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# Atomistic simulations of plasma-wall interactions on the materials side: methods and some recent results

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# Greets from the capital of a snowy Finland

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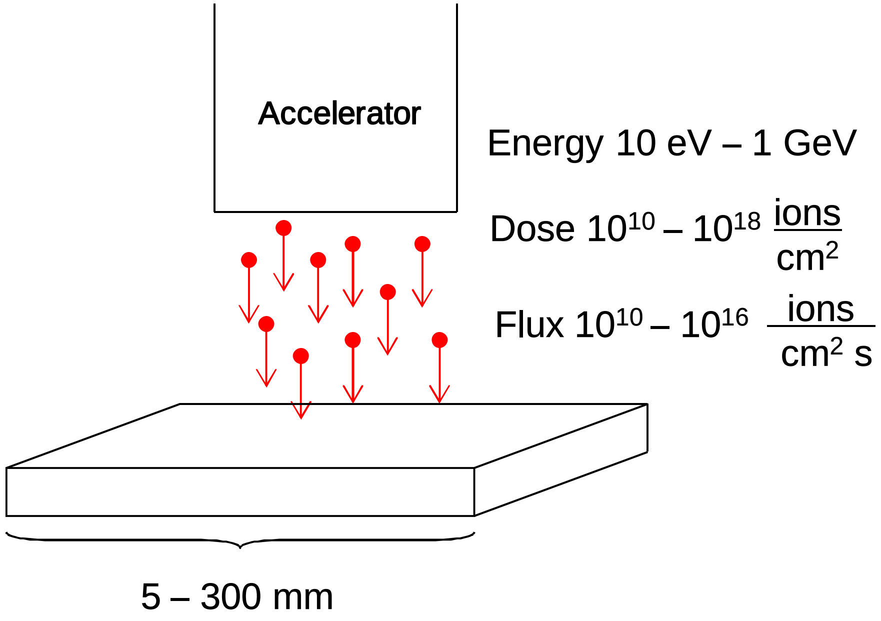
# Contents

- Background
    - Irradiation effects in materials
    - Plasma-wall interactions in fusion reactors
        - Relation to ion irradiation
- What is needed to model irradiation effects?
    - The conventional methods:
        - Binary collision approximation (BCA)
        - Molecular dynamics (MD)
        - Kinetic Monte Carlo (KMC)
    - Features specific to ion irradiation and plasma-wall interactions
- Some results on plasma-wall interactions
    - Swift chemical sputtering of carbon
    - Hydrogen in W by DFT, MD, KMC, rate equations

Irradiation effects in materials

# 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.



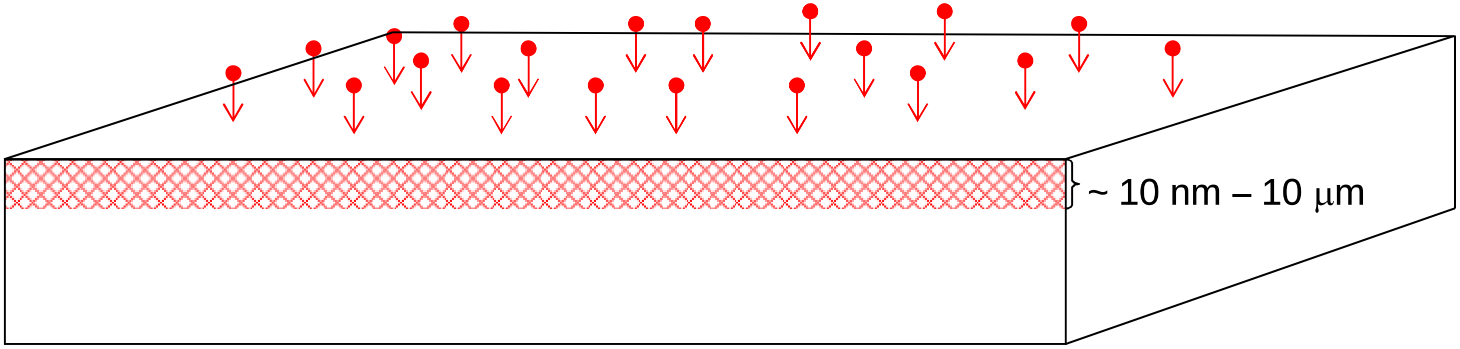
Accelerator

Energy 10 eV – 1 GeV

Dose $10^{10} – 10^{18} \frac{\text{ions}}{\text{cm}^2}$

Flux $10^{10} – 10^{16} \frac{\text{ions}}{\text{cm}^2\ \text{s}}$

5 – 300 mm

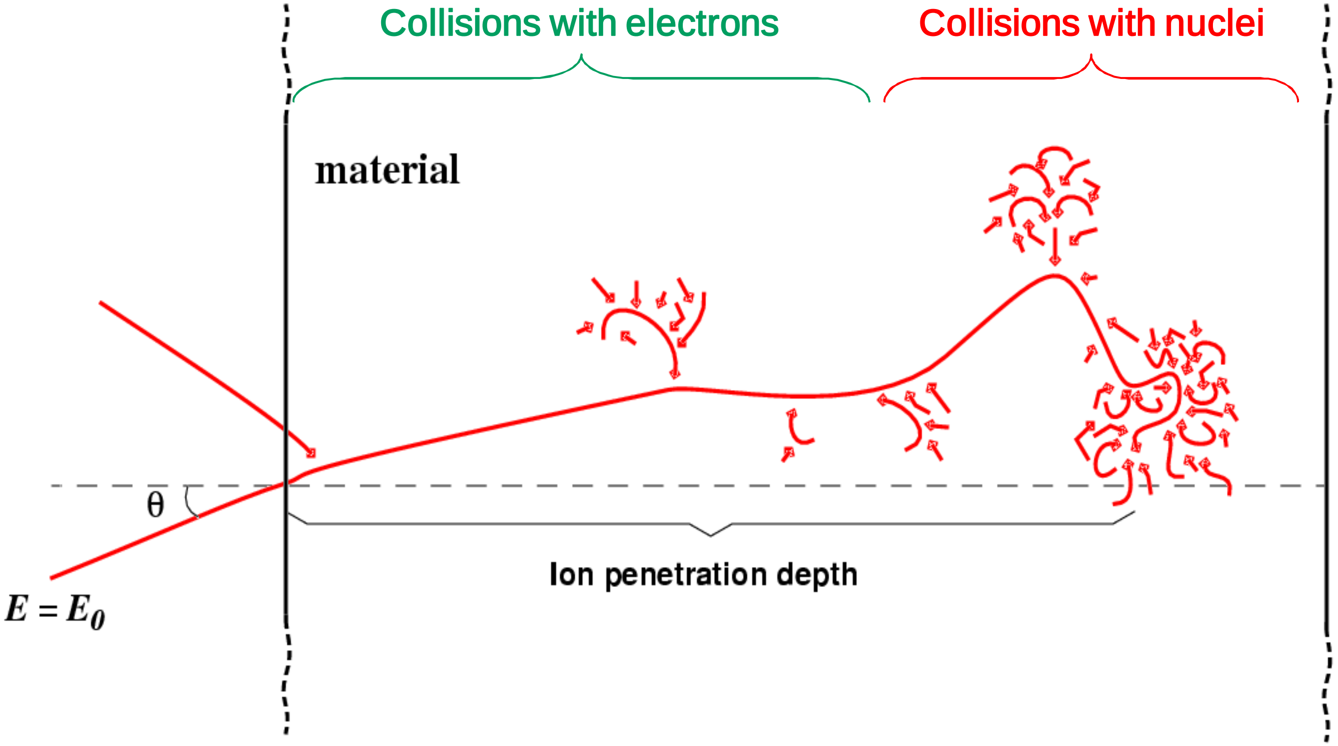


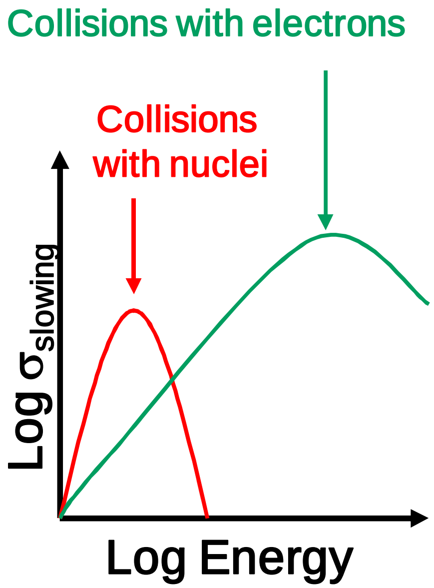
~ 10 nm – 10 μm

## Irradiation effects:

# Basic physics

- Schematical illustration of the ion slowing-down process

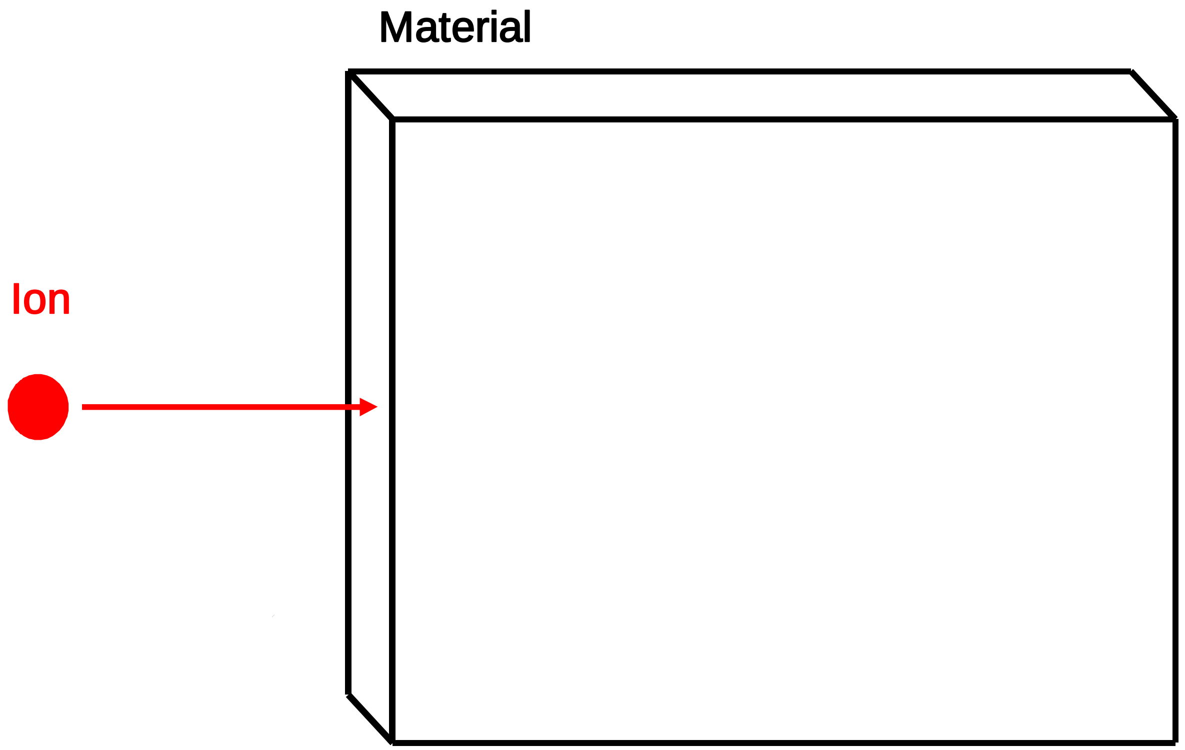




Plasma-wall interactions:

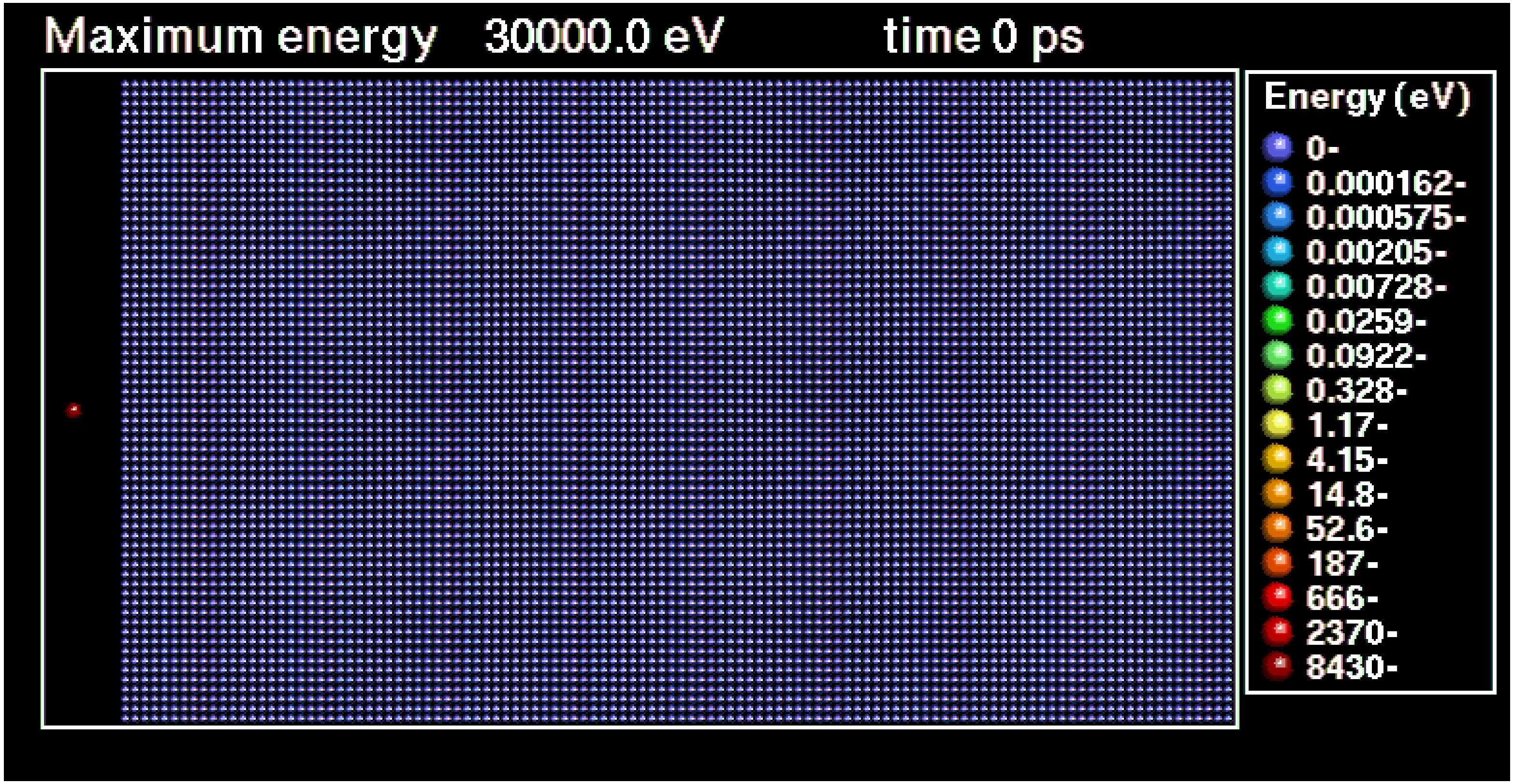
# Animation view

- An atom-level MD computer simulation can make it much clearer what irradiation effects really looks like
  - More on the method later…

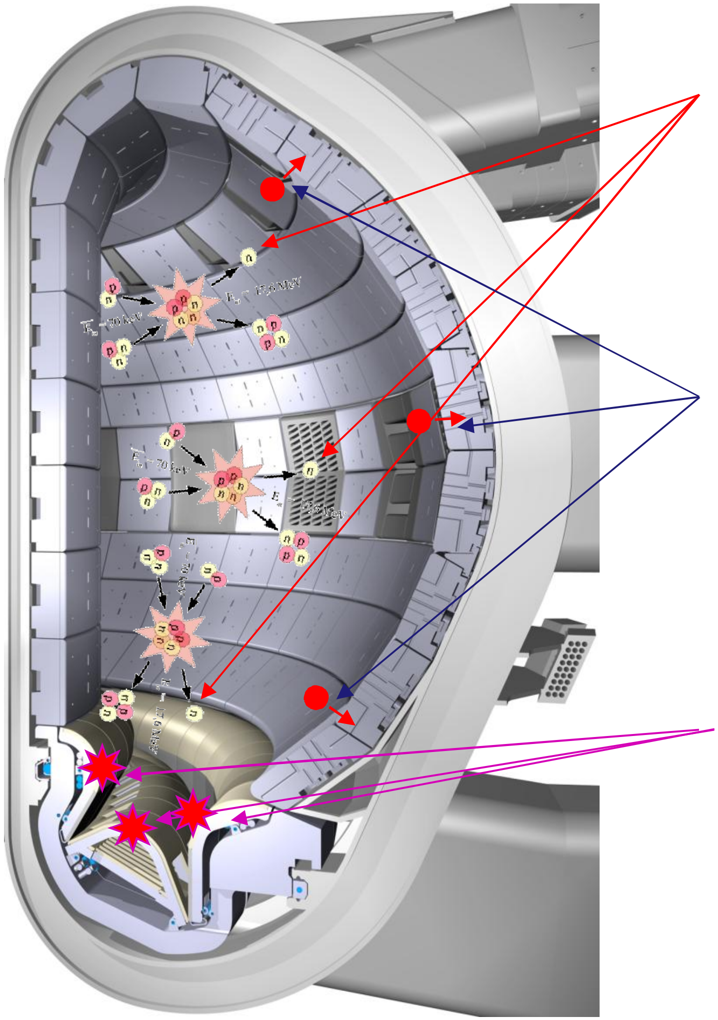


Plasma-wall interactions:

# Animation view



# Plasma-wall interactions in fusion reactors – they are ion irradiation



D+T fusion reaction in ITER and future fusion power plants will produce lots of 14.4 MeV neutrons and 3.5 MeV alphas

The alphas & other ions & neutrals leaking from the plasma bombard the main wall

- He energy ~ 1 MeV
- Others ~ 10 keV – 1 MeV
- Flux high

Divertor is bombarded by D, T and He leaking from the plasma

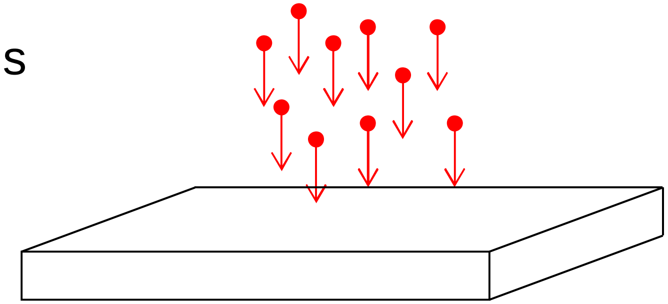
- Energies ~ 1 eV – 1 KeV
- Flux very high, ~ $10^{20}$ ions/cm$^2$s

[Thanks to Dr. Taina Kurki-Suonio for useful discussions on this issue]

Plasma-wall interactions:

# Plasma-wall energies and fluxes

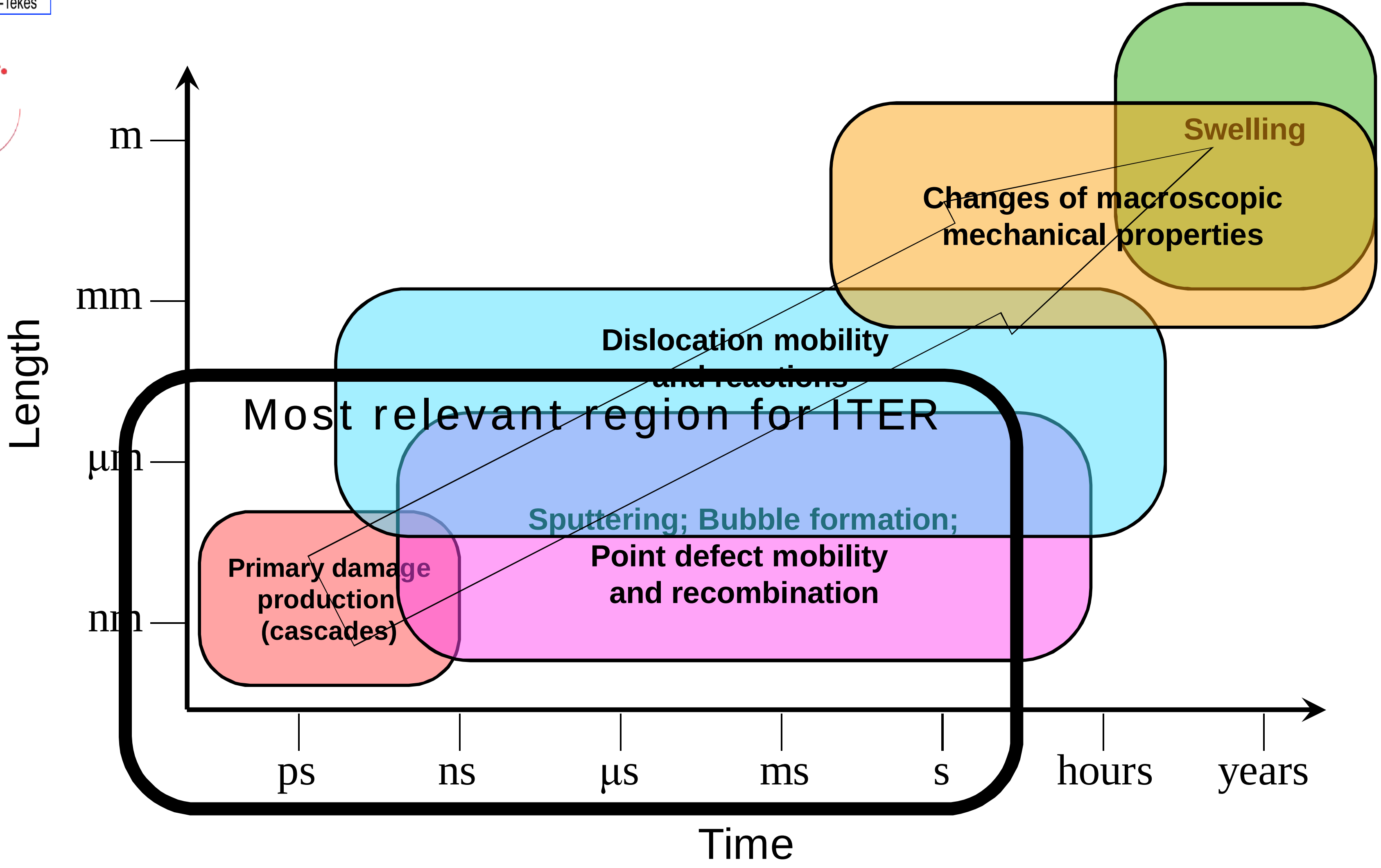
- How do ions hit a material?
- From an accelerator, with a well-defined single energy $E_0$ with very little energy spread
  - Time between impacts ~ μs – s on a nanometer scale => each impact independent of each other



- But from a plasma more complex: energy distribution likely has Maxwell-Boltzmann distribution + ions are accelerated over sheath potential before hitting materials
- If fluxes large, impacts can be close to each other in time
- In an arc plasma, they can actually be overlapping in time!

