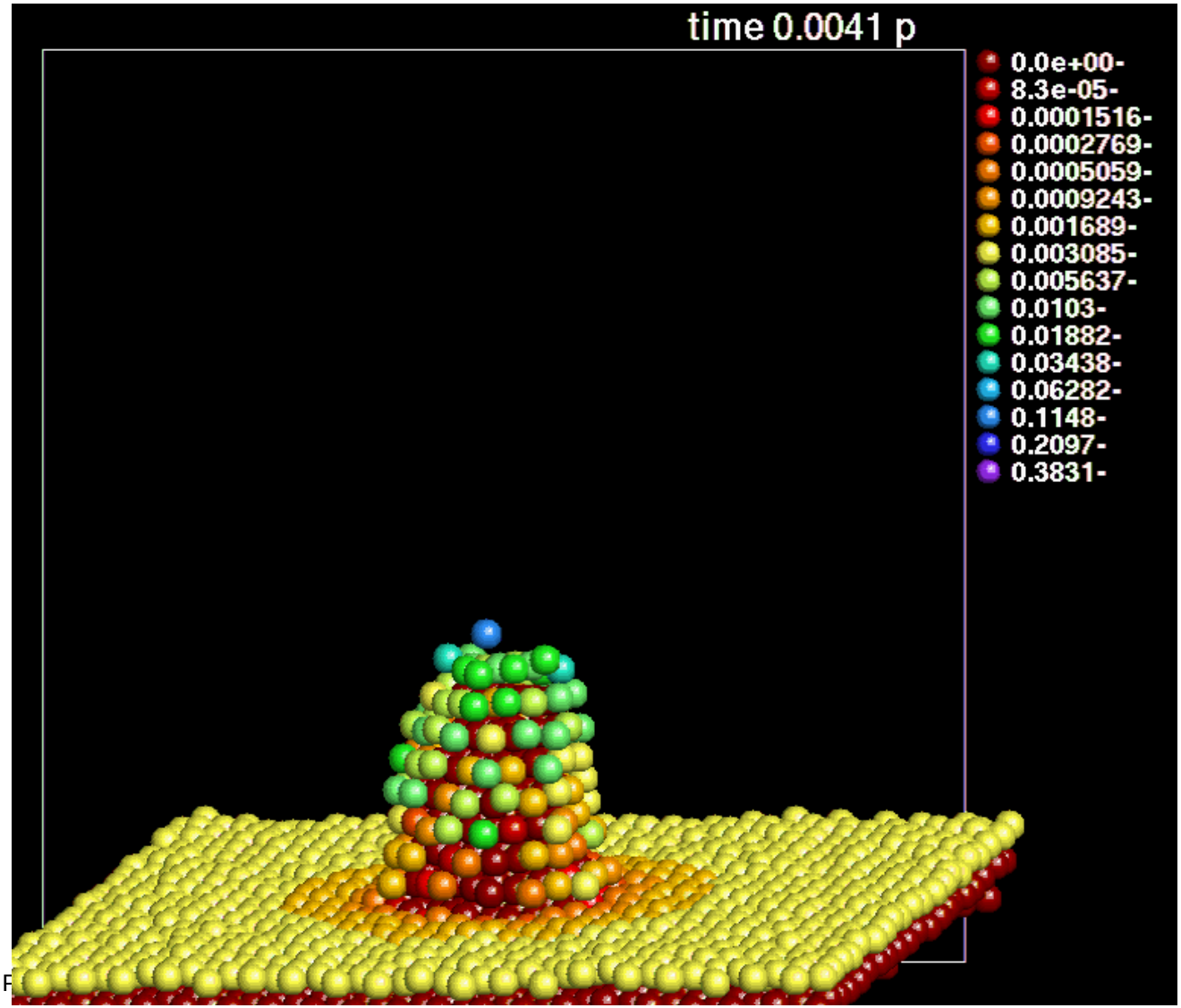
φ=const
(conductive material)