Plasma-wall interactions:

# What happens physically in the materials?



Swelling

Changes of macroscopic mechanical properties

Dislocation mobility and reactions

Most relevant region for ITER

Sputtering; Bubble formation;

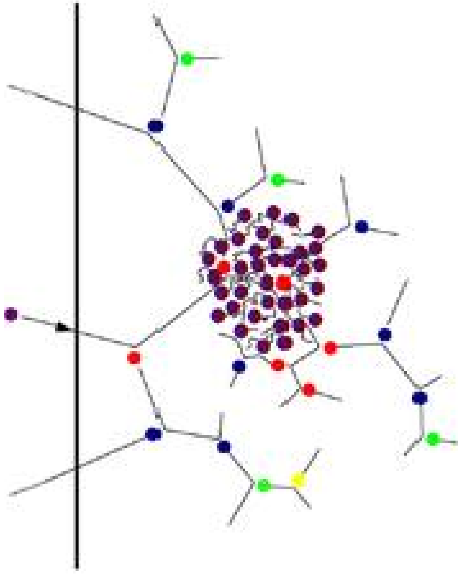
Point defect mobility and recombination

Primary damage production (cascades)

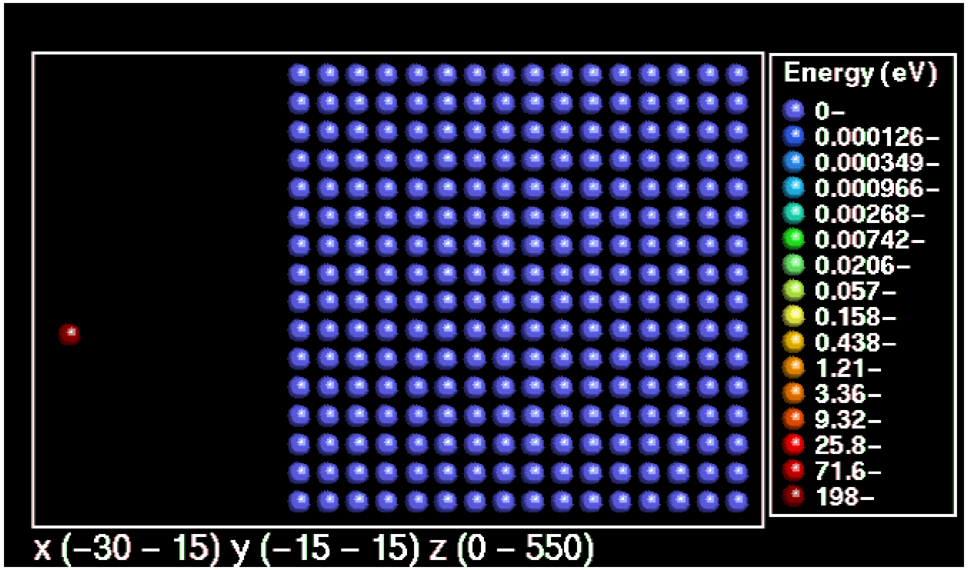
Plasma-wall interactions:

# The rich materials science of plasma-wall interactions

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



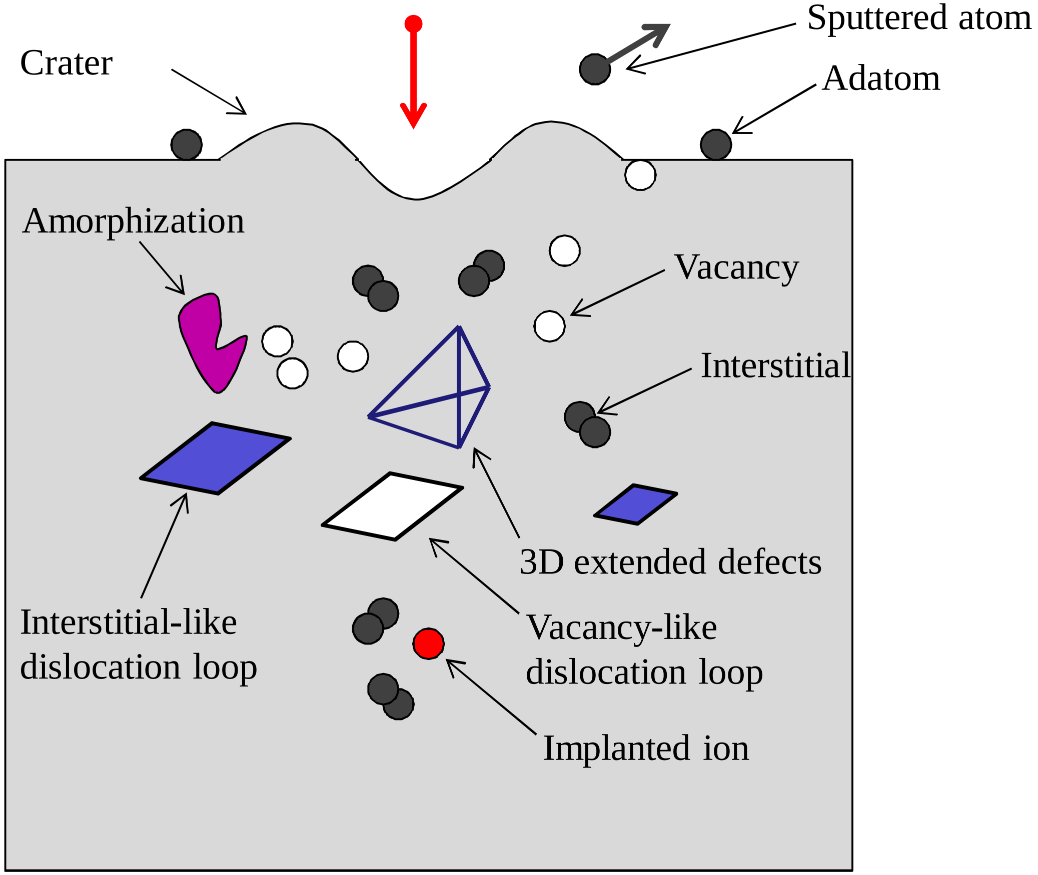
[Wikipedia by Kai Nordlund]



Plasma-wall interactions:

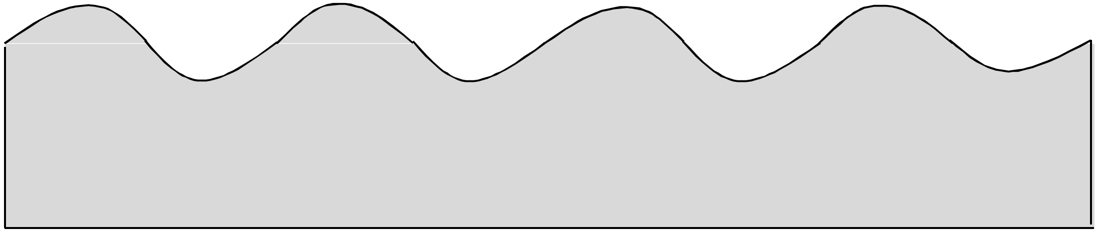
# The rich materials science of plasma-wall interactions

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



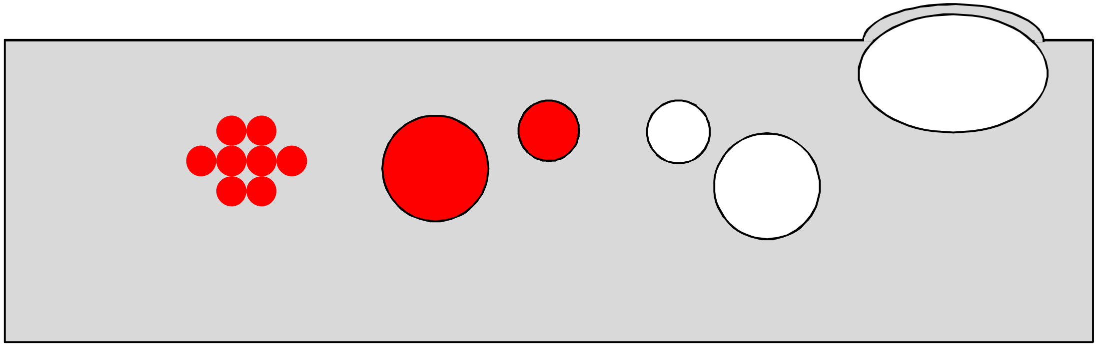
# The rich materials science of plasma-wall interactions: high fluences

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



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

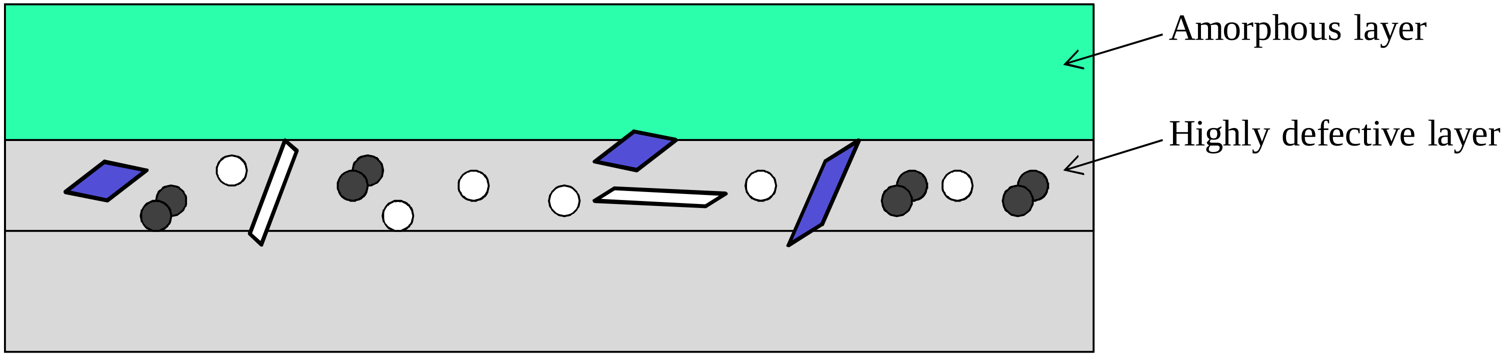
  - Precipitate/nanocluster, bubble, void or blister formation inside solid



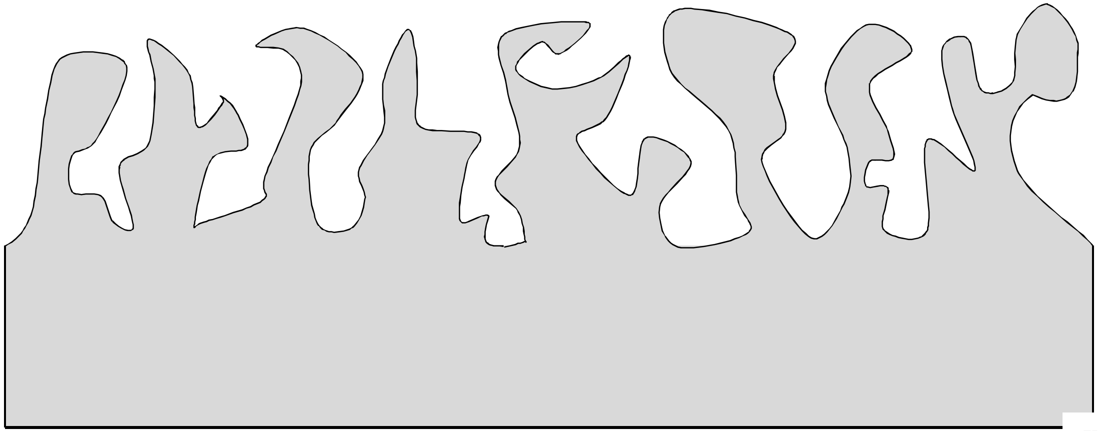
[Bubbles e.g: K. O. E. Henriksson, **K. Nordlund**, J. Keinonen, D, Physica Scripta **T108**, 95 (2004); Nanocrystals e.g. 75S. Dhara, Crit. Rev. Solid State Mater. Sci. 32, 1 [2007)]

# The rich materials science of plasma-wall interactions: high fluences

- Phase changes, e.g. amorphization:

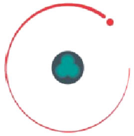


- Spontaneous porousness formation, "fuzz"
  - Highly fusion-relevant now, He -> W does it



[http://vlt.ornl.gov/research/20110119_highlight_doerner.pdf]

# Consequences of plasma-wall interactions for fusion

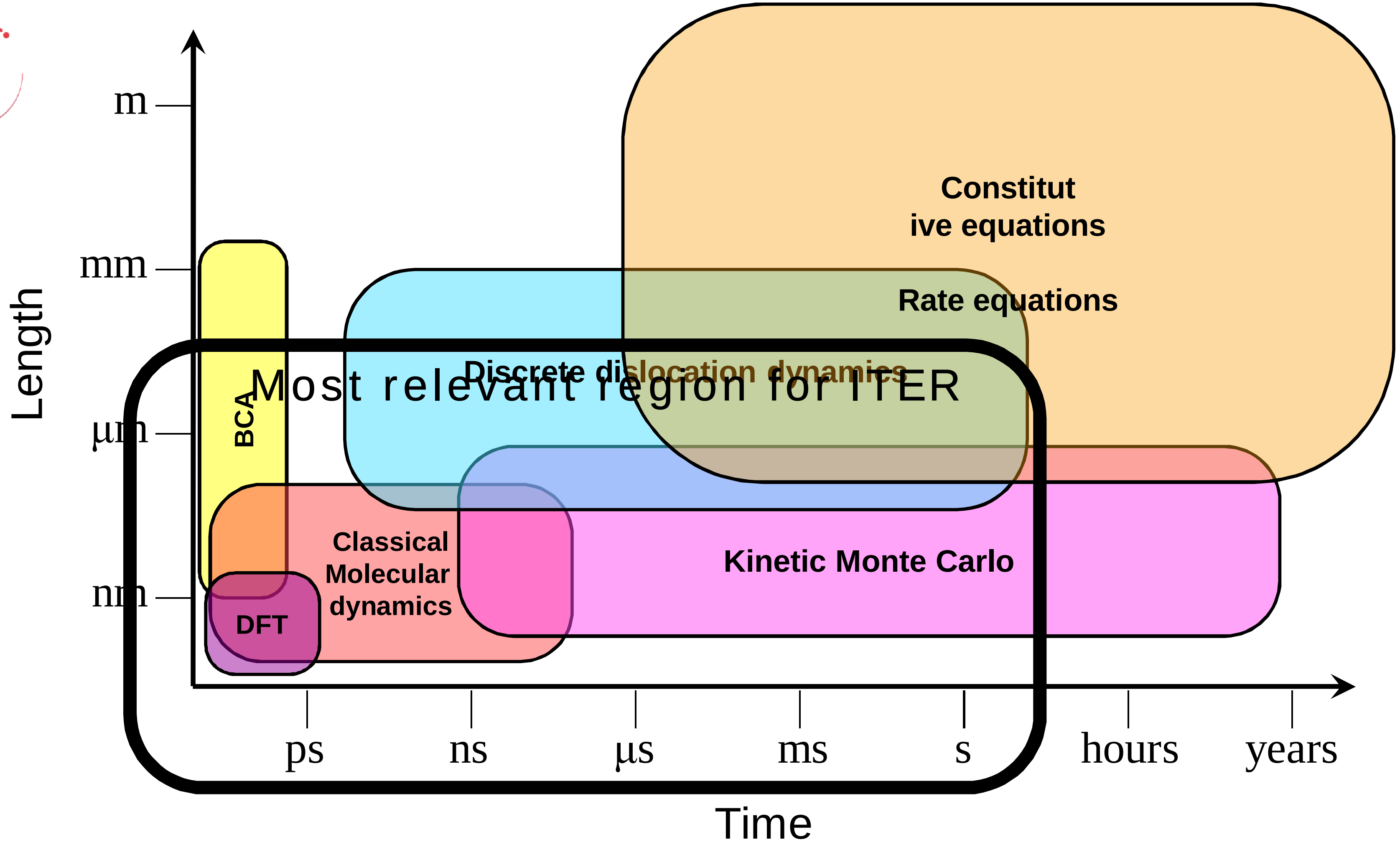


- How are all these relevant for fusion?
  - Implantation => T retention => VERY BAD
  - Sputtering => erosion => BAD
  - Sputter heavy impurities into edge plasma => cooling => GOOD
  - Sputter heavy impurities into main plasma => cooling => BAD
  - Sputtered molecules can migrate => redeposition => BAD
  - Damage the material => worse heat conduction => BAD
  - Damage the material => material becomes brittle, may crack=> BAD
  - Produce gas bubbles => blisters => flaking => dust => BAD

- So it is very problematic from many points of view, and improved understanding is needed to understand and avoid harmful effects!

Plasma-wall interactions:

# What is needed to model all this?



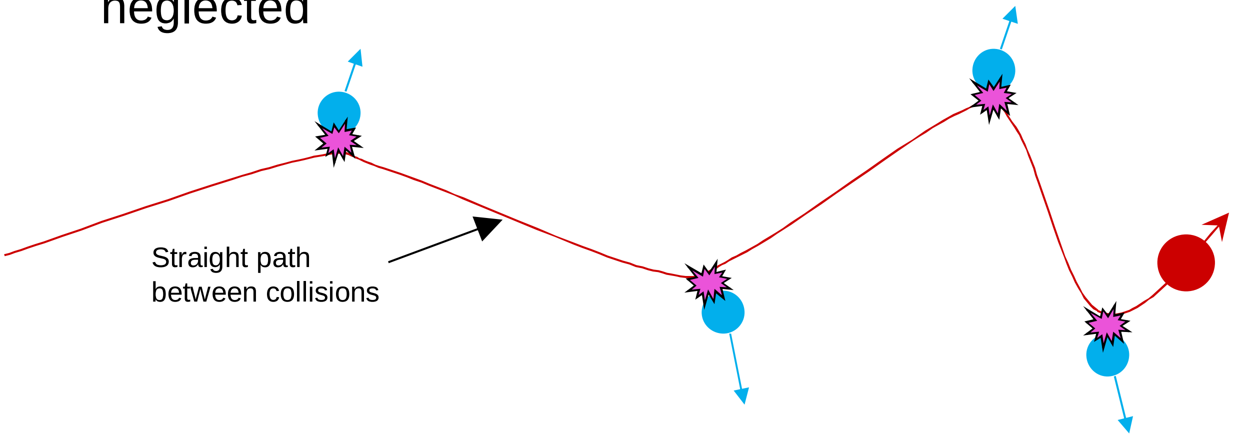
Plasma-wall interactions:

# What is needed to model the atomic level?

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

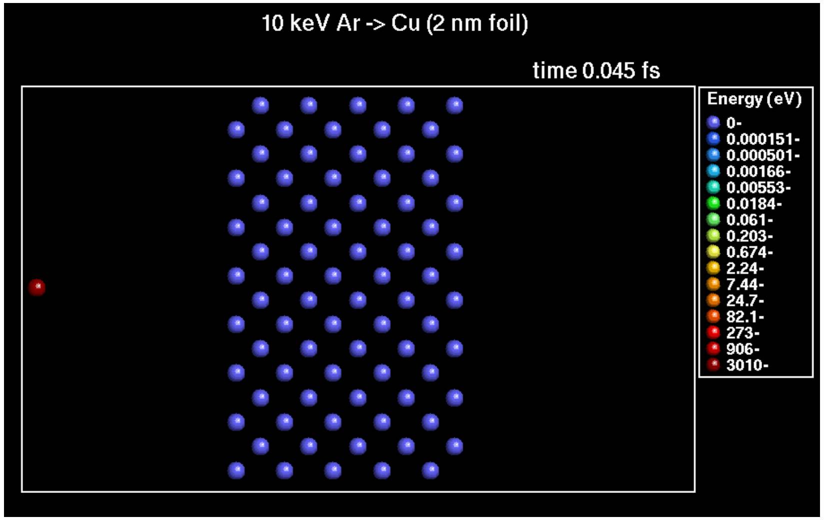
# BCA = Binary collision approximation

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

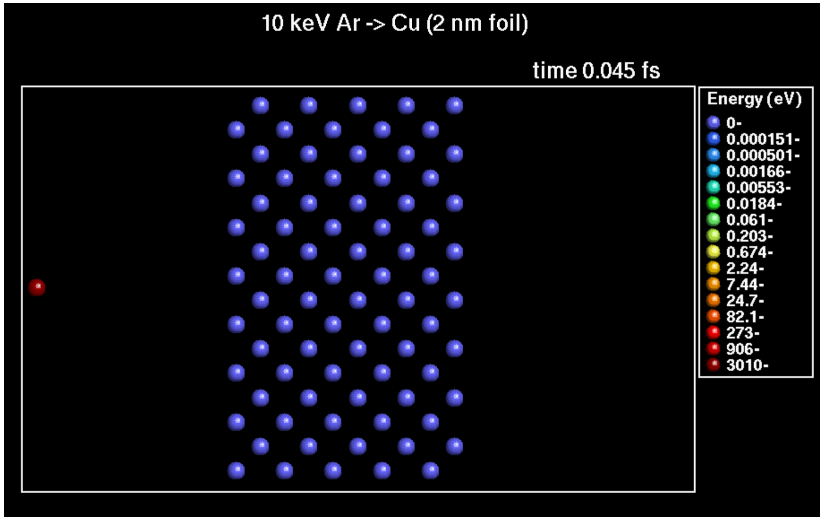


# Illustration of BCA vs. MD

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

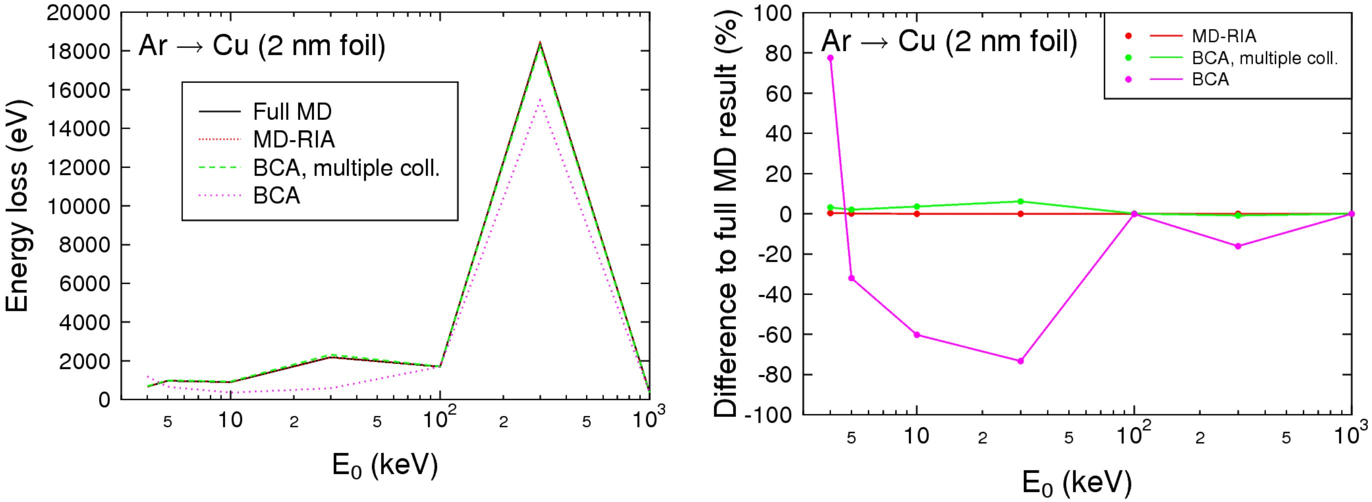


- Binary collision approximation (implemented within MD code)



# Illustration of BCA vs. MD

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



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

# Illustration of BCA vs. MD

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

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

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

# Different implementations

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

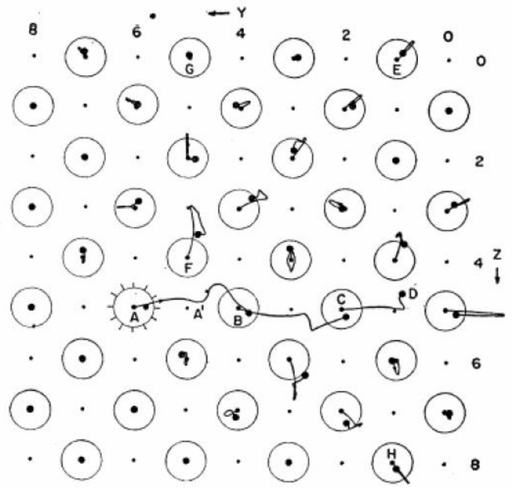
# BCA today and in the future?