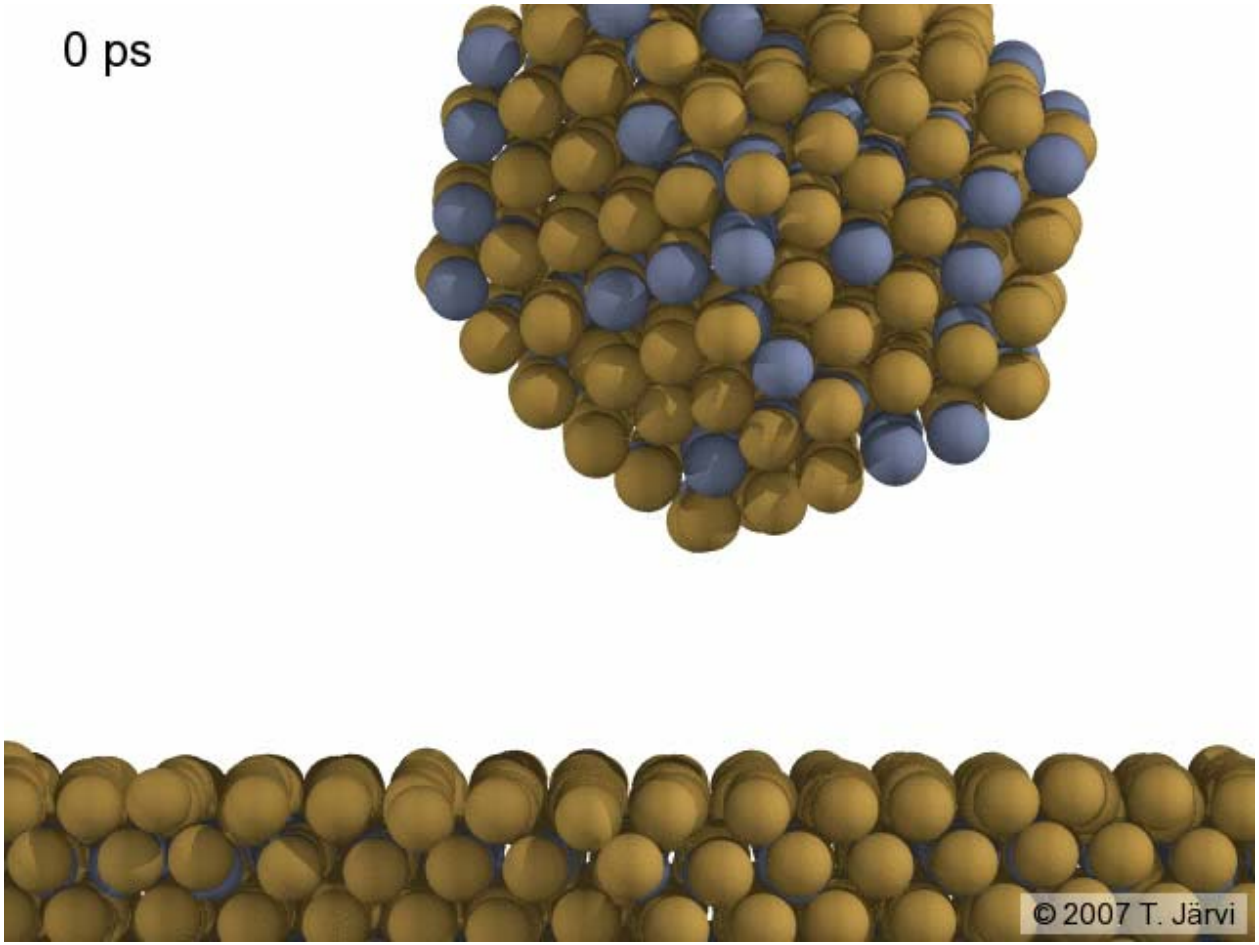


Special case for CLIC simulations: HELMOD

Example: Short tip on Cu (100) surface at the electric field 10 GV/m at 500 K

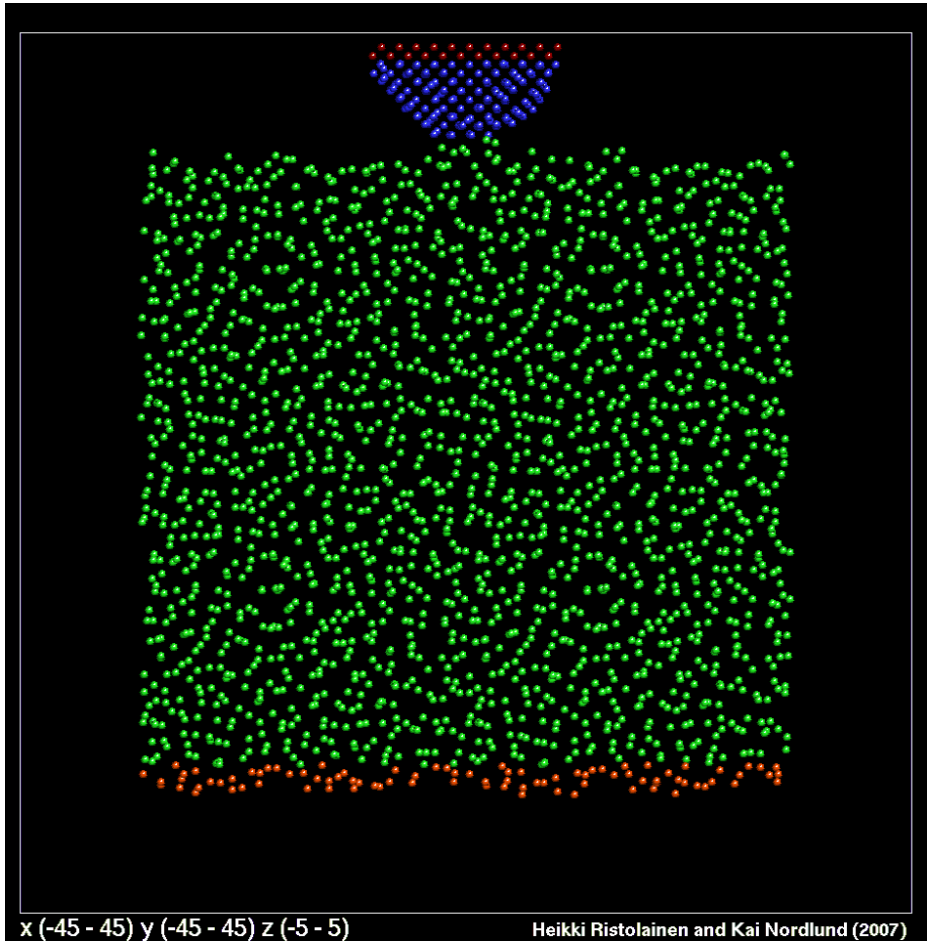


Example 1: MD of soft landing of Cu_3Ni nanocluster on Cu surface



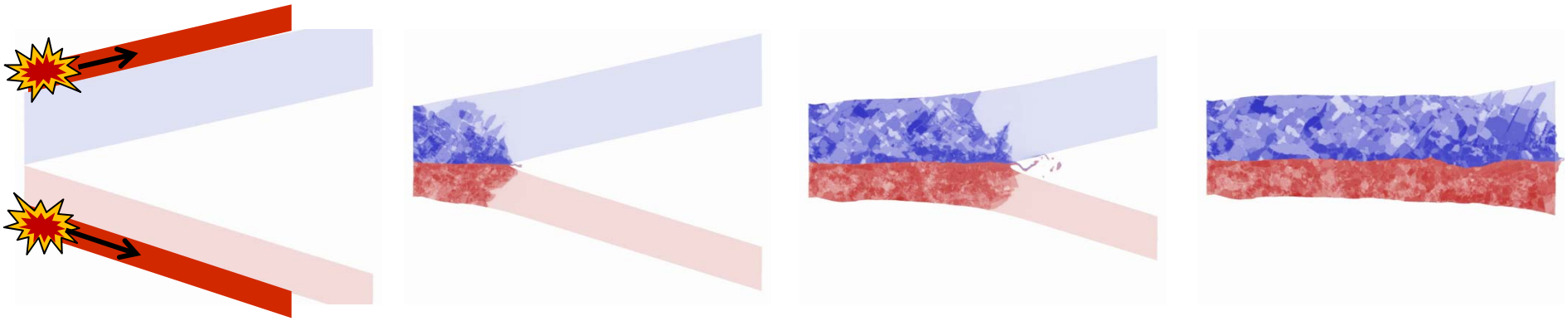
Example 2: Nanoindentation

- Nanoindentation can be very well simulated by MD
- Example: diamond indentation of a-Si



Example 3: explosive welding

- Fe and Cu explosively welded together
  - Explosion front velocity 1.5 km/s can be exactly matched on MD timescale: 1.5 m/s = 1.5 nm/ps.
- We have simulated on the atomic scale explosive welding
- Results showed that local melting is a prerequisite for jet formation



[Saresoja, Nordlund, Kuronen, Adv. Engr. Mater 14 (2012) 265]

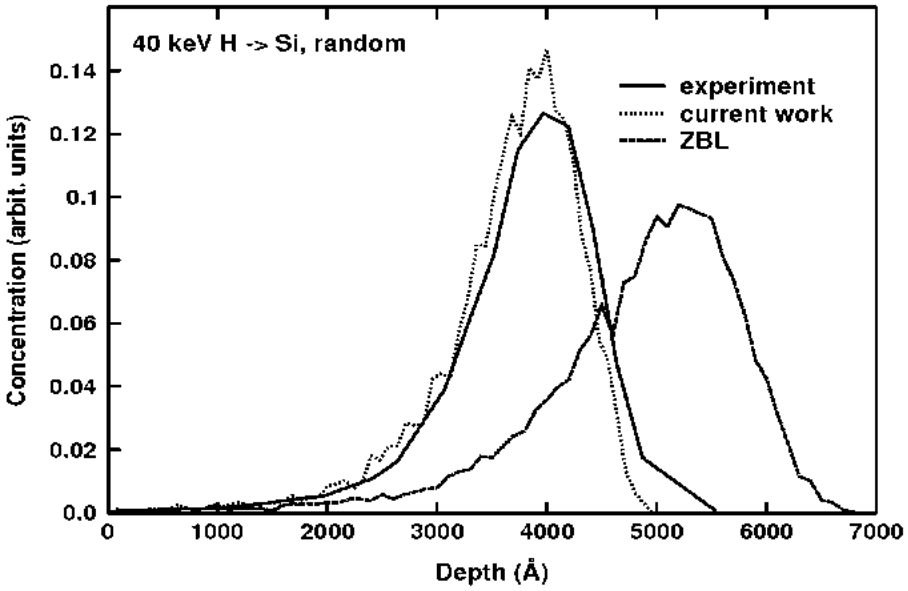
Animation

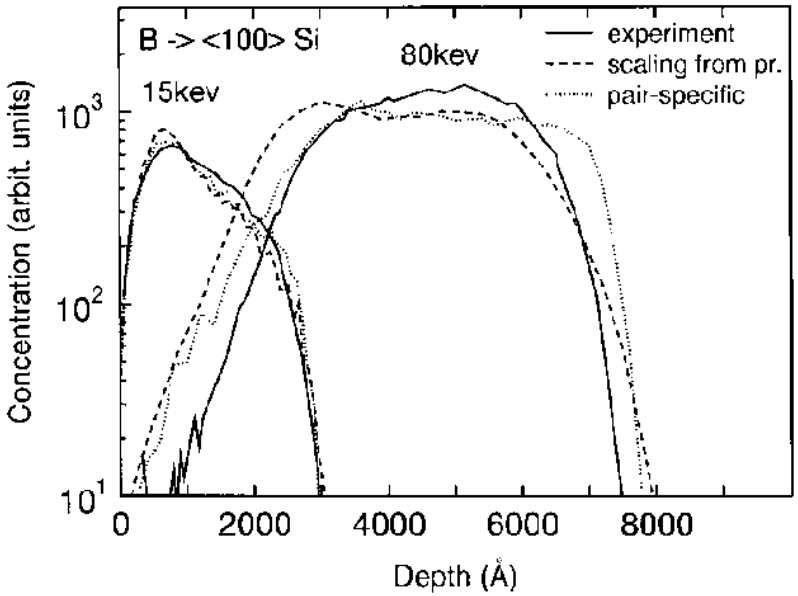
 [Saresoja, Nordlund, Kuronen, Adv. Engr. Mater 14 (2012) 265]

How reliable is MD?

Ion range calculations

- After 3 PhD theses in 1995-2005, we reached the state where we can reproduce **all** experimentally measured ion implantation depth profiles
  - Also in demanding channeling geometries



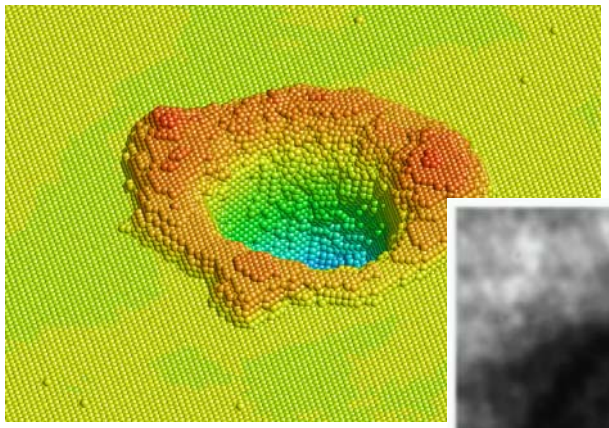


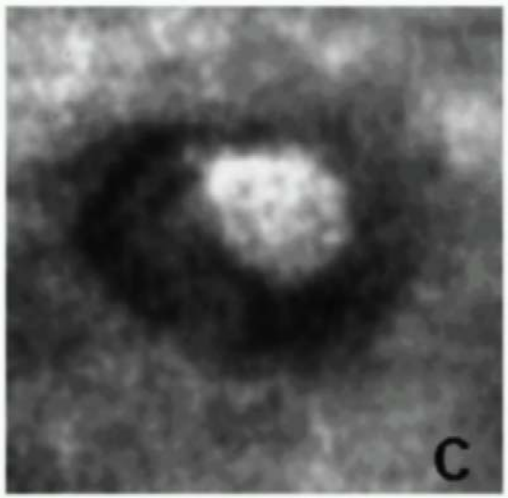
[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen,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

How reliable is MD?