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

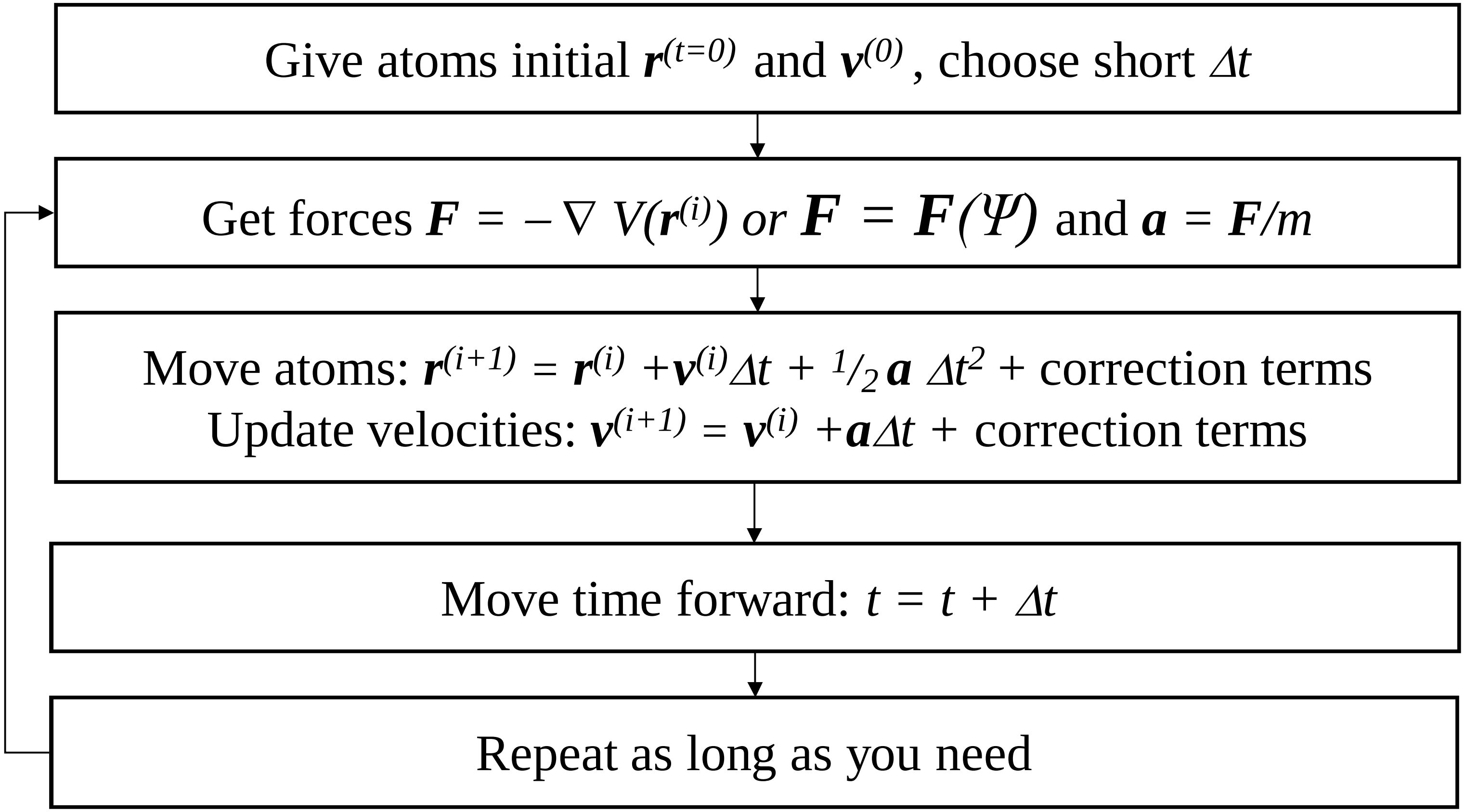
MD method in equilibrium calculations

# MD = Molecular dynamics

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



# MD algorithm



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

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

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

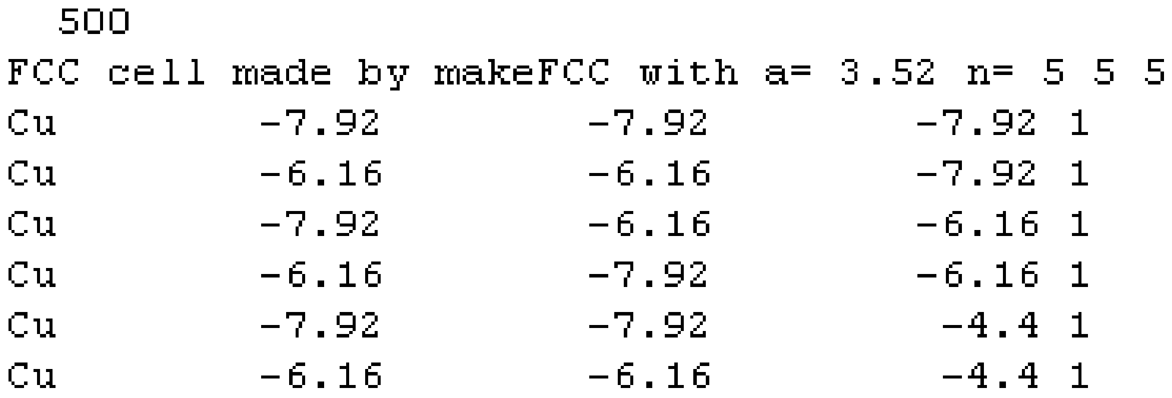
Update velocities: $\boldsymbol{v}^{(i+1)} = \boldsymbol{v}^{(i)} + \boldsymbol{a}\Delta t$ + correction terms

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

Repeat as long as you need

# MD – atom representations

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



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

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

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

# MD – Solving equations of motion

- The solution step $\mathbf{r}^{(i+1)} = \mathbf{r}^{(i)} + \mathbf{v}^{(i)}\Delta t + {}^{1}/_{2}\,\mathbf{a}\,\Delta t^{2}$ + 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:

$\mathbf{r}^{(i+1),p} = \mathbf{r}^{(i)} + \mathbf{v}^{(i)}\Delta t + {}^{1}/_{2}\,\mathbf{a}\,\Delta t^{2}$ + more accurate terms

↓

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

↓

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

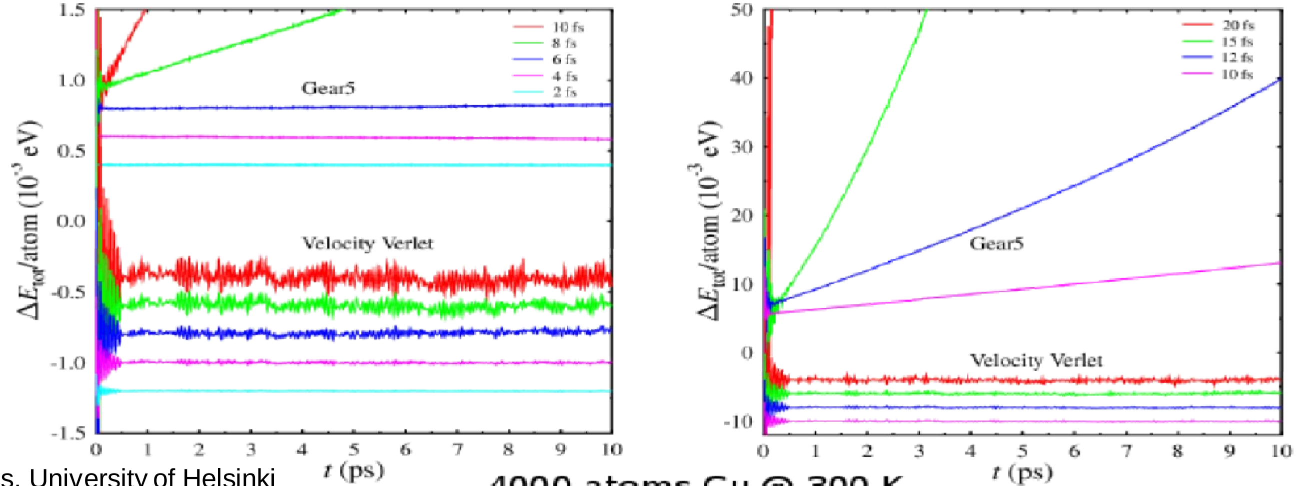
- Another, much more accurate: Gear5, Martyna
  - I recommend Gear5, Martyna-Tuckerman or other methods more accurate than Verlet,

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

MD method in equilibrium calculations

# MD – time step selection

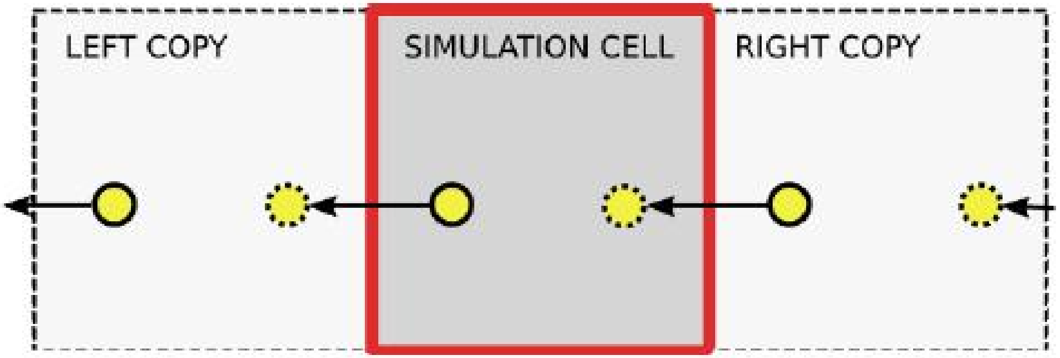
- Time step selection is a crucial part of MD
  - Choice of algorithm for solving equations of motion and time step are related
- Way too long time step: system completely unstable, “explodes”
- Too long time step: total energy in system not conserved
- Too short time step: waste of computer time
  - Pretty good rule of thumb: the fastest-moving atom in a system should not be able to move more than 1/20 of the smallest interatomic distance per time step – about 0.1 Å typically



4000 atoms Cu @ 300 K

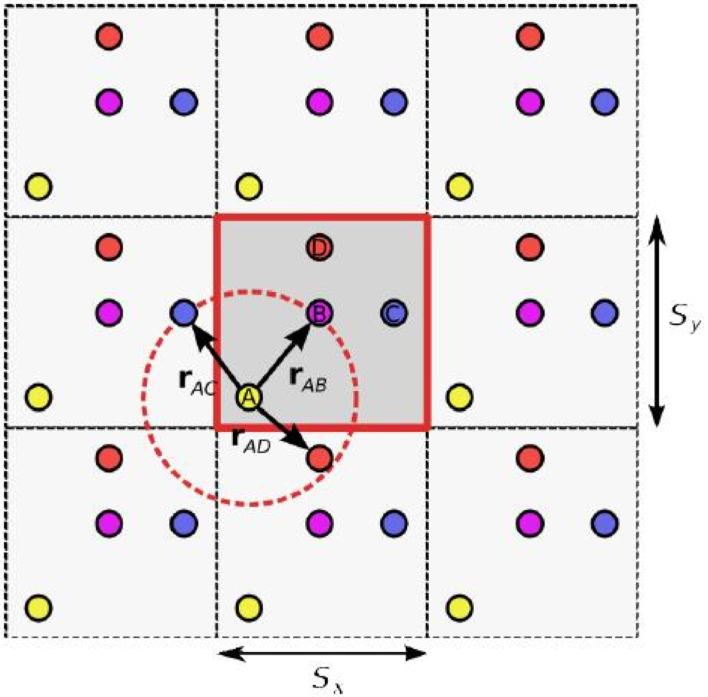
# MD – Periodic boundary conditions

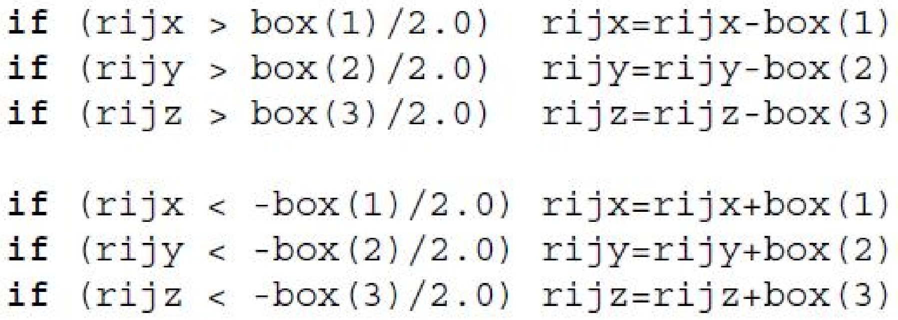
- A real lattice can be extremely big
  - E.g. 1 cm^3 of Cu: 2.1e22 atoms => too much even for present-day computers
  - Hence desirable to have MD cell as segment of bigger real system
- Standard solution**: periodic boundary conditions**
  - This approach involves “copying” the simulation cell to each 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:



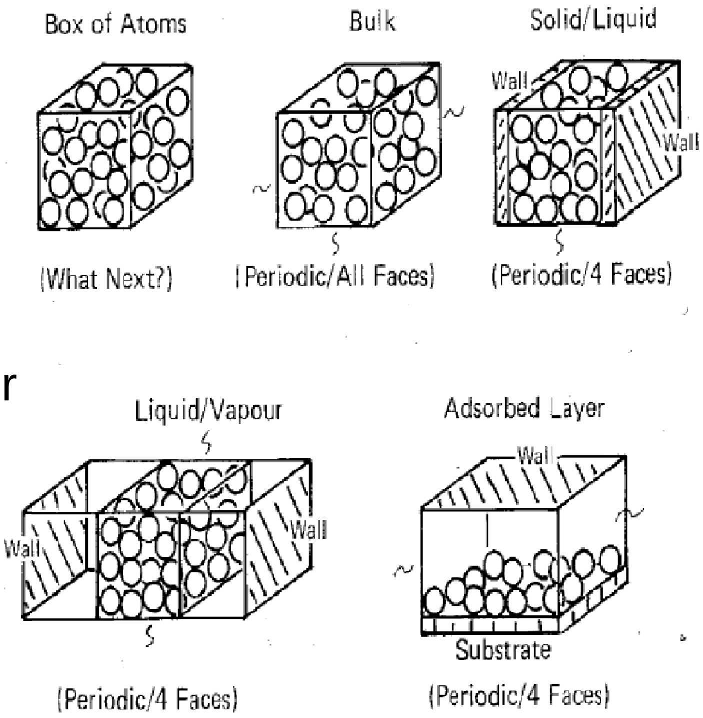


```
if (rijx > box(1)/2.0)   rijx=rijx-box(1)
if (rijy > box(2)/2.0)   rijy=rijy-box(2)
if (rijz > box(3)/2.0)   rijz=rijz-box(3)

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



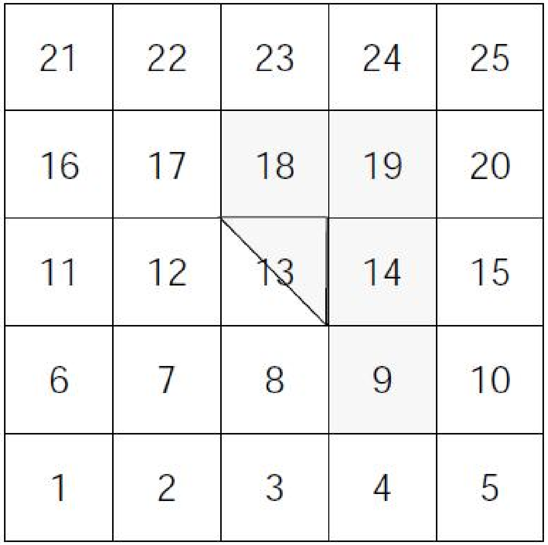
# MD – Temperature and pressure control

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

MD method in equilibrium calculations

# 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



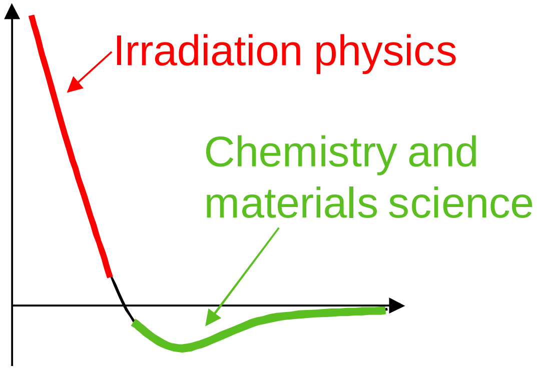
| | | | | |
|---|---|---|---|---|
| 21 | 22 | 23 | 24 | 25 |
| 16 | 17 | 18 | 19 | 20 |
| 11 | 12 | 13 | 14 | 15 |
| 6 | 7 | 8 | 9 | 10 |
| 1 | 2 | 3 | 4 | 5 |

# Nonequilibrium extensions

- 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)].

# 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

## What is needed to model irradiation effects?

### 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 $\Delta x_{max}$ *is the maximum allowed distance moved* during any *t (e.g. 0.1 Å),* $\Delta E_{max}$ *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.

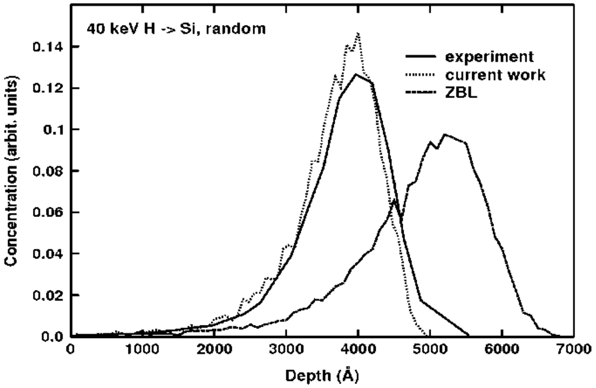
- This relatively simple algorithm has been demonstrated to be able to handle collisions with energies up to 1 GeV

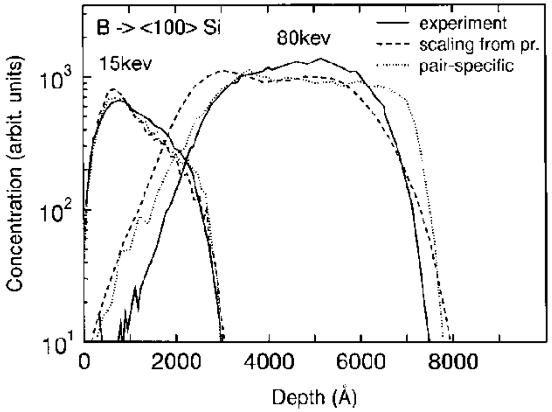
[K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)].

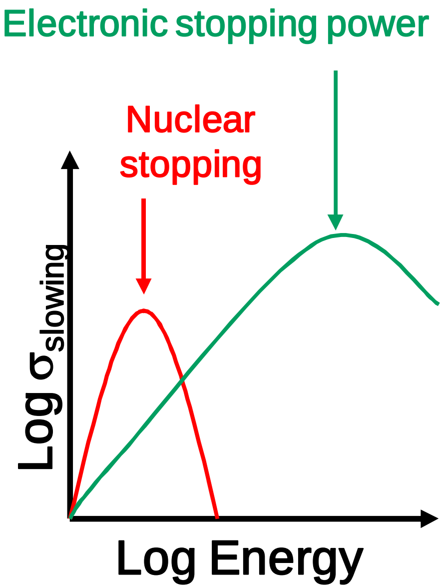
## What is needed to model irradiation effects?

## 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:





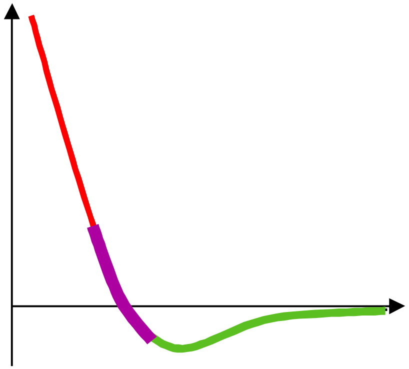


[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen,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



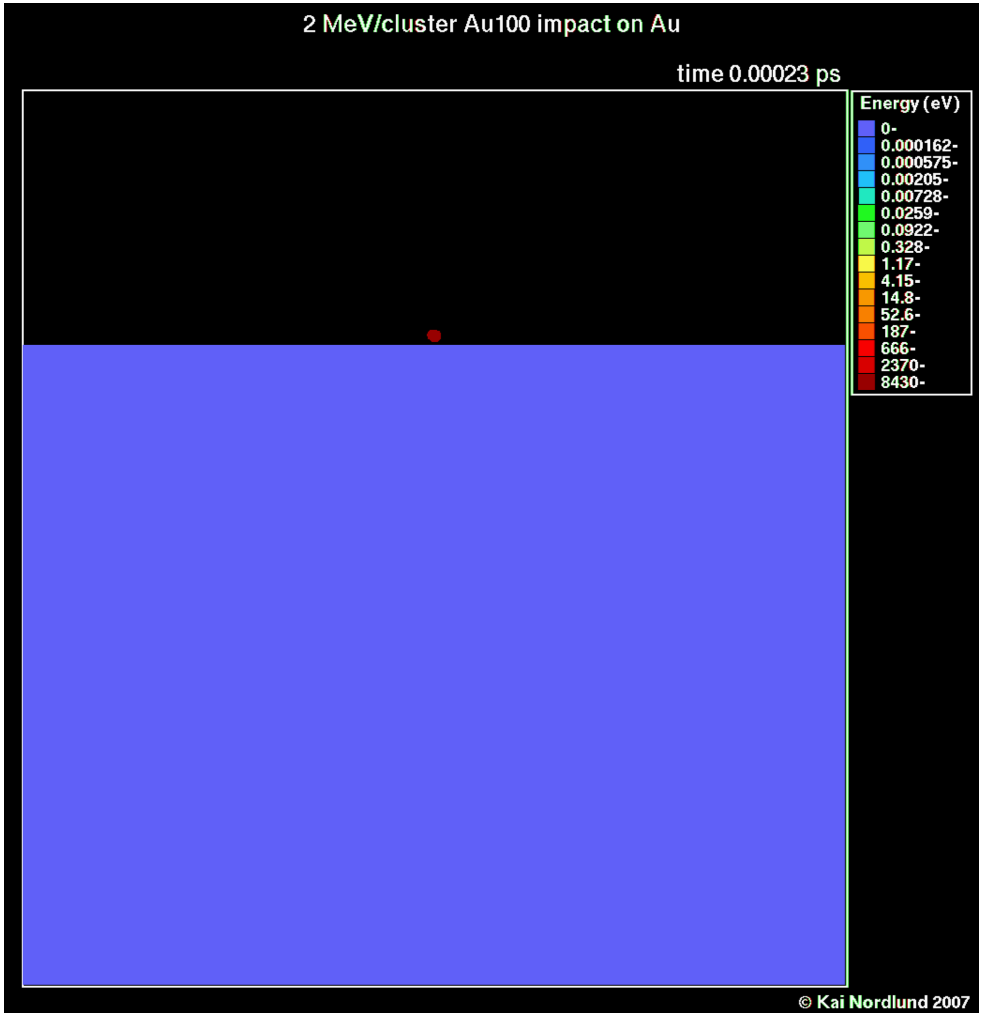
  - Can be adjusted to experimental high-pressure data and threshold displacement energies

[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



2 MeV/cluster Au100 impact on Au

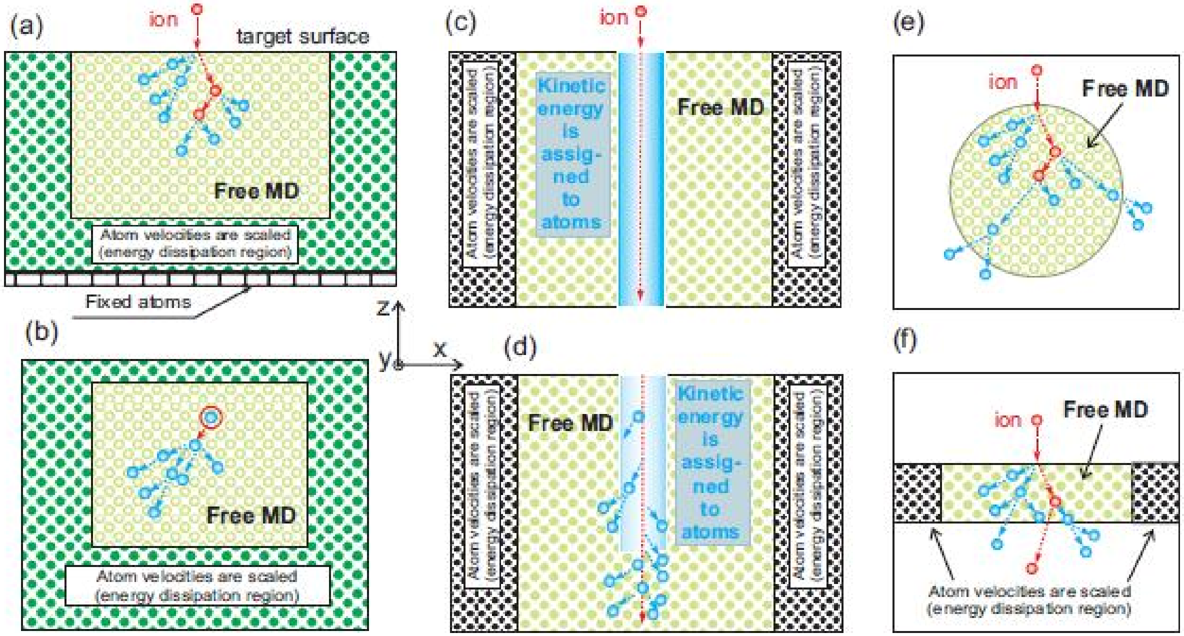
© Kai Nordlund 2007

What is needed to model irradiation effects?

# 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:

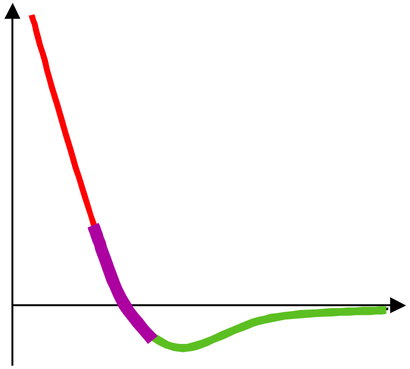
a) surface, b) bulk recoil, c-d) swift heavy ion, e) nanocluster, f) nanowire



[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

## 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
- We (and other groups in the field) 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

[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

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

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

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

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

Figure out possible changes in $r_i$ and $N$ , then repeat

# Comments on KMC algorithm

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

Kinetic Monte Carlo

# 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

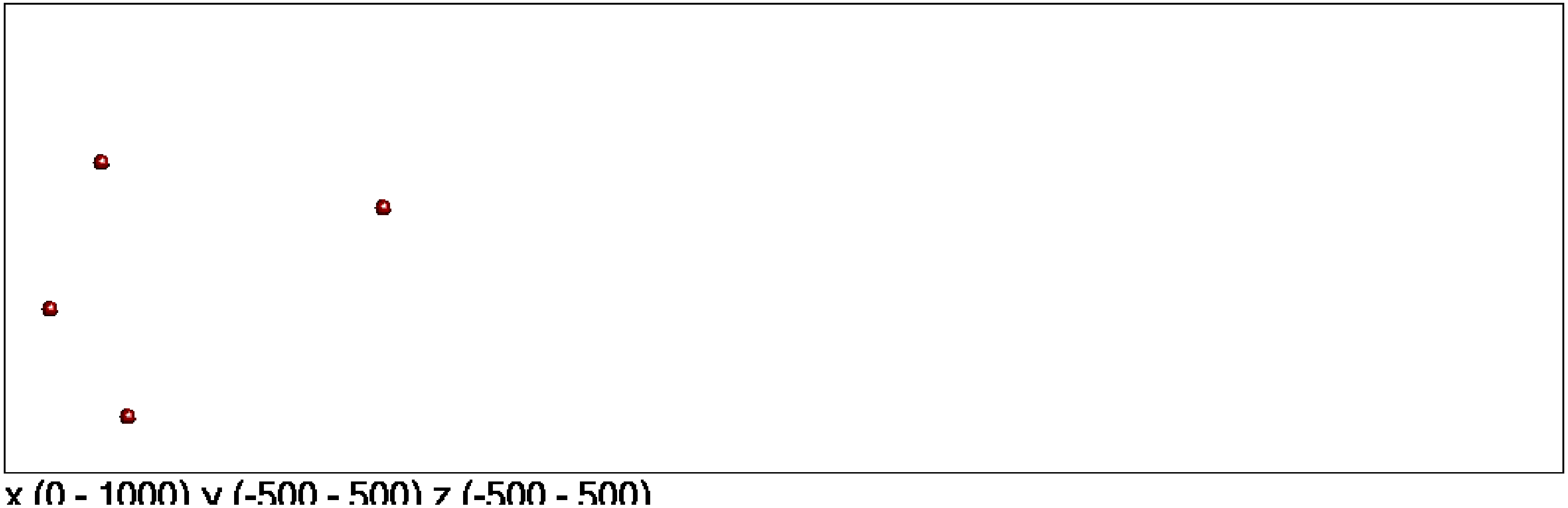
$$r_i = r_0 e^{-E_A / k_B T}$$

- 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

Kinetic Monte Carlo

# 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).]

### Interatomic potential development

# Equilibrium potentials

- For molecular dynamics we use **and develop** bond-order or embedded atom method type 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 done in systematic approach introduced by Prof. Karsten Albe (TU Darmstadt)

### Interatomic potential development

# “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 $\beta$ can be set directly from the experimental dimer interatomic distance, energy and vibration frequency!

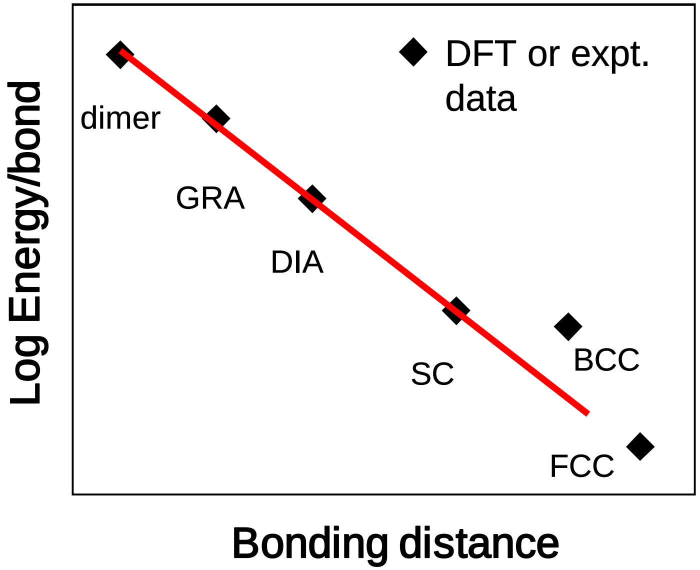
Interatomic potential development

# “Albe” fitting formalism

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

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

for all coordinations



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

# “Albe” fitting formalism

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

Second-moment approximation exponential

No power of 3

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

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

ik-dependent angular term

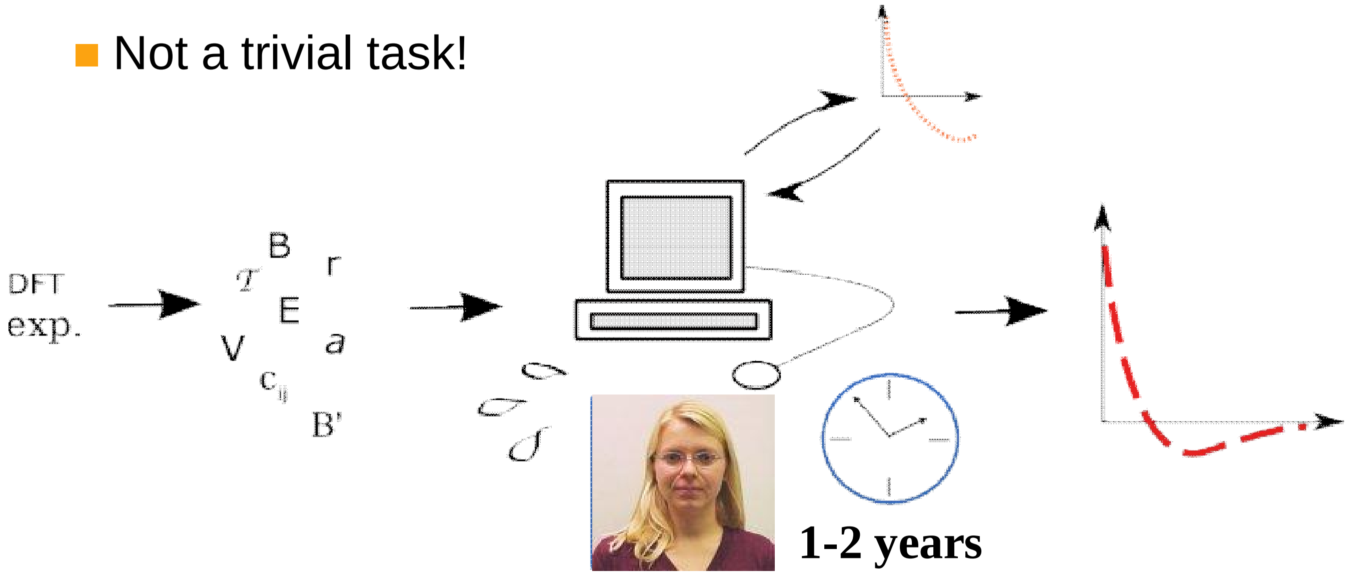
- This form for $b_{ij}$ conforms exactly to $b_{ijk} \propto \frac{1}{\sqrt{\text{coordination of } i}}$

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

Methods:

# The “blood, sweat and tears” part

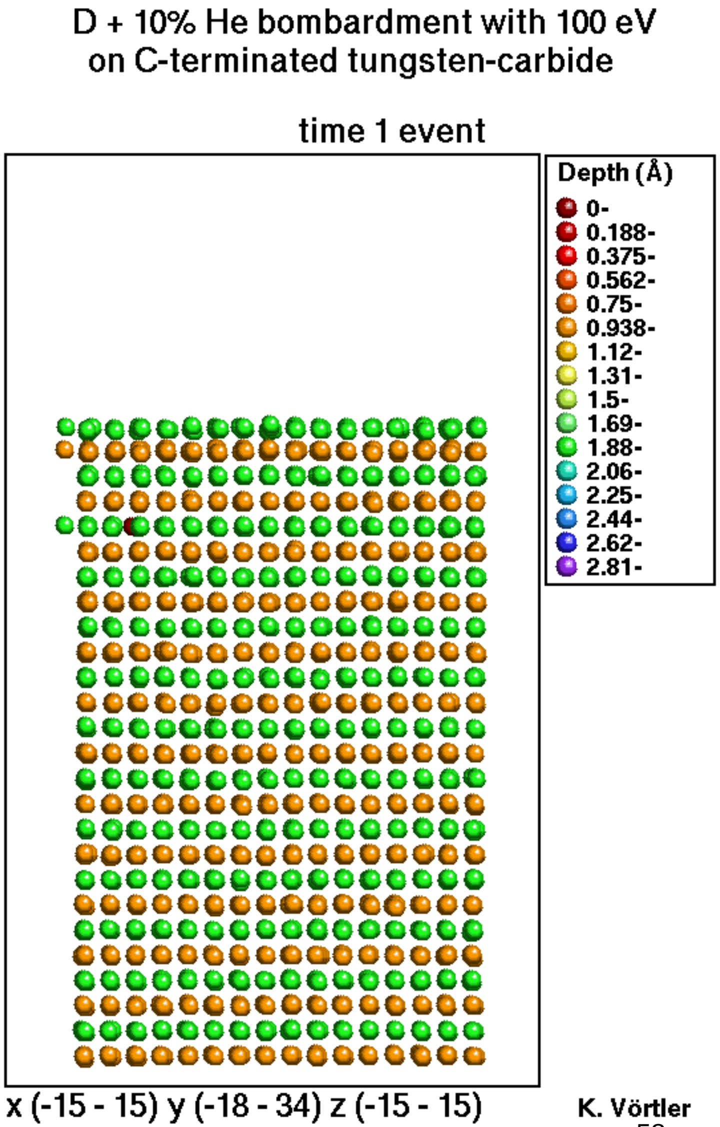
- There are all in all **11** parameters that must be specified
- Constructing a good potential means finding suitable values for these
  - This is done by fitting to different experimental or density-functional theory values of ground state and hypothetical phases
  - Not a trivial task!



Methods:

# Potentials developed

- 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



# Further reading on methods

- A full course on MD:
  - http://www.physics.helsinki.fi/courses/s/atomistiset/
- A full course on MC, including KMC:
  - http://beam.acclab.helsinki.fi/~knordlun/mc/2005/index.html
- 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
  - Crystallographic defect, vacancy defect, interstitial defect, dislocation
  - Collision cascade, threshold displacement energy
  - Binary collision approximation

*If you are not happy about any of these, do not complain to me but just fix it directly in wikipedia!*