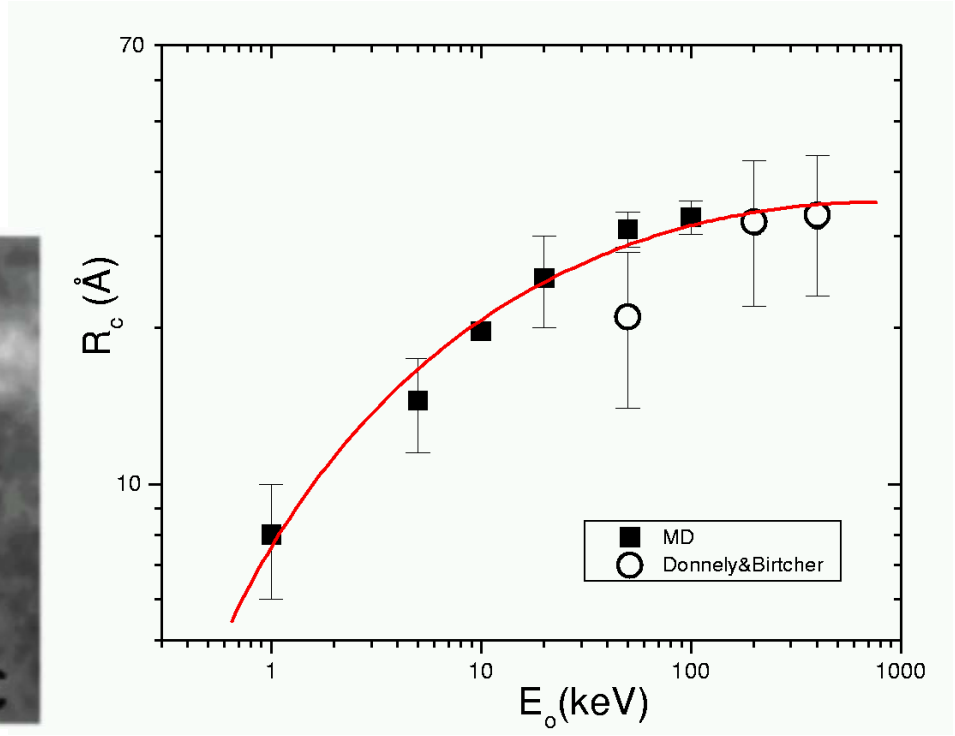
Craters: simulation vs. experiment

- We have studied surface crater formation extensively
- Experimental and simulated crater sizes agree well with experiments
- Also mechanism fully understood





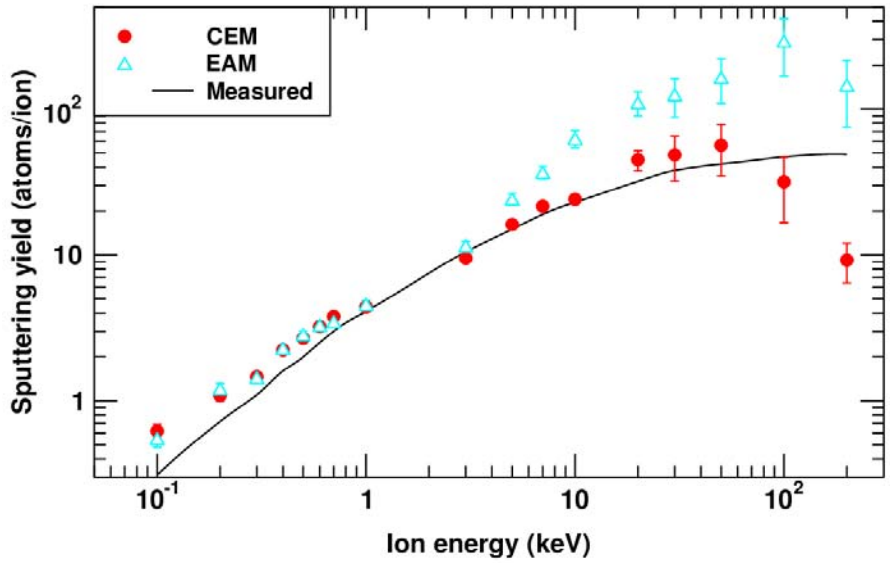
[Birtcher and Donnelly, PRB 1997]



[Bringa, Nordlund, Keinonen, Phys. Rev. B 64 (2001) 235426]

Sputtering yields

- In another of our big topics, we have examined systematically how reliable our interatomic potentials really are
- We compared the so called EAM and MD/MC CEM potentials with experiments on Au irradiation of Au(111)
  - Qualitative results the same
  - Crater sizes about the same
  - But sputtering yields have large differences at some energies!
  - The CEM potential agrees almost perfectly

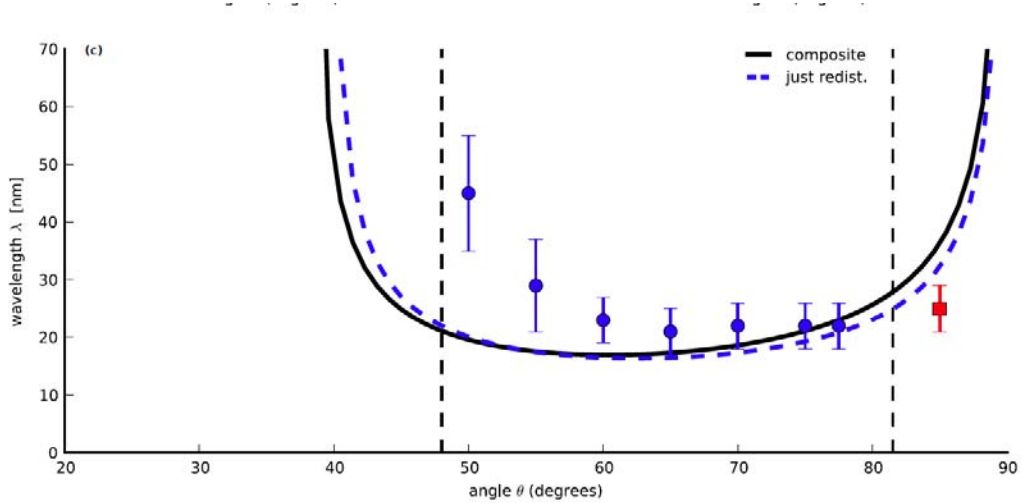


[Samela et al, Nucl. Instr. Meth. Phys. Res. B (2005)]

How reliable is MD?

Ion ripple wavelengths

- First principles (= no empirical input) ripple wavelengths compared to experiments:

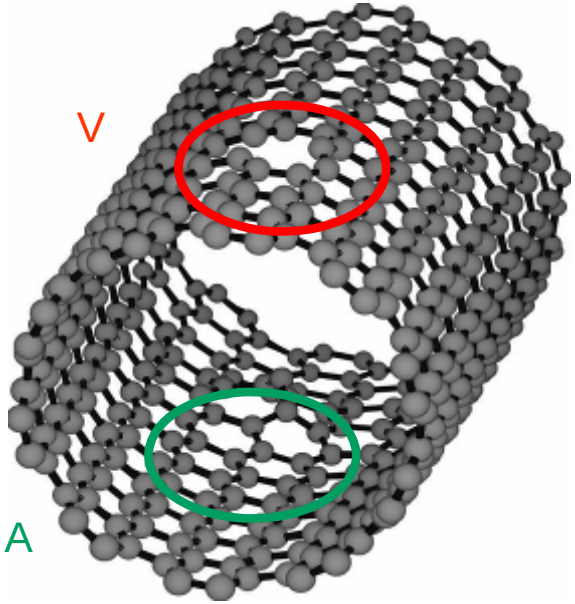


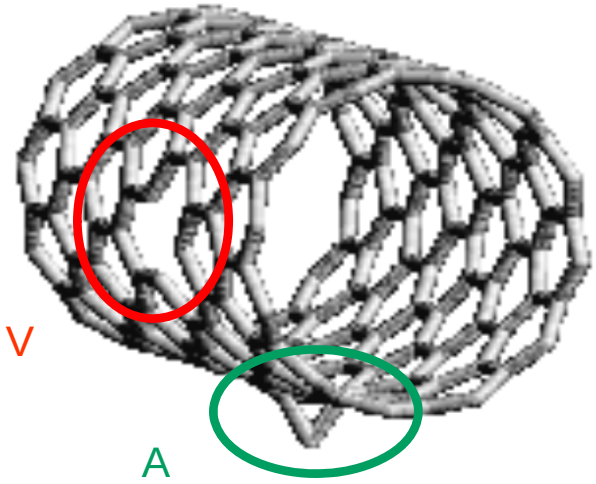
[Norris et al, Nature Communications 2 (2011) 276]

- Very good agreement considering no adjustable parameters

Case 1: Defects in carbon nanotubes

- In 2000-2005 we predicted several features of irradiation defect production in carbon nanotubes:





- **The most abundant defects in irradiated SWNTs are vacancies.**
  [Krasheninnikov et al, Phys. Rev. B 63 (2001) 245405]

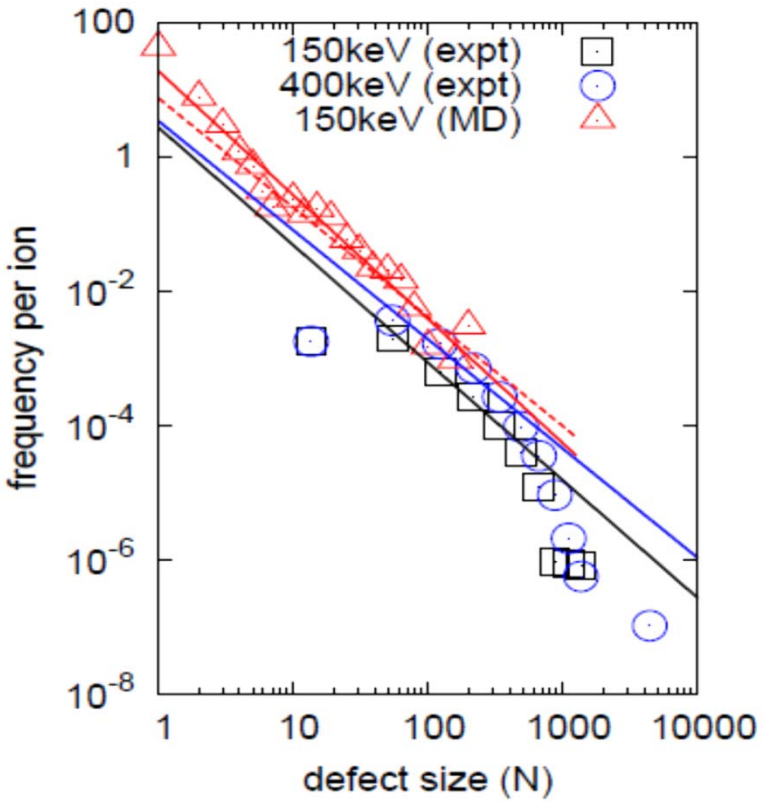
- **Carbon atoms absorbed on nanotube walls (adatoms) play the role of interstitials, and are highly mobile**
  [Lehtinen et al, Phys. Rev. Lett. 91 (2003) 017202]

- These findings were later verified experimentally by Sumio Iijima et al.

Case 2: power law damage distribution

- In 2014 we predicted that damage cluster size distributions in W follow a power law [A. E. Sand, S. L. Dudarev, and K. Nordlund, EPL **103**, 46003 (2013)]