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

CMS

HIP

# Molecular dynamics simulation of Be, Be-C and W-C mixed divertor materials.

Carolina Björkas,

Katharina Vörtler,

Andrea Meinander

Ane Lasa,

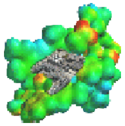
Helga Timko,

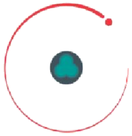
Mooses Mehine,

and Kai Nordlund

***Department of Physics and Helsinki Institute of Physics***

***University of Helsinki, Finland***





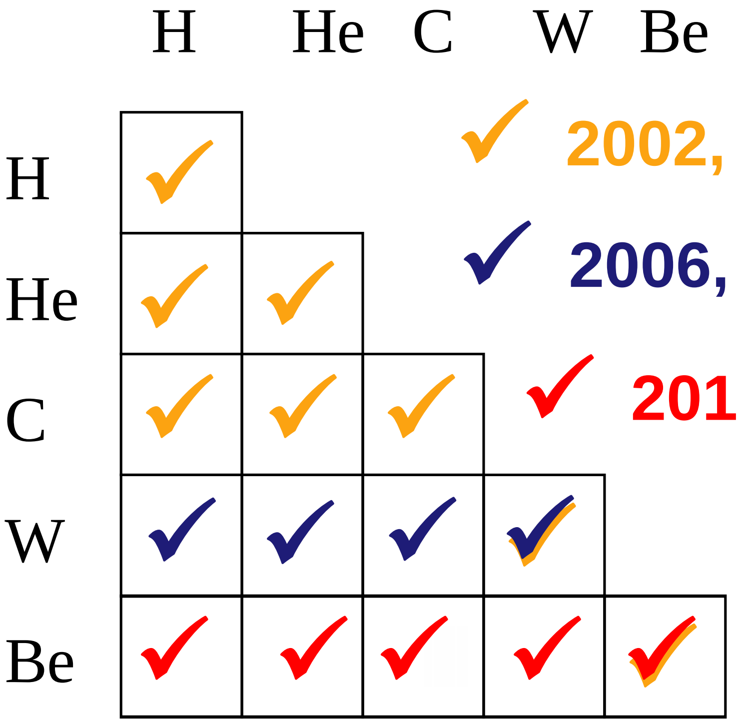
# Contents

- Motivation
- A few words on the methods
    - Potential development for BeCWH completed!
- Background: swift chemical sputtering of carbon
- Range of swift chemical sputtering:
    - Pure Be
    - WC (partly…)
    - BeC
    - Not in W!
- Phase formation in MD!
- Collecting data from MD for plasma (ERO) simulations

- Press-stop addition: He bubbles and migration in W

Method

# Plasma-wall interaction potential availability



| | H | He | C | W | Be |
|---|---|---|---|---|---|
| H | ✓ | | | | |
| He | ✓ | ✓ | | | |
| C | ✓ | ✓ | ✓ | | |
| W | ✓ | ✓ | ✓ | ✓ | |
| Be | ✓ | ✓ | ✓ | ✓ | ✓ |

✓ **2002, done by others**

✓ **2006, CarWMod**

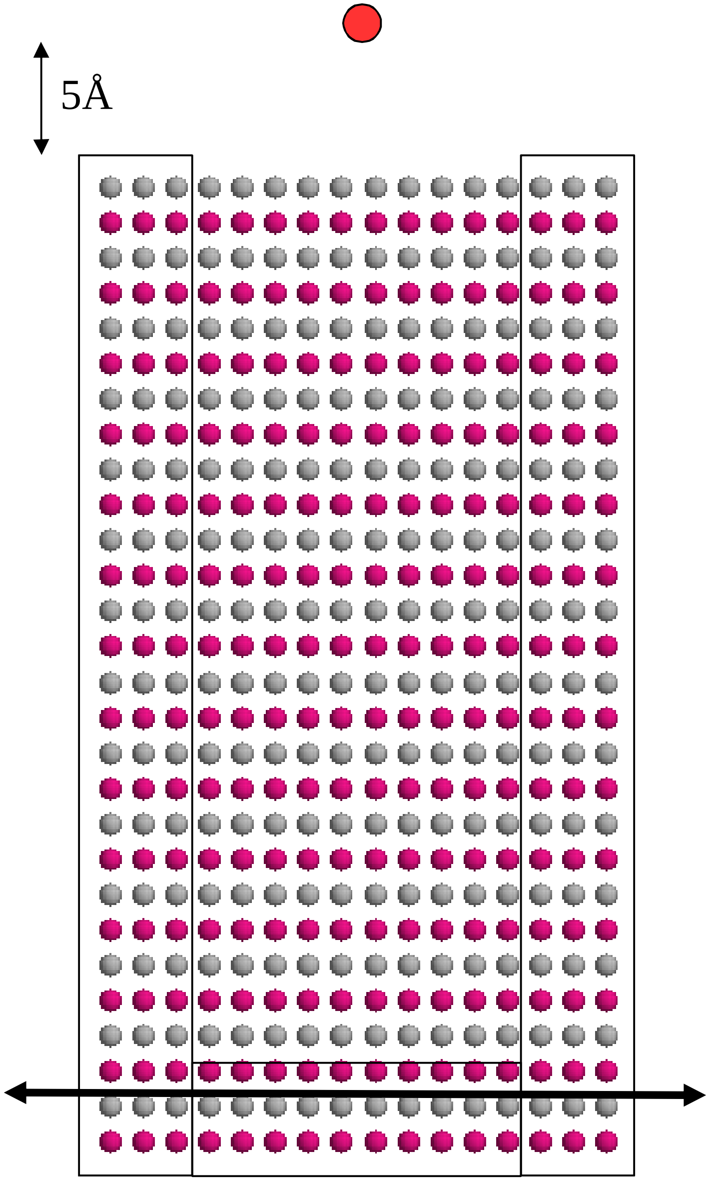
✓ **2010, BeTunCMod etc.**

[WCH: Juslin et al, J. Appl. Phys. **98**, 123520 (2005)]

[BeCWH: Björkas et al, J. Phys.: Condens. Matter 21 (2009) 445002;
BeW: Björkas et al, J. Phys. Condens. Matter fast track 22 (2010) 352206]

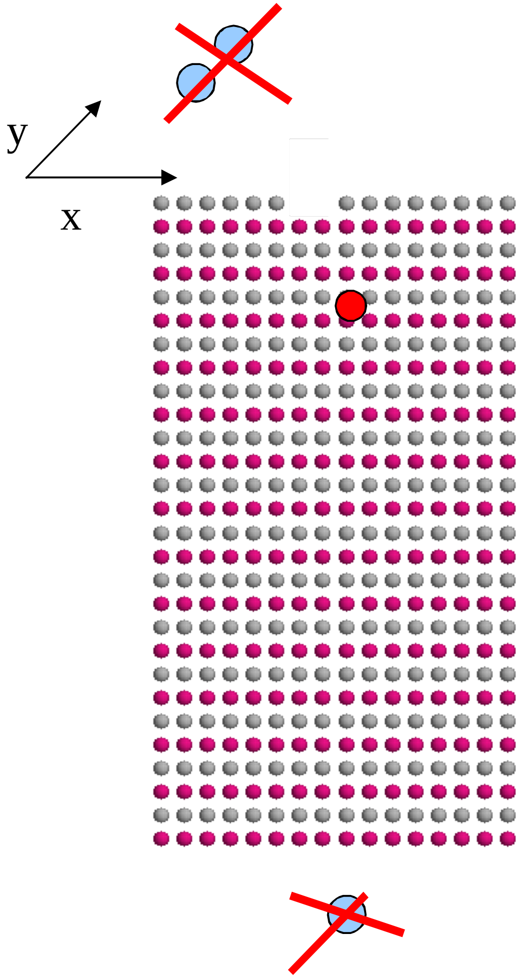
# Method: plasma-wall simulation procedure

- **Bombarding simulations**
  - Bombarding distance
  - Random recoil (90-100 % D, 0-10% plasma impurity)
  - Temperature control on cell borders
  - Bottom 2 atom layers fixed
  - Simulation time: 3-5 ps



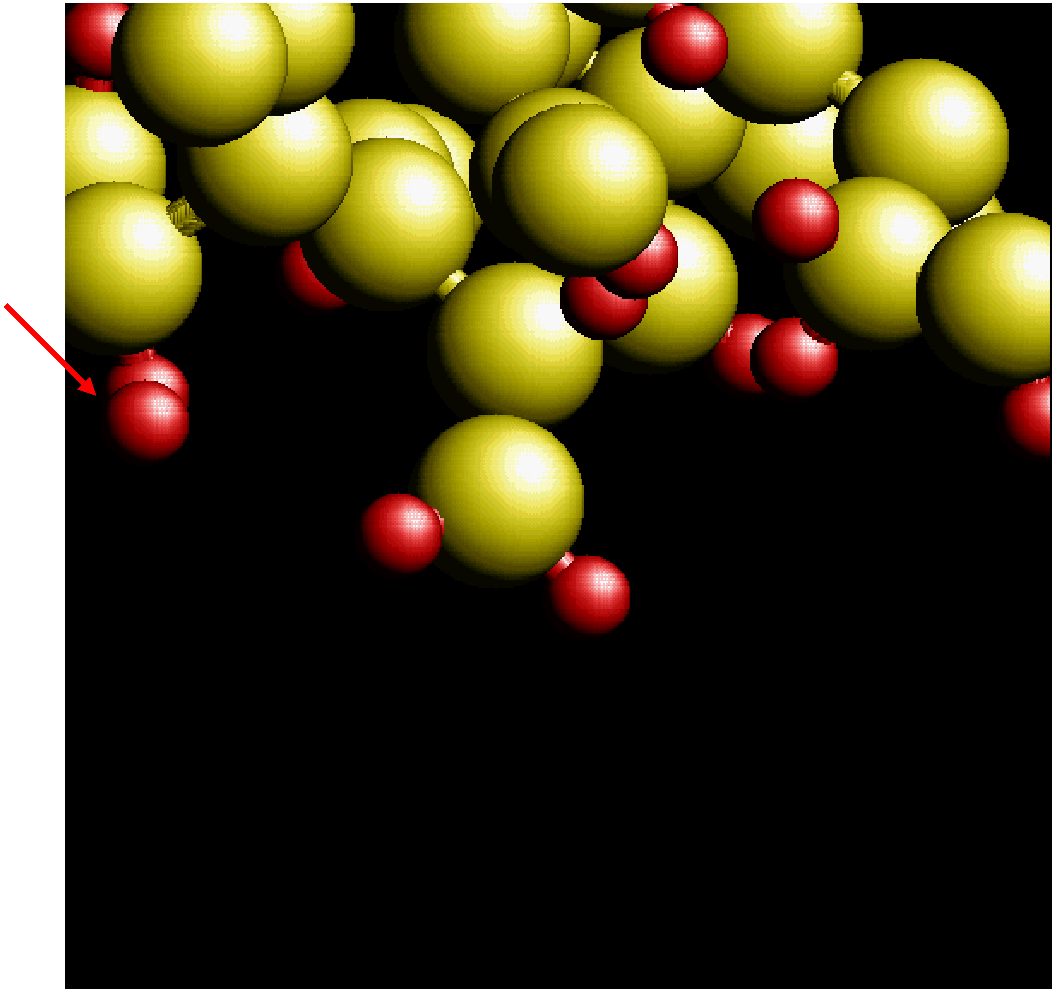
# Method: Simulation procedure

- **Prepare new cell**
  - Take out sputtered species and atoms that were implanted through the sample
  - Random shift in x- and y-direction (periodic boundaries)
- Continue bombarding using this cell => ***cumulative simulations***



# The swift chemical sputtering mechanism for carbon

- In 1999-2000 we showed that sputtering of C can occur when incoming H happens to enter in between two carbon atoms
- This mechanism was not known from before

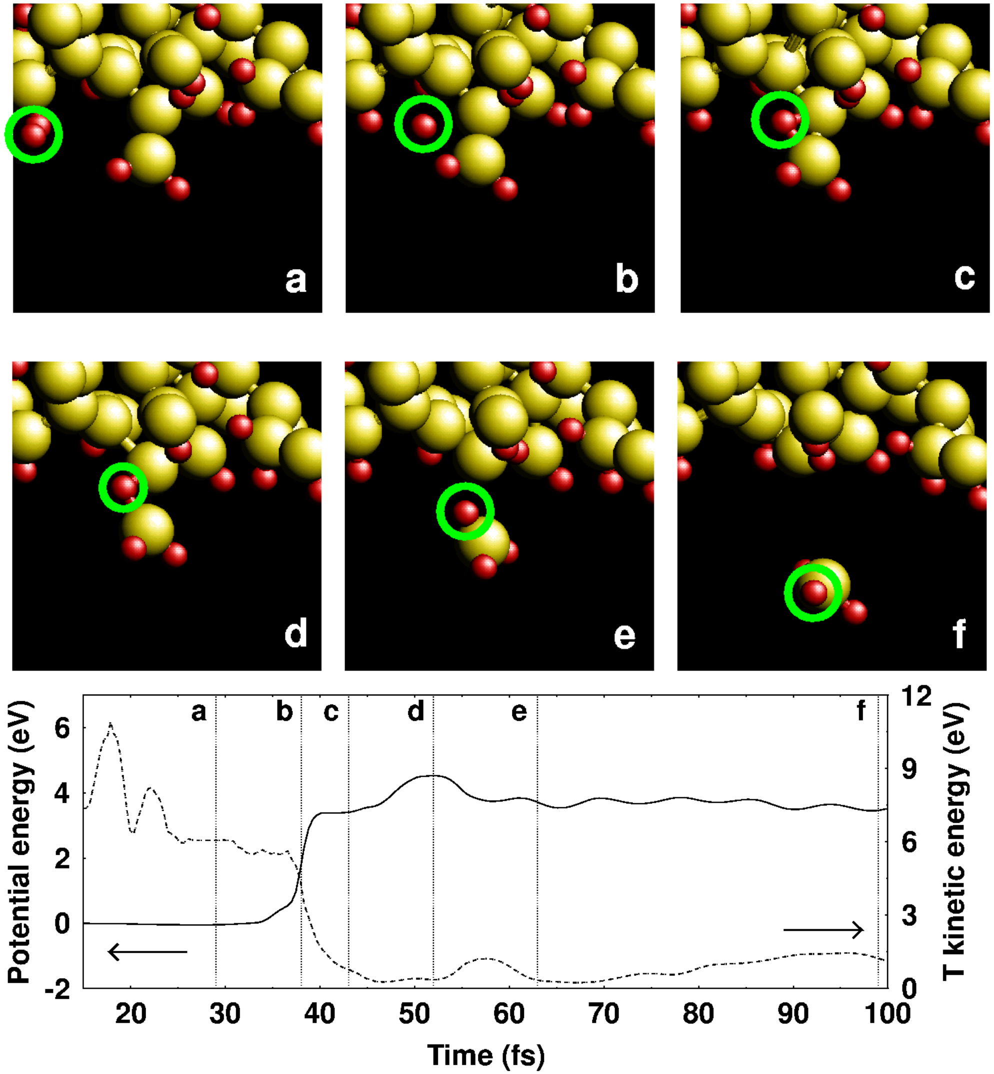


Background

# The swift chemical sputtering mechanism for carbon

- The H ion hits the middle of a C-C bond. This raises the energy enough to break the chemical bond
- Process is energetically unfavorable (endothermal)

[Salonen et al, Europhys. Lett. 52 (2000) 504; Phys. Rev. B 63 (2001) 195415; Krasheninnikov et al, Comput. Mater. Sci. 25 (2004) 427]



# The carbon sputtering mechanism

## Physical insight

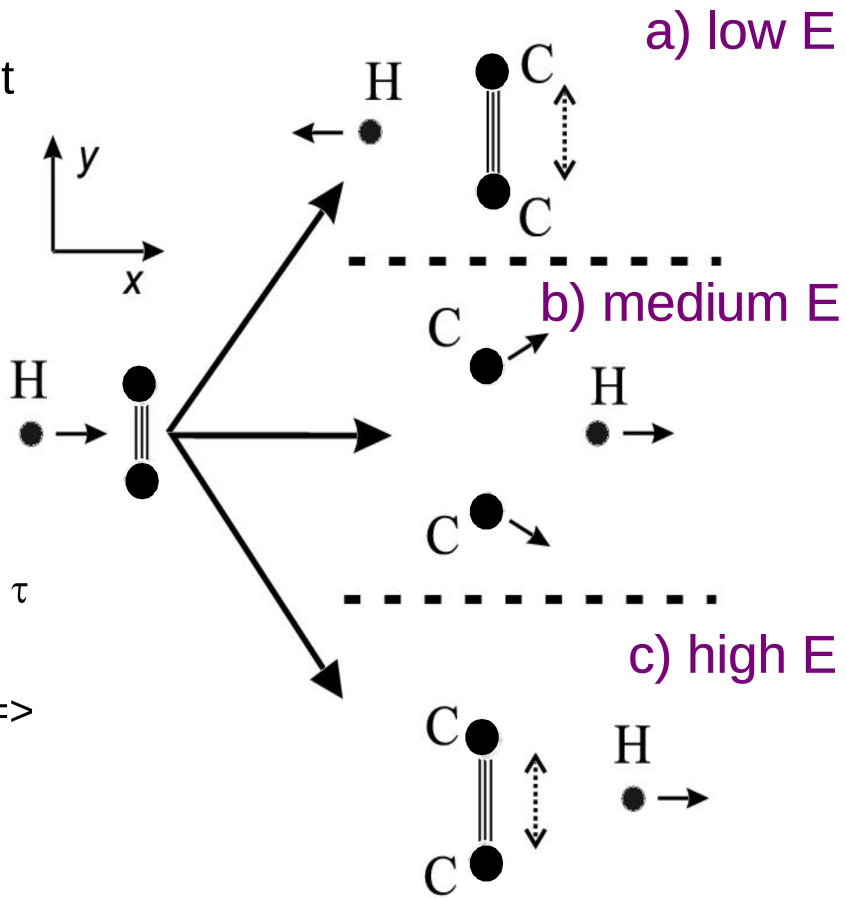
- A model system of a single H atom colliding with a C dimer gives insight to the basic mechanism
- Momentum transfer in y direction is

$$p_y = \int_{-\infty}^{\infty} f_y(t, E_{kin}[\mathrm{H}])dt \approx \bar{f}_y\bar{\tau}$$

a) low E: H does not penetrate and is reflected

b) medium E: H penetrates slowly => large $\tau$ => large $p_y$ => bond breaking occurs

c) high E: H penetrates rapidly => small $\tau$ => small $p_y$ => no bond breaking

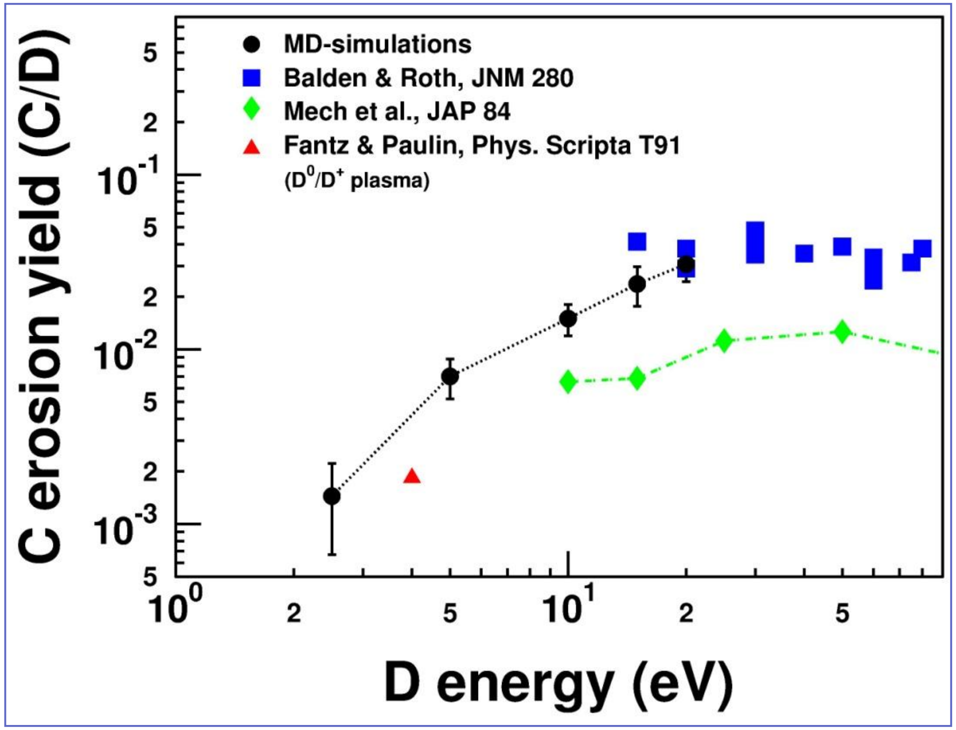


[Krasheninnikov et al, Contrib. Plasma Phys. 42 (2002) 451; Comput. Mater. Sci 25, 427 (2002)]

Background

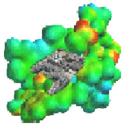
# Comparison with experiments

- The sputtering we observed is in decent agreement with experiments!
  - Even better agreement demonstrated later by P. Krstic
- At higher E and T also other mechanisms certainly are active



[Salonen, Physica Scripta T111 (2004) 133; Krasheninnikov et al, Comput. Mater. Sci. 25 (2004) 427; Nordlund et al, Pure and Appl. Chem. 78 (2005) 1203]

# Contents - update



- Motivation
- A few words on the methods
- Scientific background: swift chemical sputtering of carbon

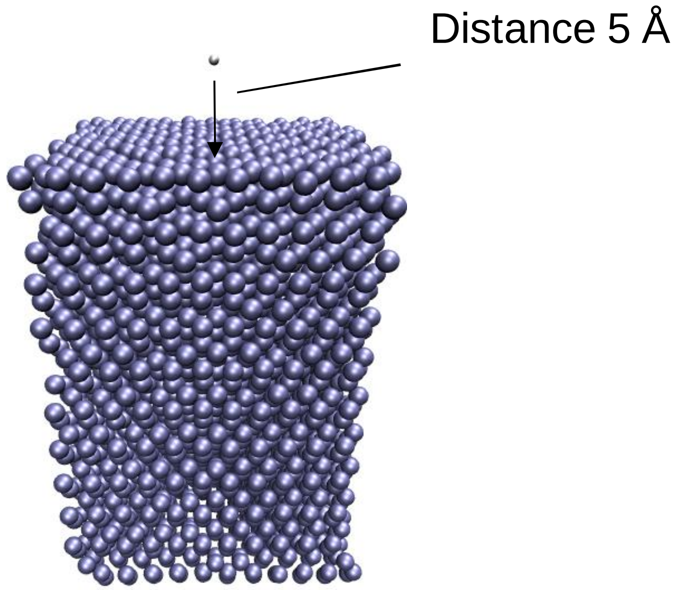
- Range of swift chemical sputtering:
  - Pure Be
  - WC
  - BeC
  - Not in W!
- Phase formation in MD!
- Collecting data from MD for plasma (ERO) simulations

- Press-stop addition: He bubbles and migration in W

## Swift chemical sputtering of beryllium:

# Background

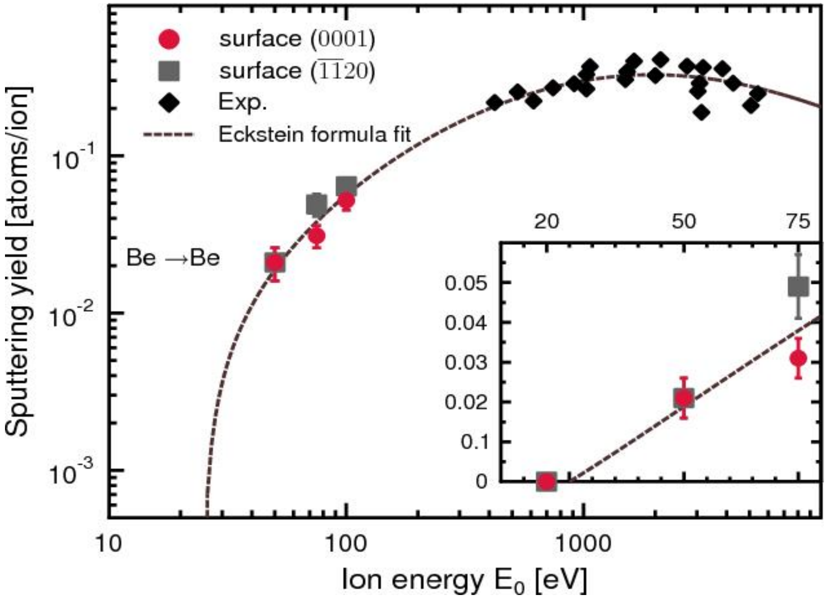
- Can metals erode chemically??
- Conventional wisdom says no, but the recent experiments by Doerner showed that ~50 eV D bombardment of Be erodes most Be in BeD molecules => cannot be physical sputtering
- We bombarded beryllium surfaces with D ions up to 100 eV



## Swift chemical sputtering of beryllium:

# Interlude: Check of model for Be self-sputtering

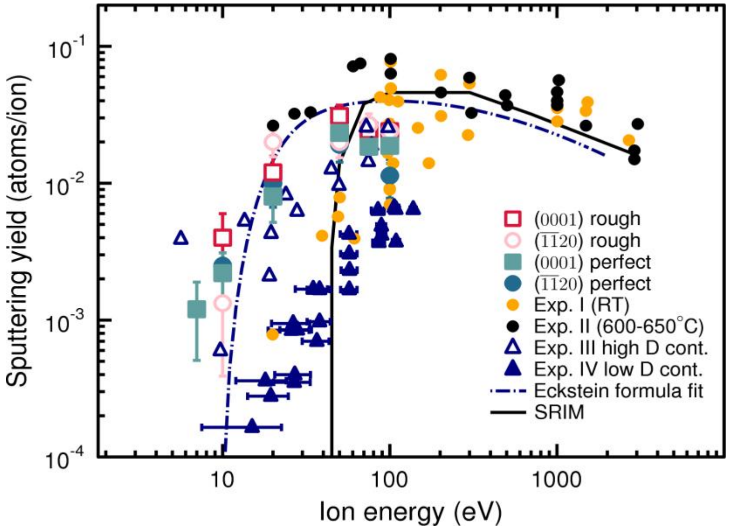
- 20 – 100 eV Be ion irradiation
  - flux ~$2 \cdot 10^{25}$ $m^{-2}s^{-1}$
  - @ room temperature
- Threshold 20 – 50 eV
- Yield agrees with exp.
  - Exp. values only at keV energies
- Be does not amorphize
  - Like a typical metal



## Swift chemical sputtering of beryllium:

# D irradiation of pure Be

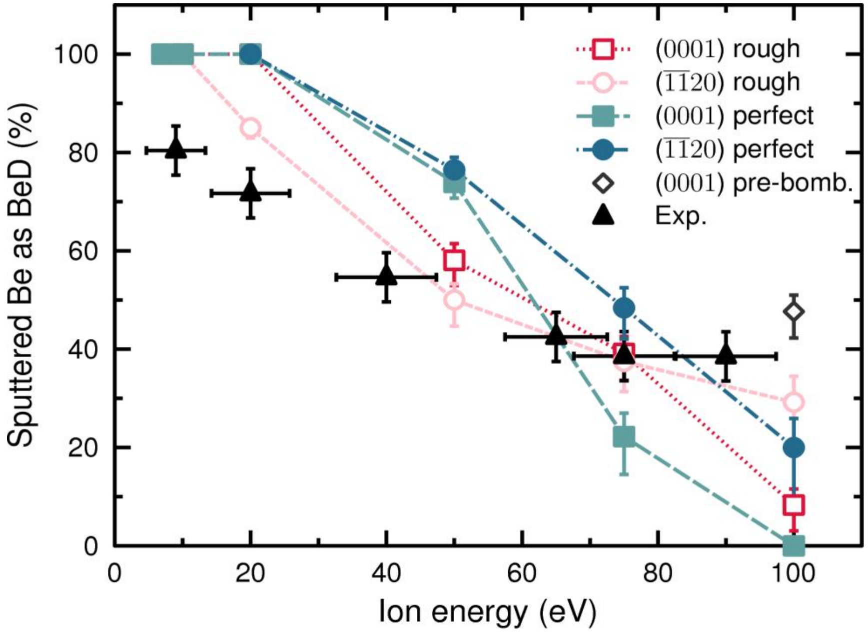
- Our simulations agree with plasma experiments done at the PISCES-B facility at low energies
    - At higher energies with the rest
- Sputtering is seen at 7 eV!



## Swift chemical sputtering of beryllium:

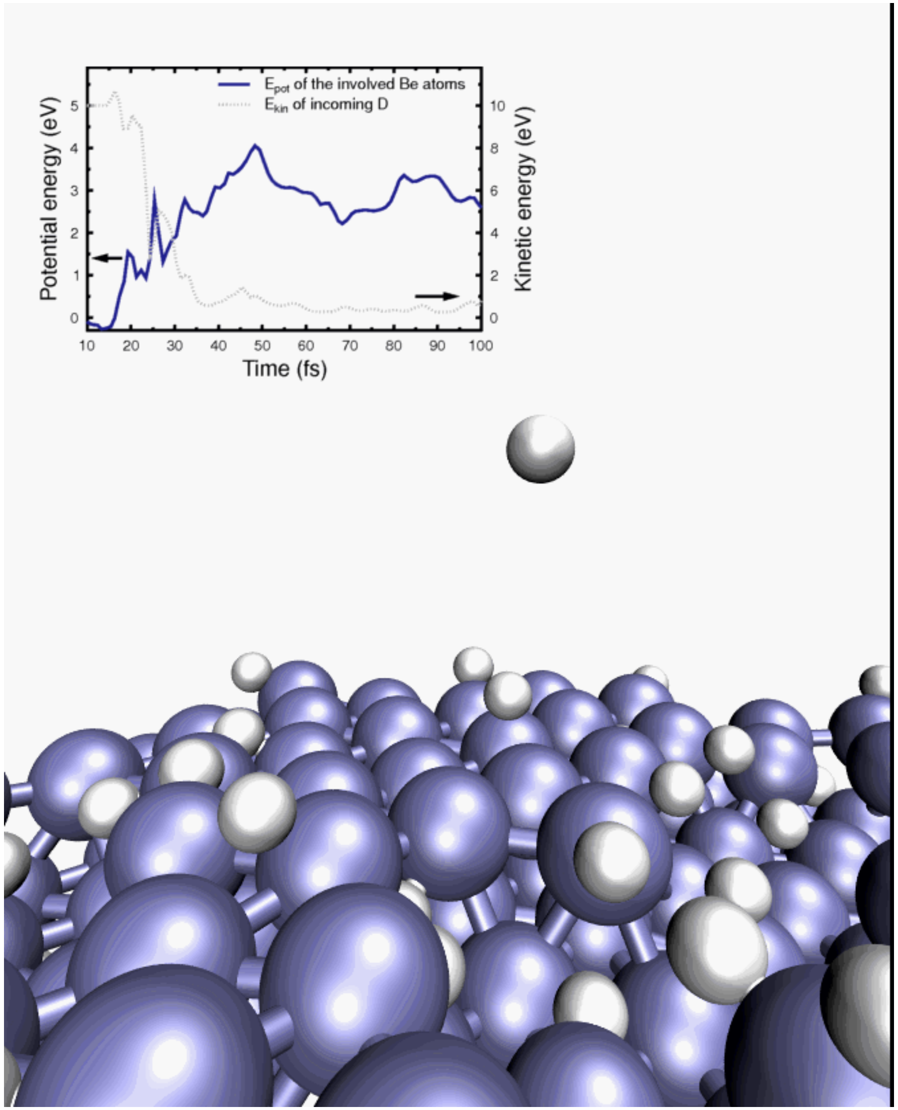