- This was verified by us and our experimental collaborators in 2015



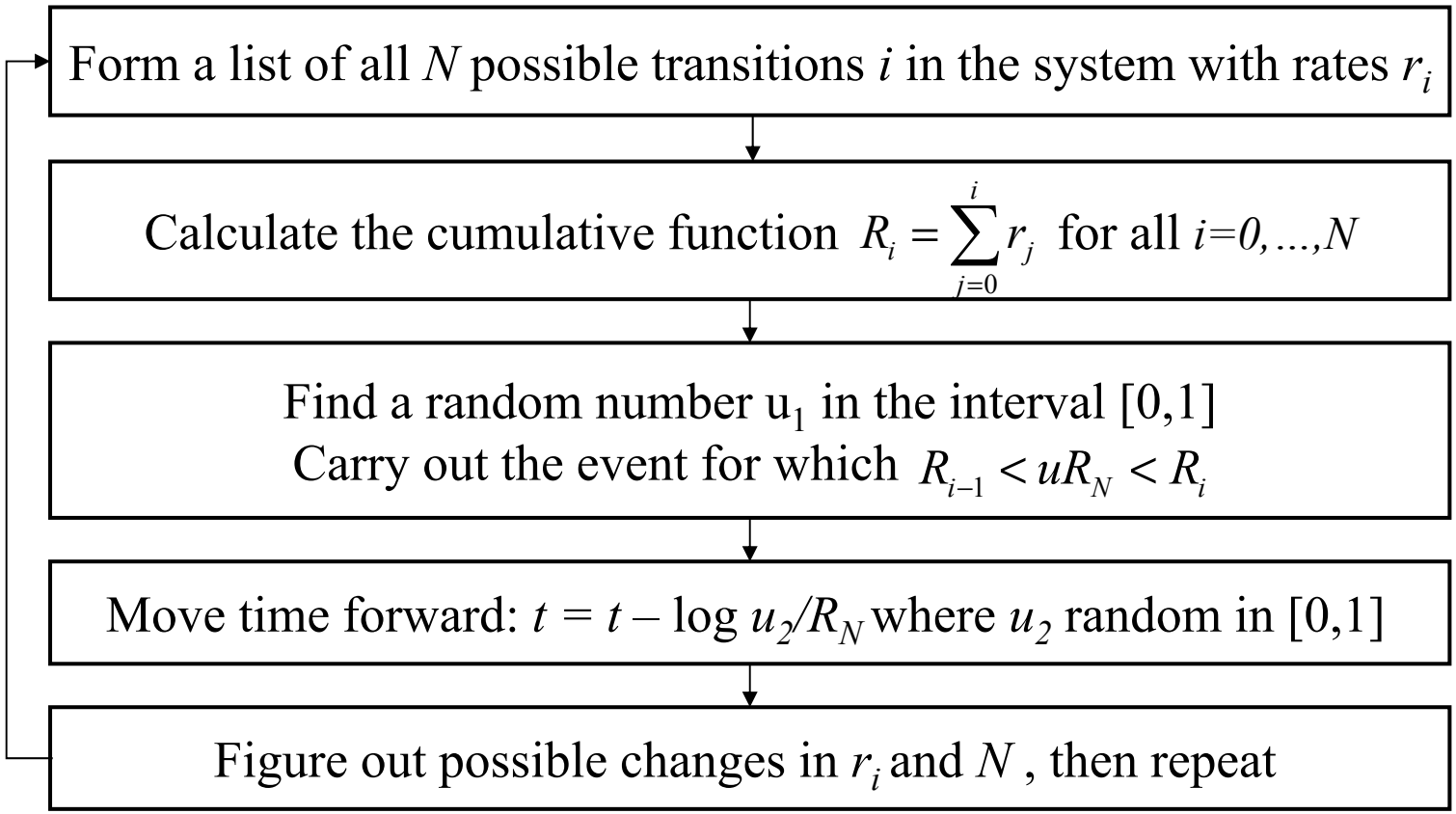
[X. Yi, A.E. Sand, D.R. Mason, M.A. Kirk, S.G. Roberts, K. Nordlund and S.L. Dudarev, EPL (2015)]

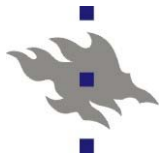
Long-time scale limit of MD

- Many real materials processes take microseconds, seconds, days or years
- This is clearly beyond the scope of molecular dynamics: the iteration time step is typically ~1 fs, and can normally not be much larger than this
  - => 1 million iterations of the MD loop only gives 1 ns time
- There ***are accelerated MD*** techniques such as "Hyperdynamics" and "Temperature-accelerated dynamics" that sometimes can get to ms or even s timescals – but limited in range of problems they can do
- Non-MD methods that can get to very long time scales:
- **Kinetic Monte Carlo (KMC)**
- **Rate equations** (numerical solution of differential equations)

[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)]

Kinetic Monte Carlo algorithm





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

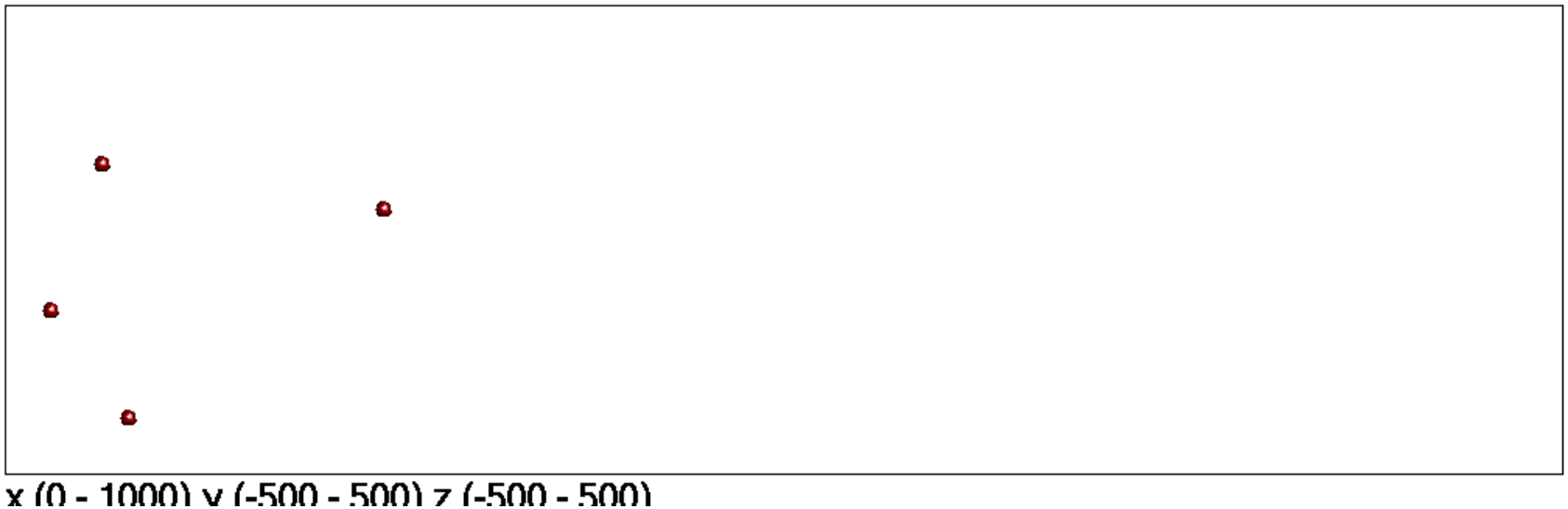
- Basic object is an impurity or intrinsic defect in lattice
- Non-defect lattice atoms are not described at all!
- Basic process is a diffusive jump, occurring at Arrhenius rate

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

- 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).]