# D irradiation of pure Be

- A large fraction of Be is eroded as BeD molecules at low energies
  - **Chemical sputtering!**
- This fraction decreases with ion energy
- The same trend is seen in the experiments by Doerner



## Swift chemical sputtering of beryllium:

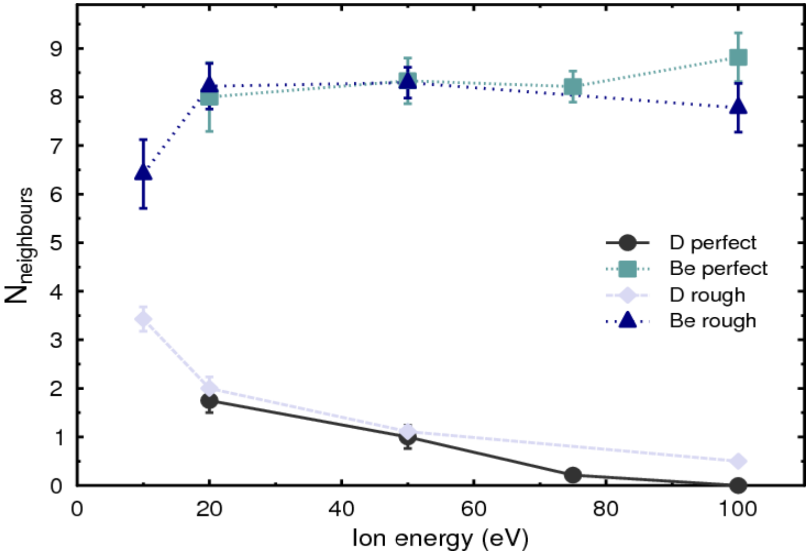
# D irradiation of Be



## Swift chemical sputtering of beryllium:

# D irradiation of Be

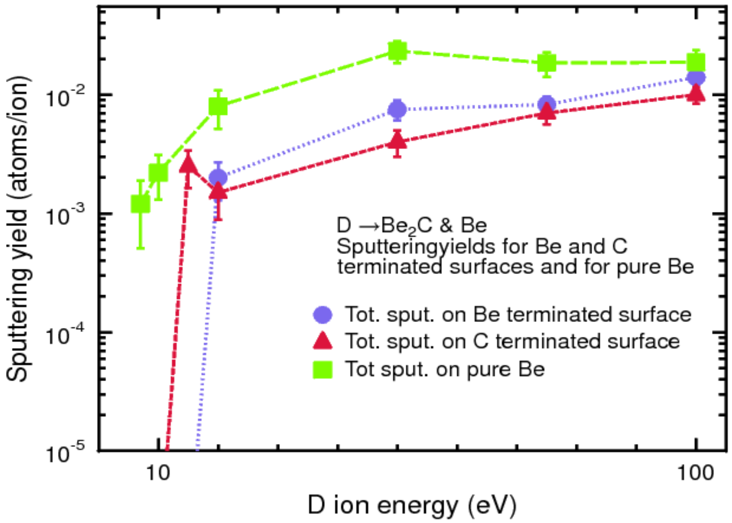
- The movie shows a swift chemical sputtering process
  - Low-energetic D ions release Be atoms from the surface by breaking Be-Be bonds
- This is possible since a surface Be atom that has bonds with D, has a weakened binding to the surface
  - At low energies, Be atoms are likely to have D neighbours
  - The figure shows the initial neighbours of the sputtered Be atoms

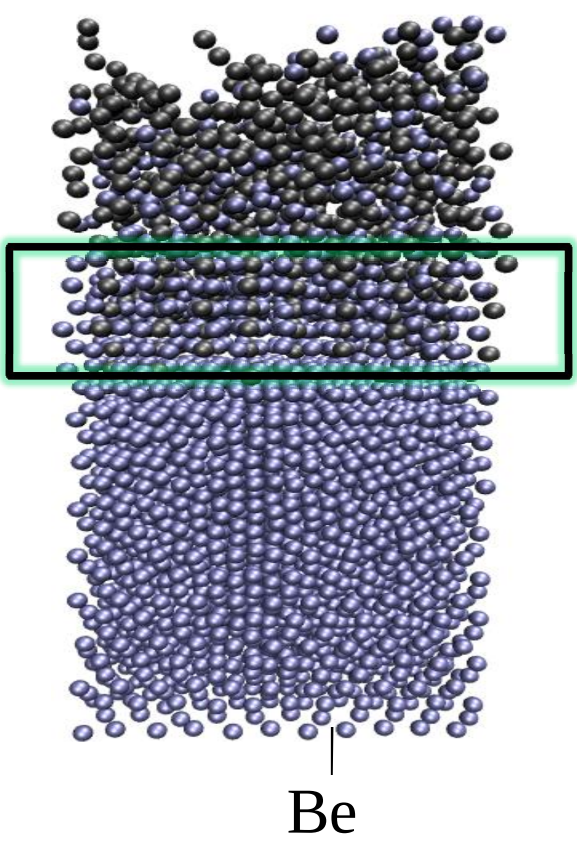


## Swift chemical sputtering of BeC

# D irradiation on $Be_2C$

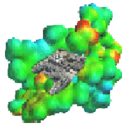
- Carbide layers will form on beryllium surfaces
  - This is believed to decrease the sputtering of pure Be and pure C
- Noticeable in our simulations

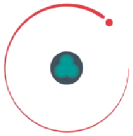




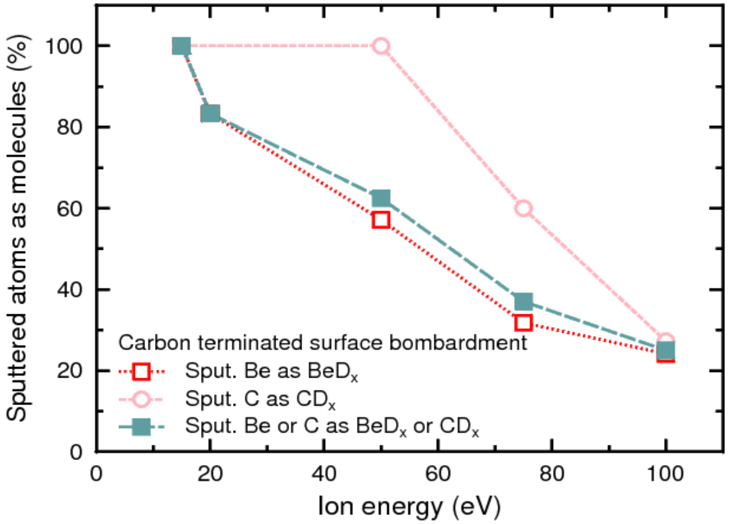
## Swift chemical sputtering of BeC

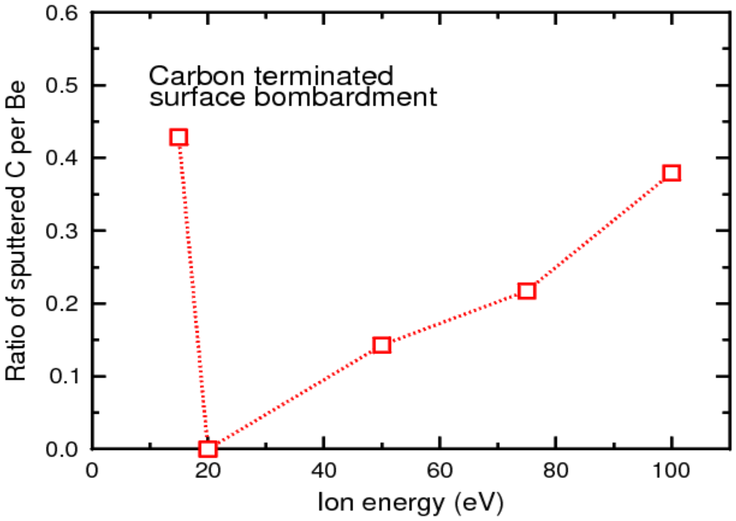
# D irradiation on Be$_2$C





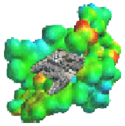
- Are there any chemical effects present?
- Yes, molecules are sputtered!
  - Same mechanism as in pure Be: the swift chemical sputtering mechanism
- Preferential sputtering of Be
  - 15 eV case interesting
  - Here, but not at 20 eV, one $CD_3$ and one $CD_4$ are released
    - Statistical fluctuations



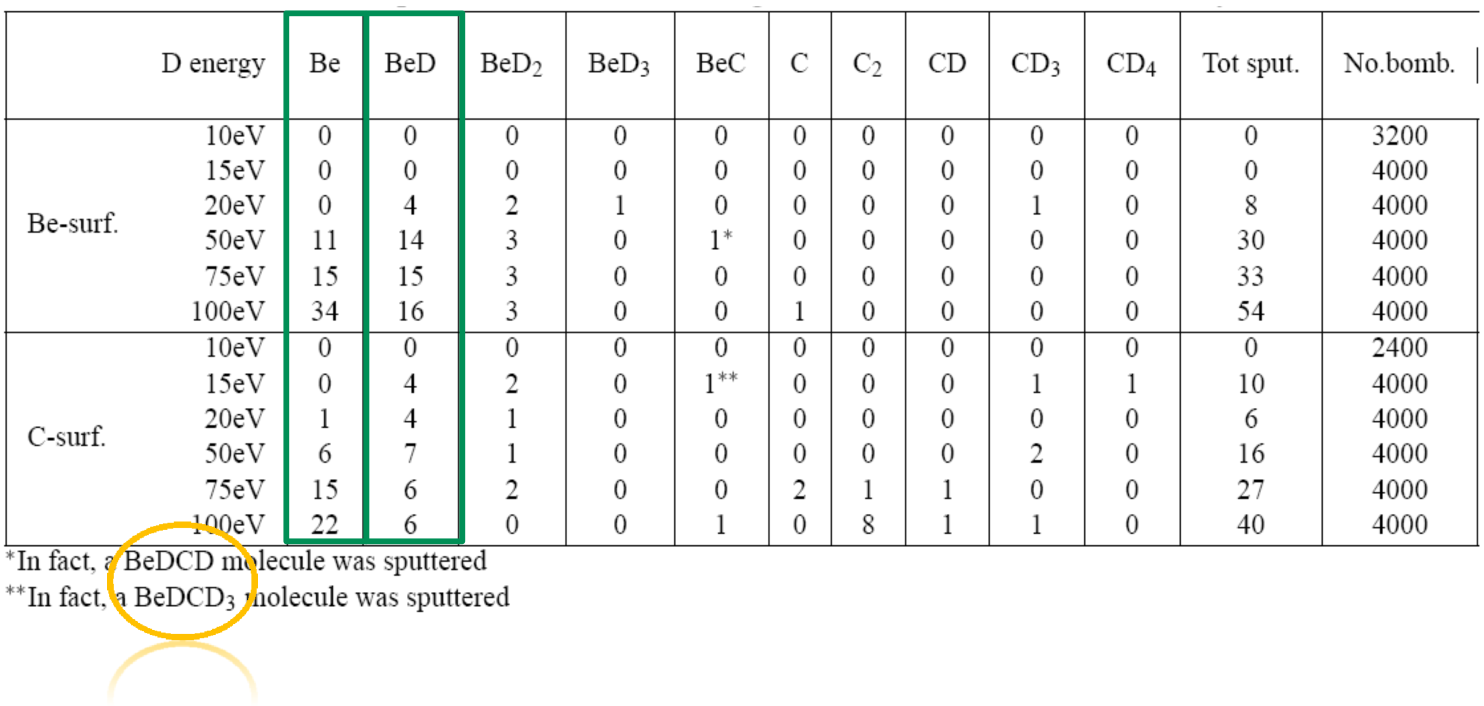


## Swift chemical sputtering of BeC

# Irradiation of $Be_2C$



- Molecules sputtered: mostly BeD

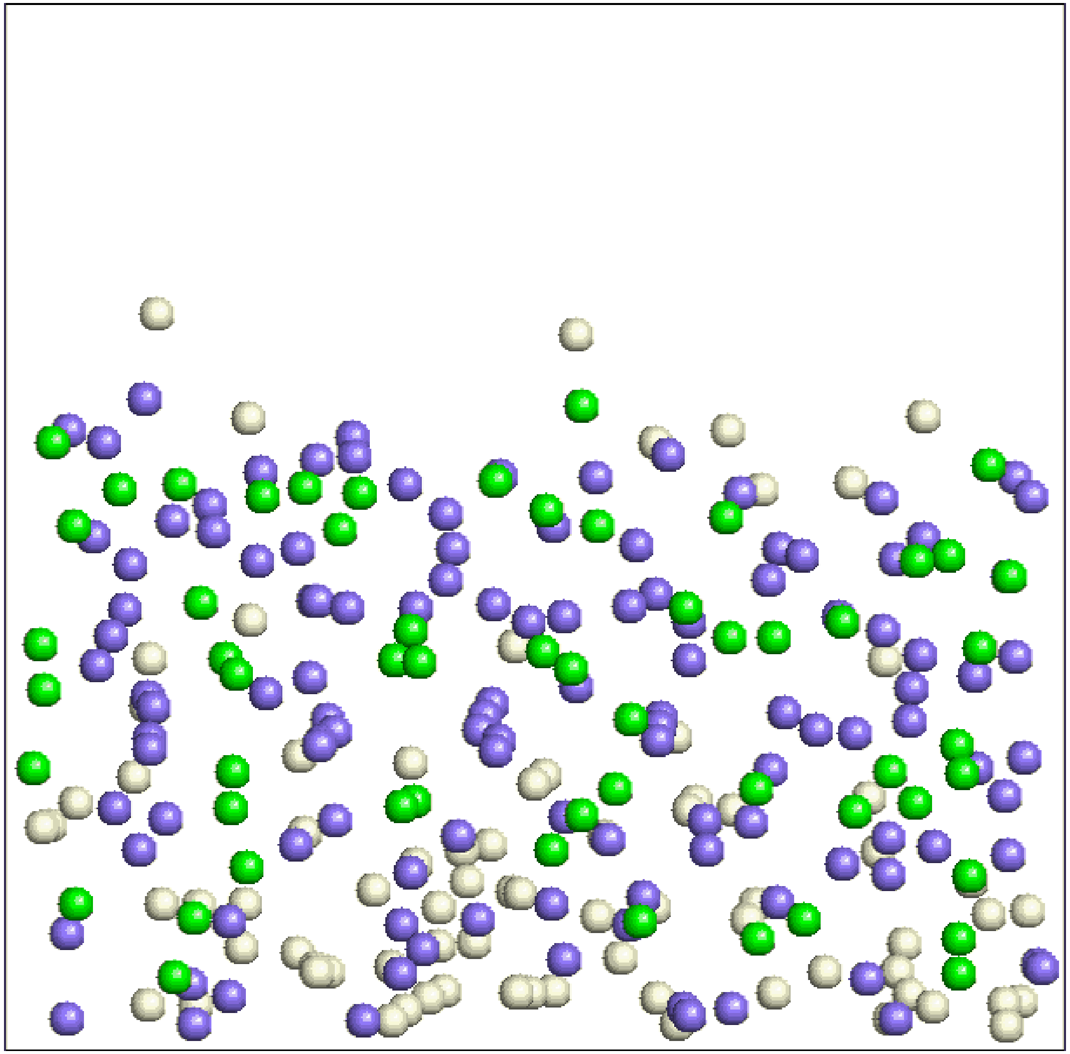


| | D energy | Be | BeD | $BeD_2$ | $BeD_3$ | BeC | C | $C_2$ | CD | $CD_3$ | $CD_4$ | Tot sput. | No.bomb. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Be-surf. | 10eV | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3200 |
| | 15eV | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4000 |
| | 20eV | 0 | 4 | 2 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 8 | 4000 |
| | 50eV | 11 | 14 | 3 | 0 | 1* | 0 | 0 | 0 | 0 | 0 | 30 | 4000 |
| | 75eV | 15 | 15 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 33 | 4000 |
| | 100eV | 34 | 16 | 3 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 54 | 4000 |
| C-surf. | 10eV | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2400 |
| | 15eV | 0 | 4 | 2 | 0 | 1** | 0 | 0 | 0 | 1 | 1 | 10 | 4000 |
| | 20eV | 1 | 4 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 4000 |
| | 50eV | 6 | 7 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 16 | 4000 |
| | 75eV | 15 | 6 | 2 | 0 | 0 | 2 | 1 | 1 | 0 | 0 | 27 | 4000 |
| | 100eV | 22 | 6 | 0 | 0 | 1 | 0 | 8 | 1 | 1 | 0 | 40 | 4000 |

*In fact, a BeDCD molecule was sputtered

**In fact, a $BeDCD_3$ molecule was sputtered

# Irradiation of $Be_2C$



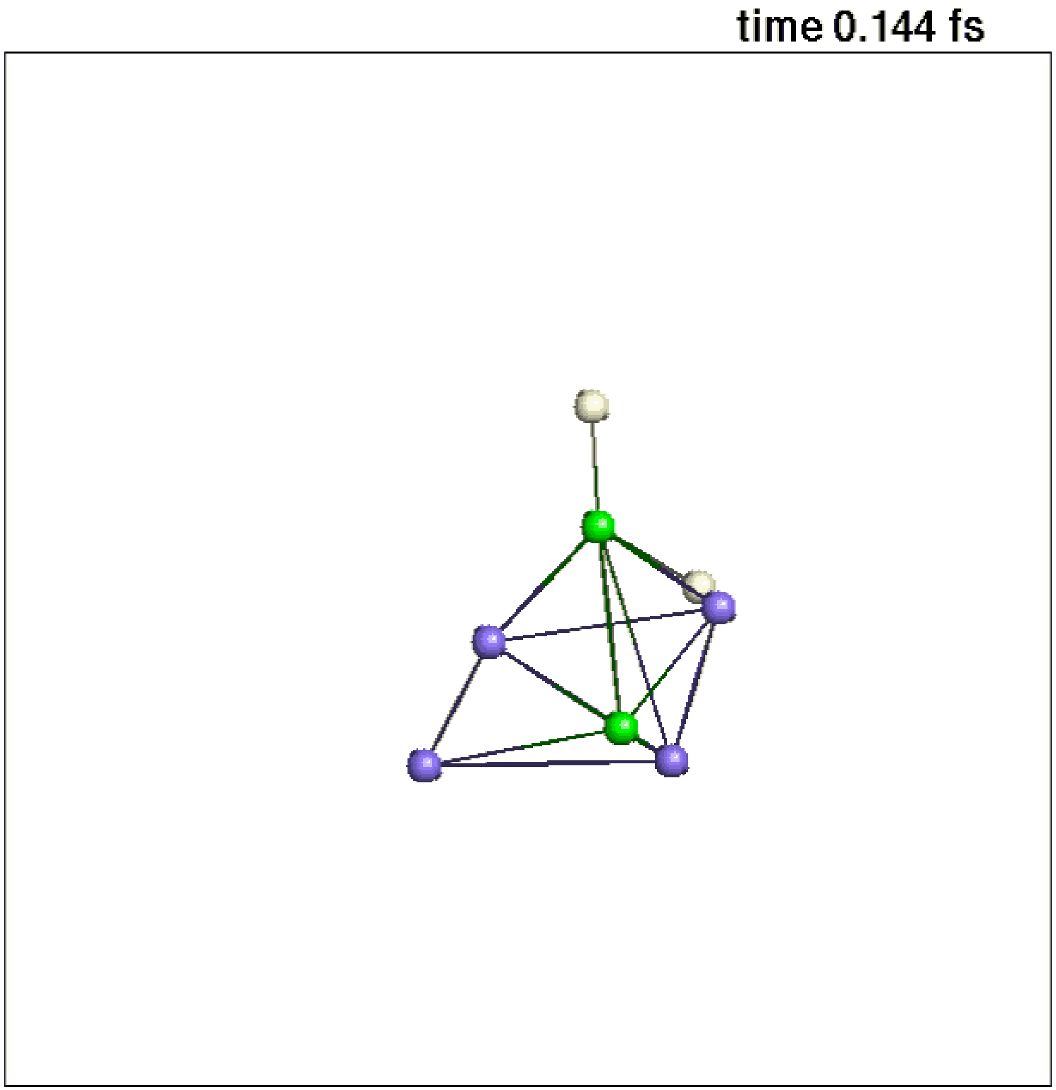
● Be

● C

○ D

## Swift chemical sputtering of BeC

# Irradiation of $Be_2C$

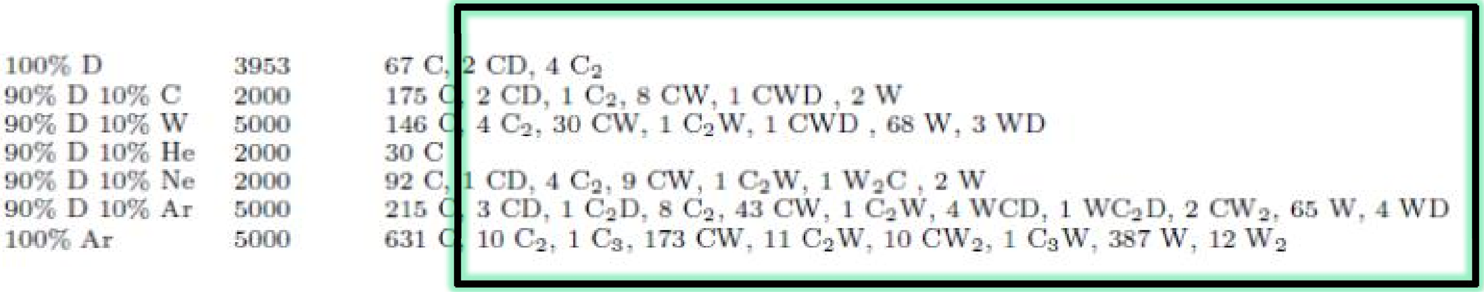


● Be
● C
○ D

## Swift chemical sputtering of BeC

# D irradiation of WC

- Molecular sputtering was also observed in WC sputtering simulations (e.g. at 300 eV):

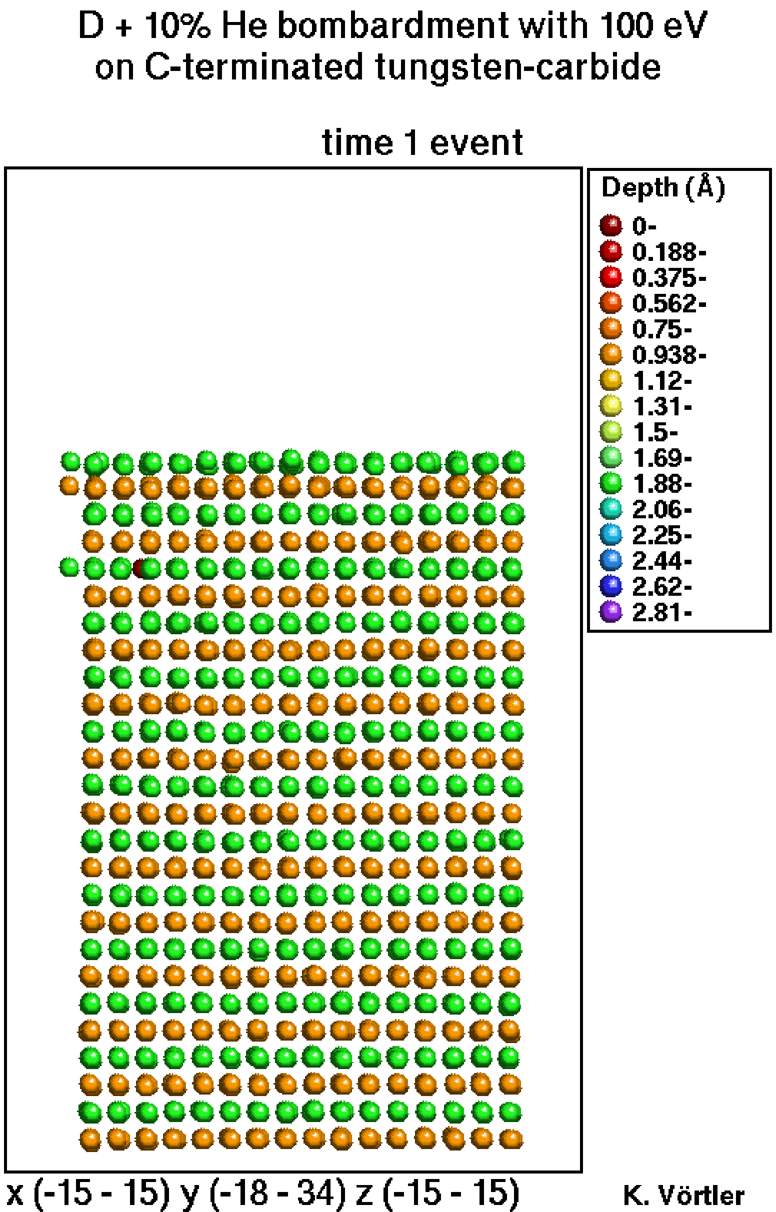


| | | |
|---|---|---|
| 100% D | 3953 | 67 C, 2 CD, 4 $C_2$ |
| 90% D 10% C | 2000 | 175 C 2 CD, 1 $C_2$, 8 CW, 1 CWD , 2 W |
| 90% D 10% W | 5000 | 146 C 4 $C_2$, 30 CW, 1 $C_2W$, 1 CWD , 68 W, 3 WD |
| 90% D 10% He | 2000 | 30 C |
| 90% D 10% Ne | 2000 | 92 C, 1 CD, 4 $C_2$, 9 CW, 1 $C_2W$, 1 $W_2C$ , 2 W |
| 90% D 10% Ar | 5000 | 215 C 3 CD, 1 $C_2D$, 8 $C_2$, 43 CW, 1 $C_2W$, 4 WCD, 1 $WC_2D$, 2 $CW_2$, 65 W, 4 WD |
| 100% Ar | 5000 | 631 C 10 $C_2$, 1 $C_3$, 173 CW, 11 $C_2W$, 10 $CW_2$, 1 $C_3W$, 387 W, 12 $W_2$ |

- A lot of different small molecules
  - Very few hydrocarbons, WC-molecules and single C preferred
- Is the mechanism the same as in Be and $Be_2C$?

## Sputtering of WC

# D irradiation of WC

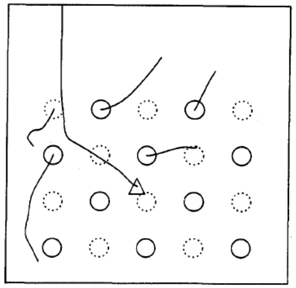


● He
● C
● W
● D

## Sputtering of WC

# D irradiation of WC

- Detailed analysis showed that the mechanism is essentially the **dimer physical sputtering** one
  - Synergetic movement of atoms in low-energy heat spikes
  - Physical in nature, mostly seen during Ar sputtering
  - So, not the same as during the low energy bombardments of beryllium and beryllium carbide



Karetta and Urbassek Appl. Phys. A 55 (1992) 364

- At lower energies, however, mechanism will again be swift chemical sputtering

# D + impurity irradiation of WC

- The impurities (10% W, C, He, Ne or Ar) resulted in
  - 10% W: Net deposition of W
  - 10% C: Net deposition of C
  - 10% He: A few molecules sputtered
  - 10% Ne: Molecules sputtered
  - 10% Ar: Many molecules sputtered

Increasing amount of sputtered molecules

- An enhancement of the sputtering yield of W was observed, so that e.g.

$$Y_{90\%D+10\%Ar} > 0.9Y_{100\%D} + 0.1Y_{100\%Ar}$$

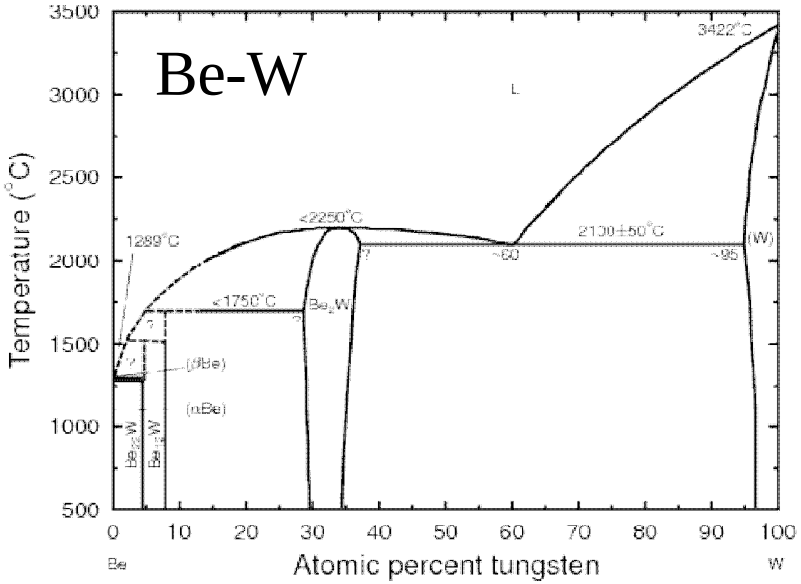
# D irradiation of pure W

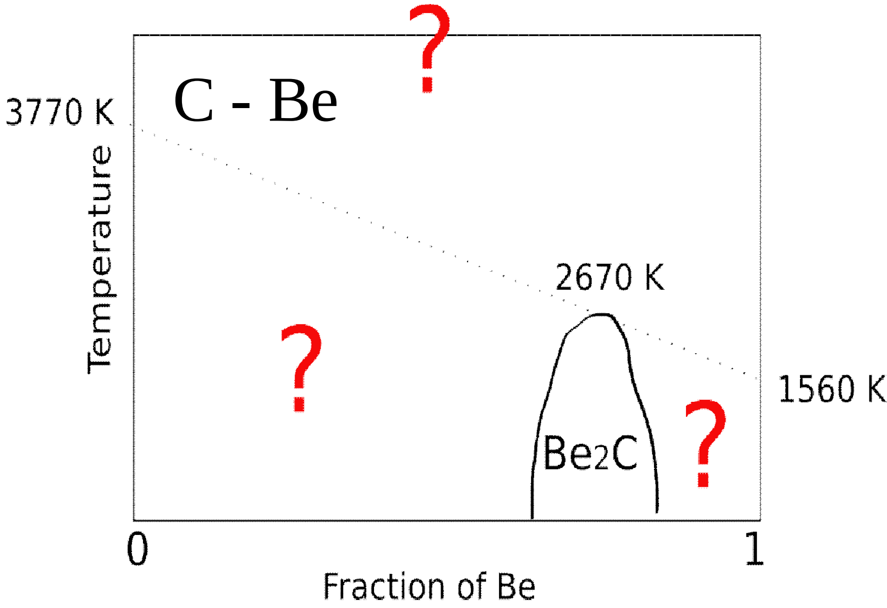
- As a sanity check for our potentials, we also ran simulations of D bombardment of pure W