Further reading on methods

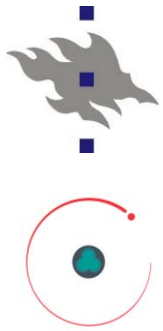
- A full course on MD:

  http://www.acclab.helsinki.fi/~knordlun/atomistiset/
- A full course on MC, including KMC:

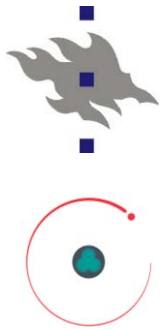
  https://moodle.helsinki.fi/course/info.php?id=11740
- Books:
  - Allen, Tildesley: “Computer simulation of liquids”, Oxford University Press 1989
    - An old classic, still fully relevant in theory parts
  - Frenkel, Smit: “Understanding molecular simulation: from algoritms to applications“, Academic Press 2002
    - More modern, has e.g. Modern interatomic potentials described
- And of course all the references given in the slides

Reliable (according to me) wikipedia pages

- I can also for a quick introduction recommend the following wikipedia pages (I have written or checked and modified them myself ☺):
  - **Sputtering**
  - **Kinetic Monte Carlo**
  - **Molecular dynamics**
  - **Interatomic potential**



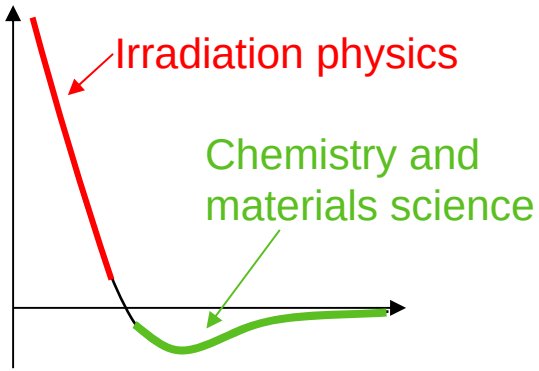
Extra slides: irradiation effect special methods



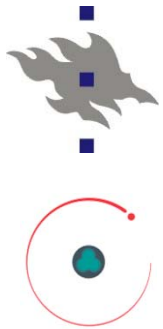
What is needed to model irradiation effects?

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!



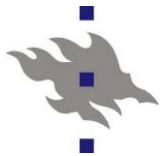
[K. Nordlund, N. Runeberg, and D. Sundholm, Nucl. Instr. Meth. Phys. Res. B 132, 45 (1997)].



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

- Example:

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

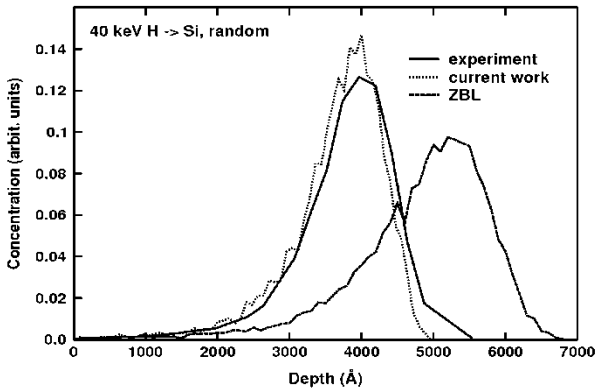
Here Δx_{max} *is the maximum allowed distance moved* during any *t (e.g. 0.1 Å),* ΔE_{max} *is the maximum allowed* change in energy (e.g. 300 eV), v_{max} *and* F_{max} *are the* highest speed and maximum force acting on any particle at *t*, respectively, $c_{\Delta t}$ prevents sudden large changes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

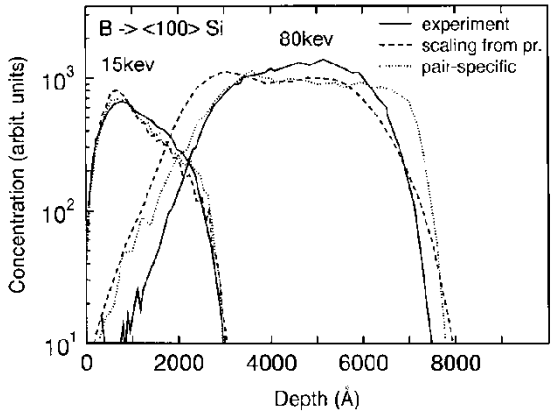
- This relatively simple algorithm has been demonstrated to be able to handle collisions with energies up to 1 GeV

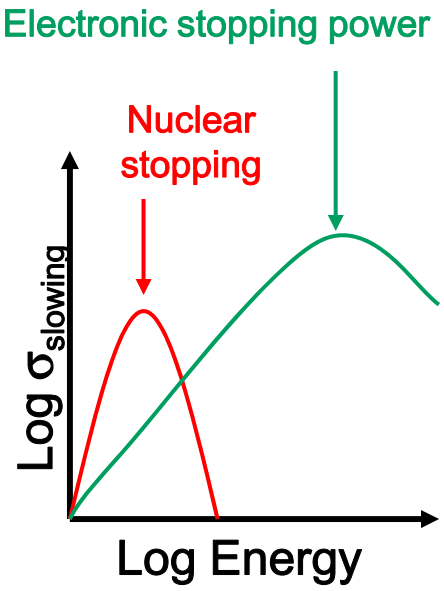
[K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)].

2) Energy loss to electronic excitations

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





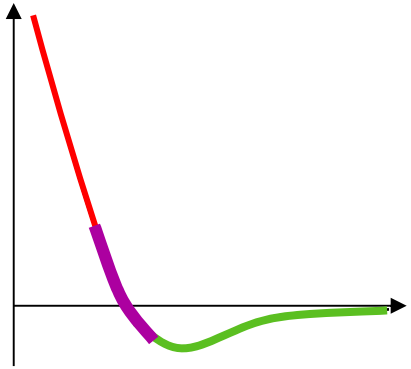


[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen,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

What is needed to model irradiation effects?