- Experiments show zero sputtering below ~ 200 eV, so we should also get none – otherwise we are in trouble with our swift chemical sputtering results!
- Fortunately we do get zero sputtering, for at least 2000 D ions up to 100 eV
  - Higher energies running still, eventually physical sputtering must appear

## Phase formation in MD

# Observations of phase formation

- Our interatomic potentials aim to describe all crucial phases of the materials involved correctly.
- Hence they should be able to reproduce the central part of the phase diagrams – to the extent they are known…

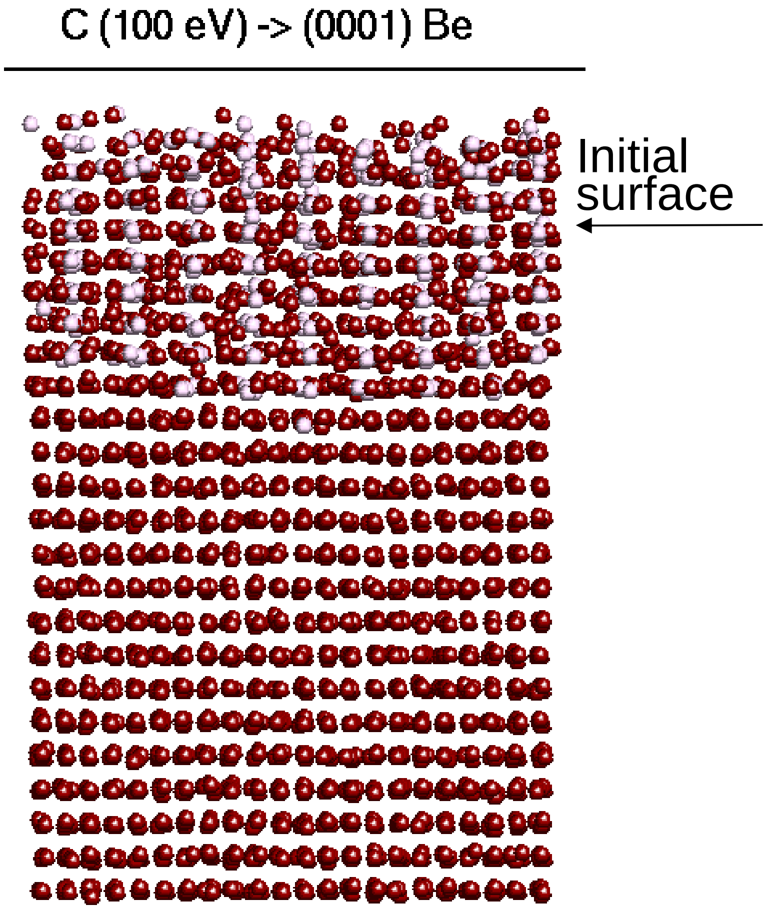




## Phase formation in MD

# C irradiation of Be

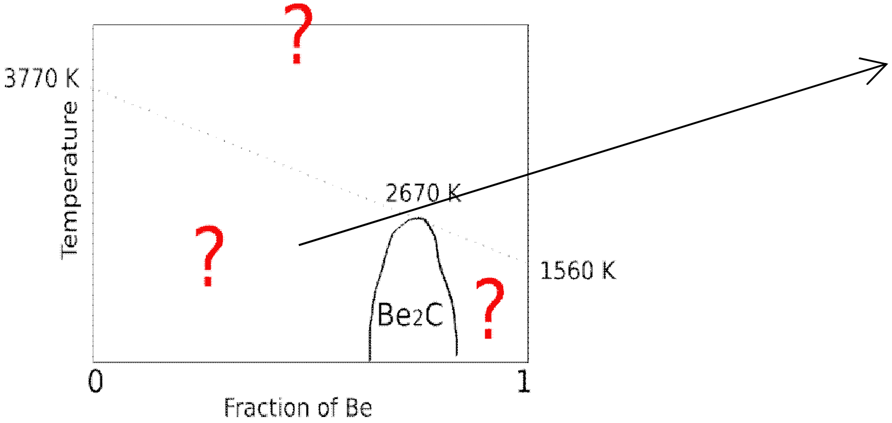
- Gratifyingly enough, we do see a lot of phases formed!
- 20 – 100 eV C ion irradiation
  - flux ~$2 \cdot 10^{25}$ m$^{-2}$s$^{-1}$
  - @ 1500 K
- Layers of $Be_2C$ are formed!

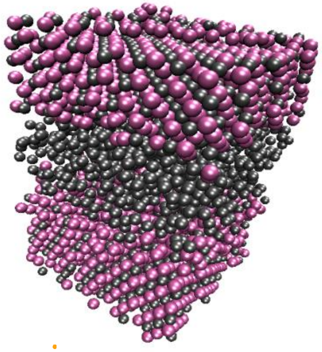


### Phase formation in MD

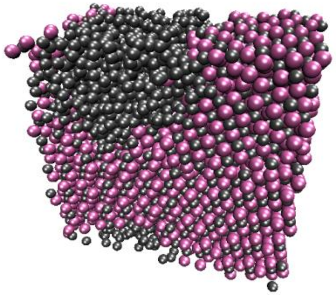
# Random mixtures of Be and C

- When making cells of random Be-C composition, we do see phase separation of BeC starting from random mixtures!
  - As expected from DFT calculations of phases and a single-intermetallic type phase diagram





layered BeC



BeC cell, mixed

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

CMS

HIP

# Simulations of H and He effects in W

Kalle Heinola,

Krister Henriksson,

Tommy Ahlgren,

Katharina Vörtler

and Kai Nordlund

*Department of Physics*

*University of Helsinki, Finland*

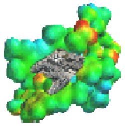
### Bubble formation and blistering in W:

## Motivation

- The main divertor material in ITER will be W
- So what about H and He damage in it?
- One of the main advantages of W is that 1-100 eV H and He cause zero damage, very little physical sputtering and no chemical sputtering
- But these ions do produce bubbles and blisters, which eventually rupture and might cause erosion

### Bubble formation and blistering in W:

# Difference of H and He bubble formation

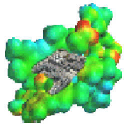


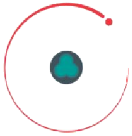
- Depth of blisters vastly different.
  - H: at micrometer depths
  - He: close to projected range (<100 Å)
- Why is this?
- We considered many possibilities:
  - Damage different: no, since also non-damaging irr. produces bubbles!!
  - Difference in diffusivity: no, about the same
  - Thermal gradients: no
  - Different kinds of W samples in experiments: no
- But how about differences in trapping behaviour?

### Bubble formation and blistering in W:

## H vs. He self-trapping

- The simplest possible trap is the self-trap: two mobile atoms A and A clustering with each other
  - Becomes immobile, acts as seed for further bubble growth
- To examine this, we used classical MD simulations and quantum-mechanical DFT calculations to examine the energy of two H or He atoms at different distances

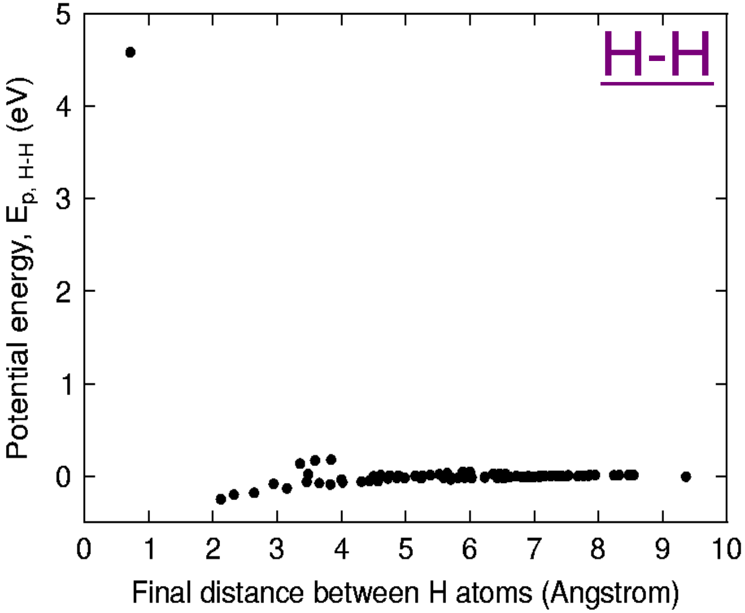


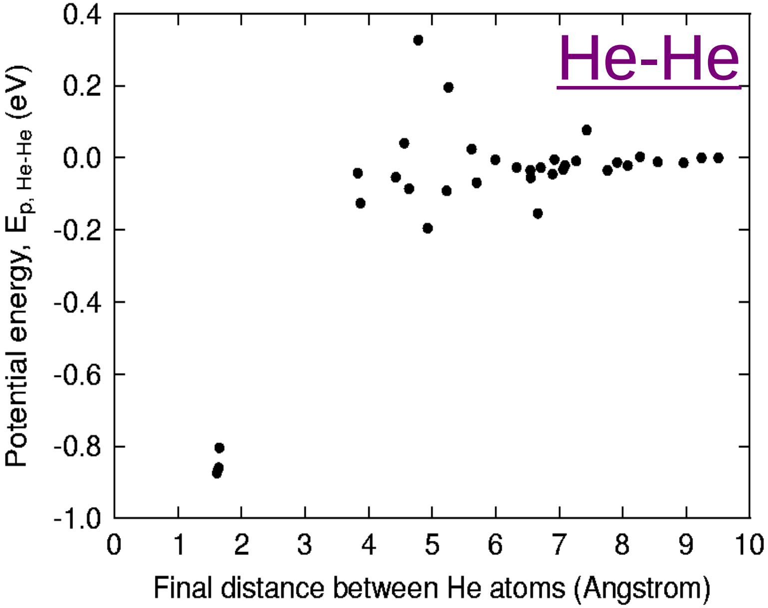


### Bubble formation and blistering in W:

# H vs. He self-trapping: energetics results

- MD energetics of H-H or He-He pair:
  - Most important features confirmed by DFT





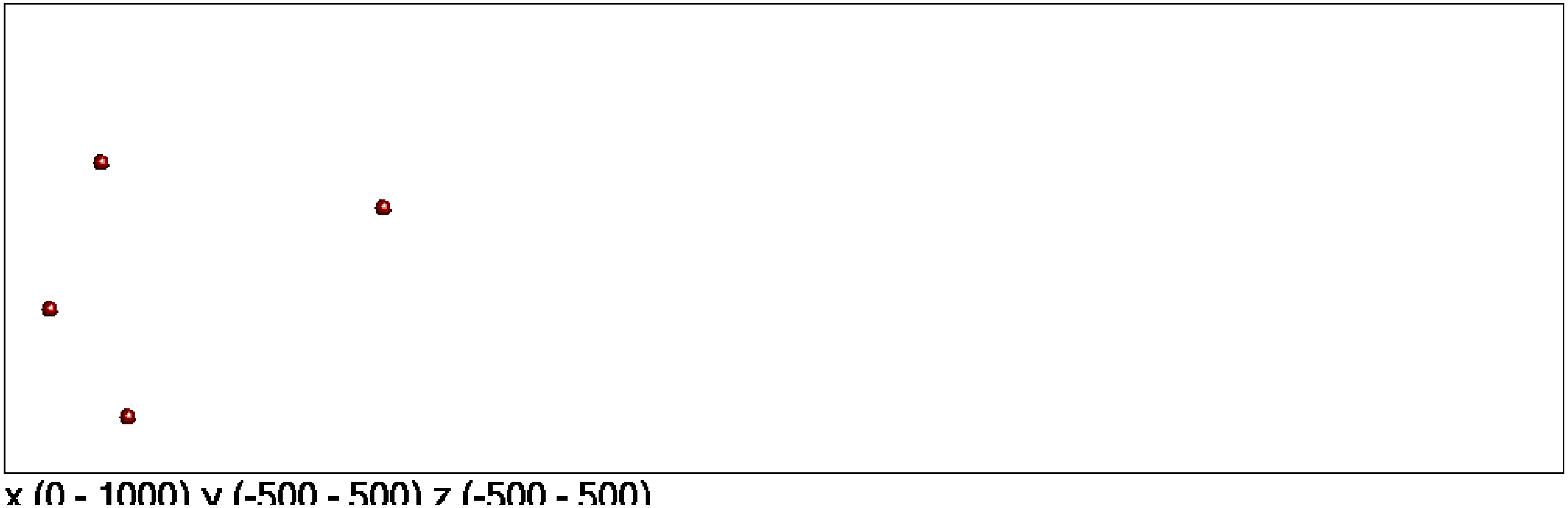
- Almost no binding for H-H, but strong (1 eV) binding for He-He!

[K. O. E. Henriksson, K. Nordlund, A. Krasheninnikov, and J. Keinonen, Appl. Phys. Lett. 87, 163113 (2005)]

### Bubble formation and blistering in W:

# Animation of KMC bubble formation

- He bubble formation: mobile atoms red, immobile He in clusters orange, large clusters green or blue



Bubble formation and blistering in W:

# He bubble depths

- This shows that He can self-trap, while H can not
- Enough to explain qualitatively He-H difference
- But to be on the safe side we also used Kinetic Monte Carlo (KMC) simulations of He migration in W to check whether He bubble depths obtained with self-trapping are the same as in experiments
- Results:

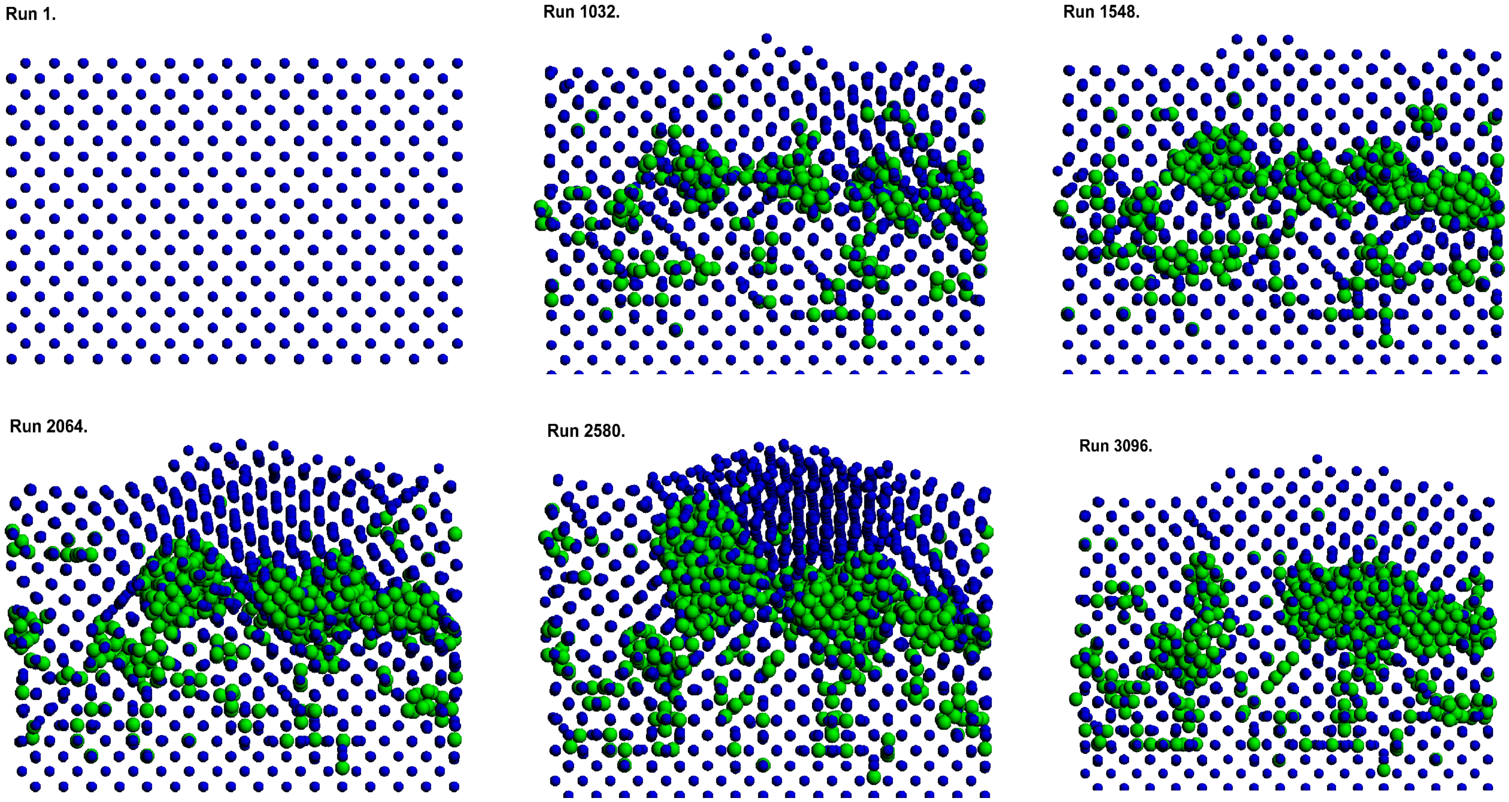
| T(K) | Our KMC | Expt. | Reference |
|---|---|---|---|
| 300 | 100 Å | 62 Å | Nicholson and Walls 1978 |
| 2370 | 2200 Å | 0 – 5000 Å | Chernikov and Zakharov 1989 |

[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)]

## Bubble formation and blistering in W:

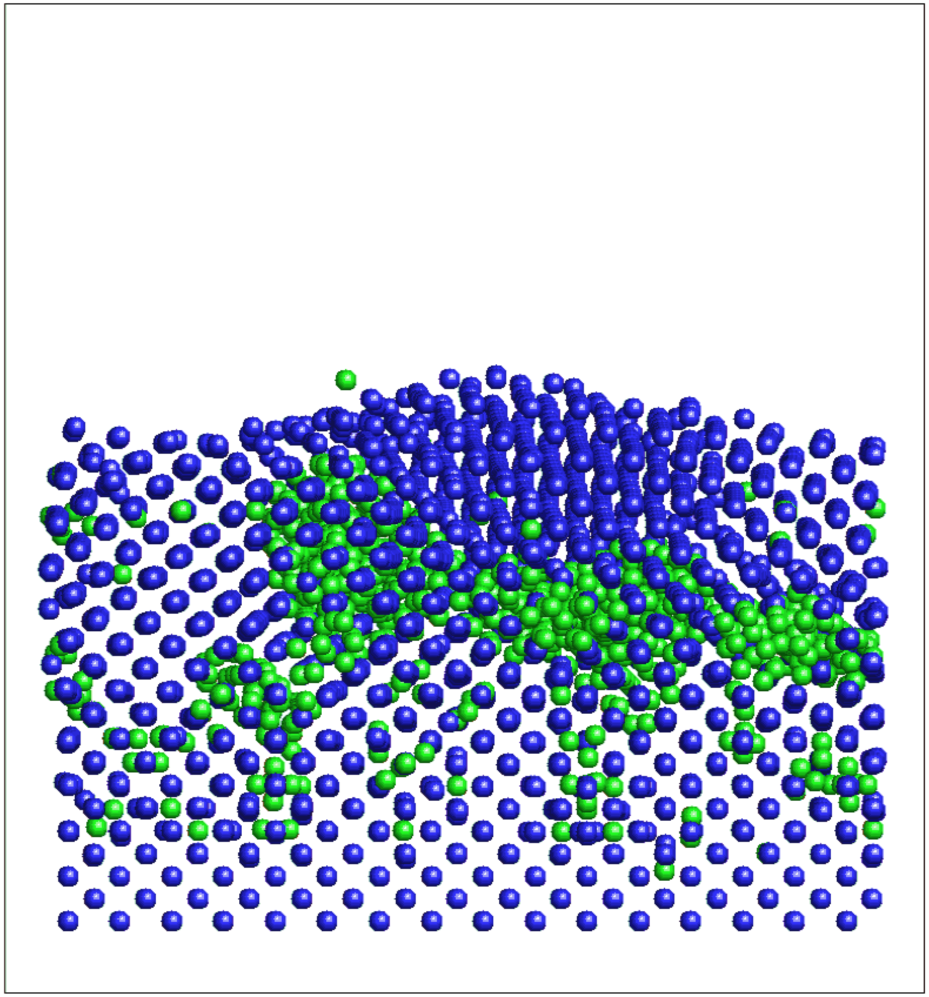
# Near-surface blistering of W by He

- MD simulation of 100 eV He -> W:



### Bubble formation and blistering in W:

## What happened after run 2580?



[K. O. E. Henriksson, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B. 244, 377 (2005)]

### Bubble formation and blistering in W:

## Blistering results

- In the He-induced blistering events observed so far, no W erosion associated with the bubble rupture has occurred
  - Sounds encouraging: low-E bombardment bubble rupture may not cause much erosion
- The results look very much like the first stages of the formation of Doerner’s W fuzz!

### Bubble formation and blistering in W:

# Recent results: traps for T in W divertors

- Neutrons induce damage also in the W divertor
- This damage may bind T coming from the fusion plasma
- Retained T limits the usage lifetime of ITER (700 g limit)
    - Hence it is important to know the nature of the damage in W, how much T it can retain, and how it can be taken out
- To this end, we are doing multiscale modelling of the damage and T binding in W