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

- Requires realistic **intermediate part** in potential



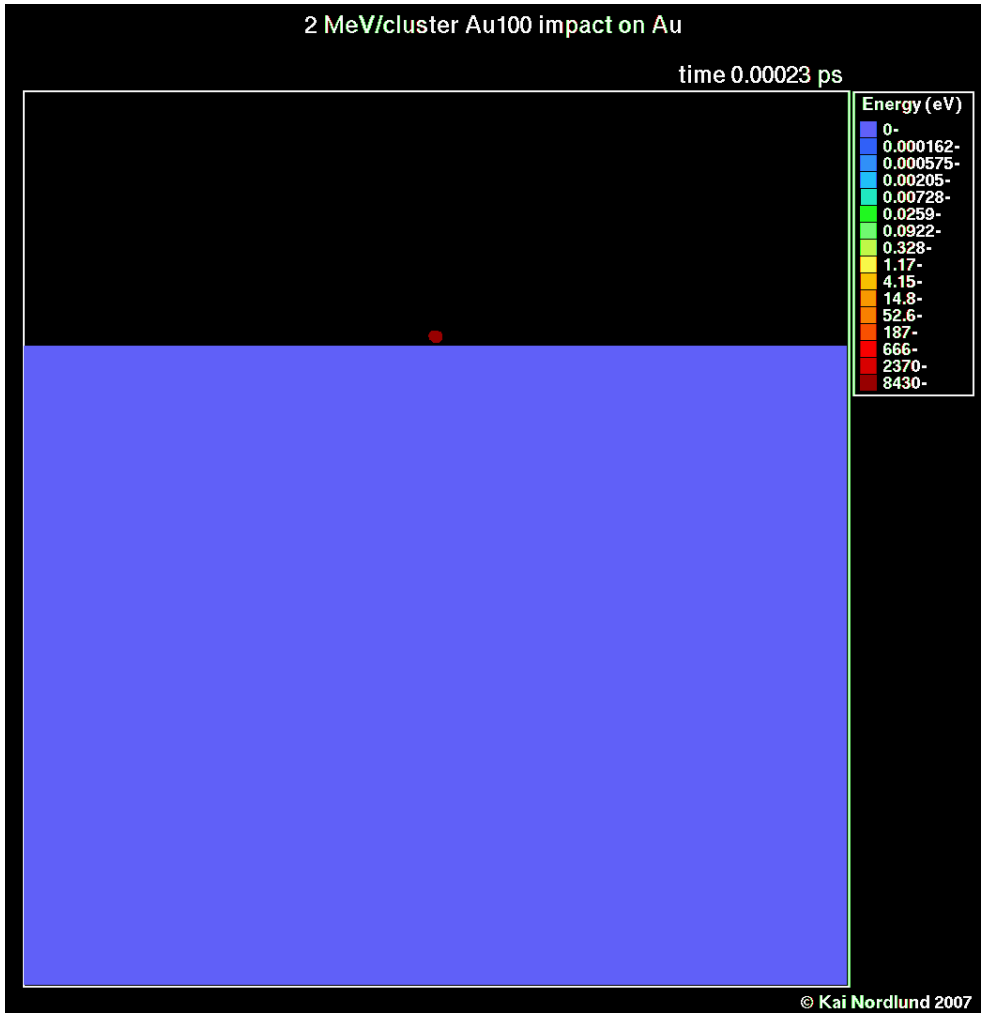
  - Can be adjusted to experimental high-pressure data and threshold displacement energies

[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

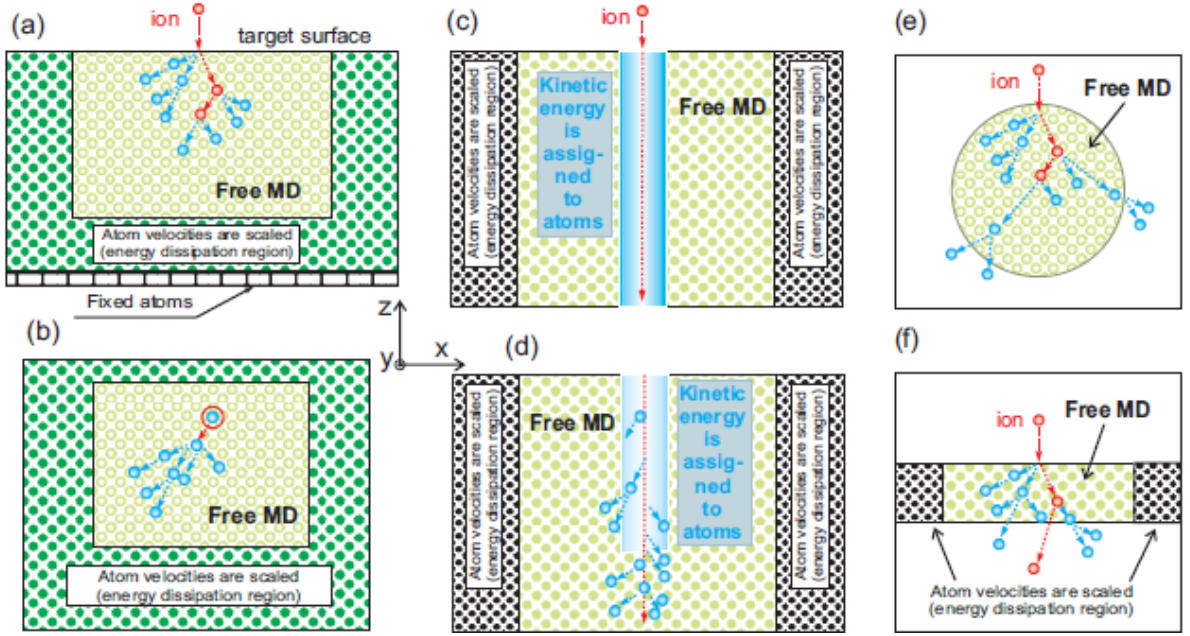
- The transition to thermodynamics occurs natuarally in MD
- But boundary conditions a challenge due to heat and pressure wave emanating from a cascade



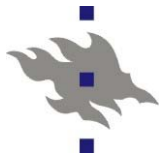
MD irradiation temperature control

- 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

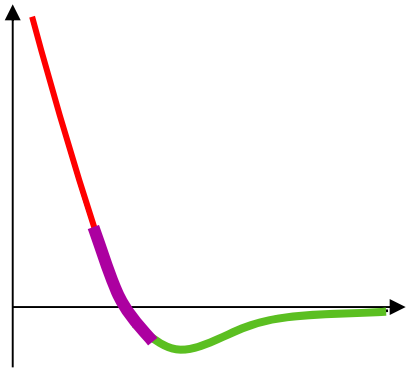


 [A. V. Krasheninnikov and **K. Nordlund**, J. Appl. Phys. (Applied Physics Reviews) **107**, 071301 (2010).



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 later