# *Multiscale* calculation of H retention with Rate Equations:

Association Euratom–Tekes

- Hydrogen in the bulk is free (=mobile) or trapped

*E.g*. system with hydrogen and monovacancies ($V_1$), $C = C(x,t)$

$$\frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial x^2}$$

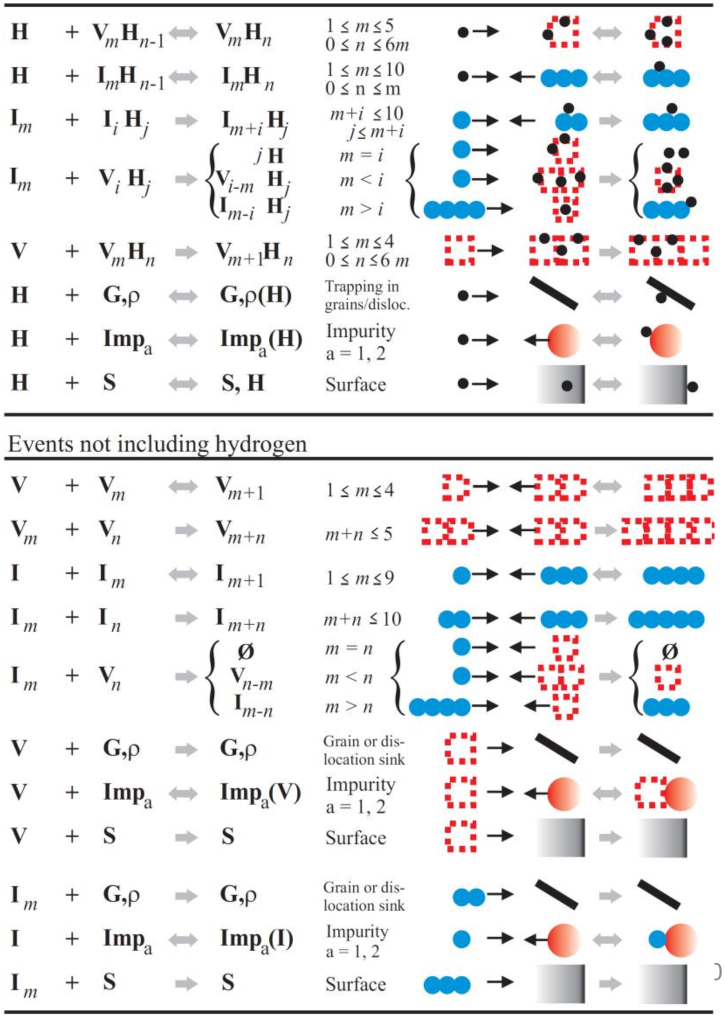
**diffusion** (free particles $D = D_0 e^{-E_m/kT}$)

- In real life:
  - several defect types trap Hydrogen
  - evolution of defects is time & temperature dependent

# *Multiscale* calculation of H retention with Rate Equations:

- Analytical method, real time & length scales, no limitations in the number of particles

$$\frac{\partial C_\alpha(x,t)}{\partial t} = D_\alpha \frac{\partial^2 C_\alpha(x,t)}{\partial x^2} + S_\alpha(x,t) \pm \sum_{\beta,\gamma=1}^{N} k^2_{\beta,\gamma} D_\beta C_\beta(x,t) \pm \sum_{\delta=1}^{N} \nu_\delta e^{-E_{A,\delta}/kT} C_\delta(x,t)$$



| | | | | | |
|---|---|---|---|---|---|
| $\mathbf{H}$ | + | $\mathbf{V}_m\mathbf{H}_{n-1}$ | ⇔ | $\mathbf{V}_m\mathbf{H}_n$ | $1 \le m \le 5$<br>$0 \le n \le 6m$ |
| $\mathbf{H}$ | + | $\mathbf{I}_m\mathbf{H}_{n-1}$ | ⇔ | $\mathbf{I}_m\mathbf{H}_n$ | $1 \le m \le 10$<br>$0 \le \mathrm{n} \le \mathrm{m}$ |
| $\mathbf{I}_m$ | + | $\mathbf{I}_i\mathbf{H}_j$ | ⇒ | $\mathbf{I}_{m+i}\mathbf{H}_j$ | $m+i \le 10$<br>$j \le m+i$ |
| $\mathbf{I}_m$ | + | $\mathbf{V}_i\mathbf{H}_j$ | ⇒ | $j\,\mathbf{H}$<br>$\mathbf{V}_{i-m}\ \mathbf{H}_j$<br>$\mathbf{I}_{m-i}\ \mathbf{H}_j$ | $m = i$<br>$m < i$<br>$m > i$ |
| $\mathbf{V}$ | + | $\mathbf{V}_m\mathbf{H}_n$ | ⇒ | $\mathbf{V}_{m+1}\mathbf{H}_n$ | $1 \le m \le 4$<br>$0 \le n \le 6\,m$ |
| $\mathbf{H}$ | + | $\mathbf{G},\rho$ | ⇔ | $\mathbf{G},\rho(\mathbf{H})$ | Trapping in grains/disloc. |
| $\mathbf{H}$ | + | $\mathbf{Imp}_\mathrm{a}$ | ⇔ | $\mathbf{Imp}_\mathrm{a}(\mathbf{H})$ | Impurity<br>a = 1, 2 |
| $\mathbf{H}$ | + | $\mathbf{S}$ | ⇔ | $\mathbf{S}, \mathbf{H}$ | Surface |

Events not including hydrogen

| | | | | | |
|---|---|---|---|---|---|
| $\mathbf{V}$ | + | $\mathbf{V}_m$ | ⇔ | $\mathbf{V}_{m+1}$ | $1 \le m \le 4$ |
| $\mathbf{V}_m$ | + | $\mathbf{V}_n$ | ⇒ | $\mathbf{V}_{m+n}$ | $m+n \le 5$ |
| $\mathbf{I}$ | + | $\mathbf{I}_m$ | ⇔ | $\mathbf{I}_{m+1}$ | $1 \le m \le 9$ |
| $\mathbf{I}_m$ | + | $\mathbf{I}_n$ | ⇒ | $\mathbf{I}_{m+n}$ | $m+n \le 10$ |
| $\mathbf{I}_m$ | + | $\mathbf{V}_n$ | ⇒ | Ø<br>$\mathbf{V}_{n-m}$<br>$\mathbf{I}_{m-n}$ | $m = n$<br>$m < n$<br>$m > n$ |
| $\mathbf{V}$ | + | $\mathbf{G},\rho$ | ⇒ | $\mathbf{G},\rho$ | Grain or dislocation sink |
| $\mathbf{V}$ | + | $\mathbf{Imp}_\mathrm{a}$ | ⇔ | $\mathbf{Imp}_\mathrm{a}(\mathbf{V})$ | Impurity<br>a = 1, 2 |
| $\mathbf{V}$ | + | $\mathbf{S}$ | ⇒ | $\mathbf{S}$ | Surface |
| $\mathbf{I}_m$ | + | $\mathbf{G},\rho$ | ⇒ | $\mathbf{G},\rho$ | Grain or dislocation sink |
| $\mathbf{I}$ | + | $\mathbf{Imp}_\mathrm{a}$ | ⇔ | $\mathbf{Imp}_\mathrm{a}(\mathbf{I})$ | Impurity<br>a = 1, 2 |
| $\mathbf{I}_m$ | + | $\mathbf{S}$ | ⇒ | $\mathbf{S}$ | Surface |

# *Multiscale* calculation of H retention with Rate Equations:

- Analytical method, real time & length scales, no limitations in the number of particles
- System with hydrogen, vacancies ($V_n$), interstitials ($I_n$), grains, …

$$\frac{\partial C_\alpha(x,t)}{\partial t} = D_\alpha \frac{\partial^2 C_\alpha(x,t)}{\partial x^2} + S_\alpha(x,t) \pm \sum_{\beta,\gamma=1}^{N} k^2_{\beta,\gamma} D_\beta C_\beta(x,t) \pm \sum_{\delta=1}^{N} \nu_\delta e^{-E_{A,\delta}/kT} C_\delta(x,t)$$

$$D = D_0 e^{-E_m/kT}$$

◌ **energetics from DFT**

◌ **sink strength and reaction radii from MD**

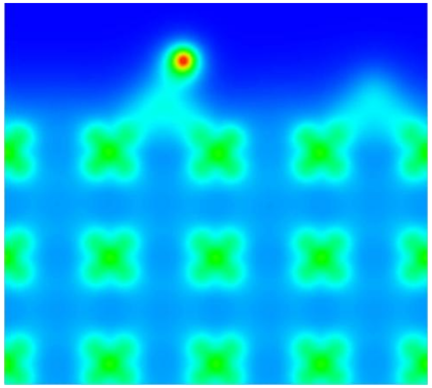
◌ **source term from BCA, MD, experiments, etc**

# *Multiscale* calculation of hydrogen retention in W: Computational tools

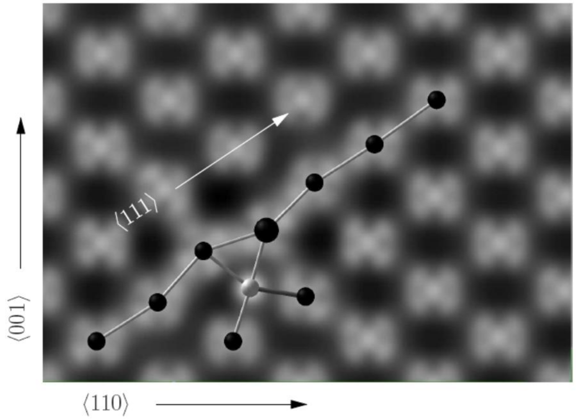
Association
Euratom–Tekes

- Energetics from first-principle calculations
  - **DFT** (density functional theory) with VASP 4.6.35
    - W properties: bulk bcc, fcc and A15 as well as $W_2$ molecule
    - W point defect properties (mono-vacancy and SIA)
    - W (100) surface reconstruction
    - H diffusivity in W and on the (100) surface
    - H detrapping from W mono-vacancy

H @ W(100)
surface



H @ ‹111› SIA



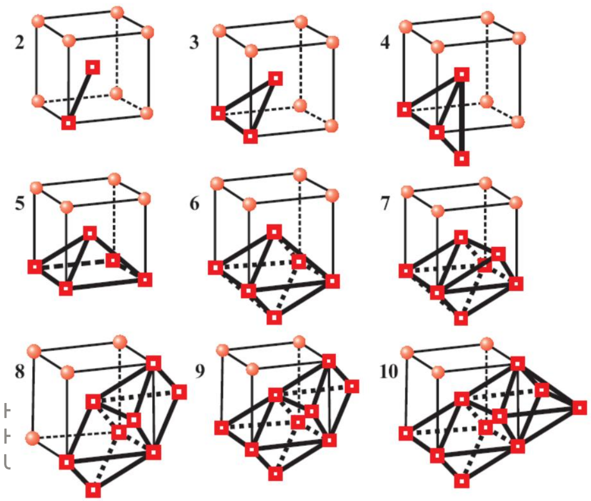
*Ahlgren, Heinola, et al, J. Appl. Phys.* ***107****, 033516 (2010)*
*Heinola, Ahlgren, J. Appl. Phys.* ***107****, 113531 (2010)*
*Heinola, Ahlgren, Phys. Rev.* ***B 81****, 073409 (2010)*
*Heinola, Ahlgren, et al, Phys. Rev.* ***B 82****, 094102 (2010)*

# *Multiscale* calculation of hydrogen retention in W: Computational tools

- Energetics from first-principle calculations
  - **DFT** (density functional theory) with VASP 4.6.35

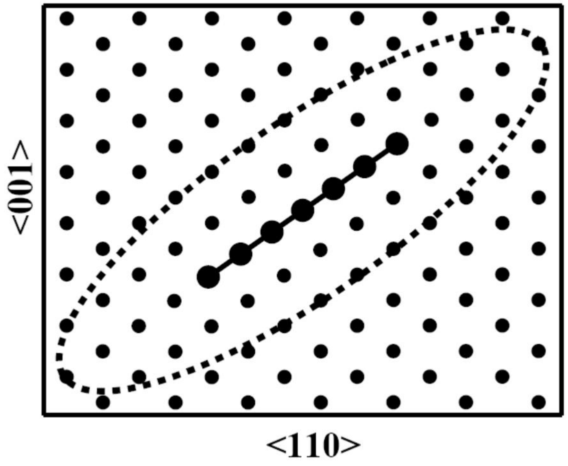
↓

- Defect properties in clusters with **MD**
  - **MD** potential from **DFT** + experiments
  - clustering & annihilation radii (*R*)
  - W in W projected ranges with low energies
  - thousands of W atoms



← Vacancy cluster properties

Frenkel pair annihilation radius →



*Ahlgren, Heinola, et al, J. Appl. Phys.* ***107****, 033516 (2010)*

# *Multiscale* calculation of hydrogen retention in W: Computational tools

- Energetics from first-principle calculations
  - **DFT** (density functional theory) with VASP 4.6.35
- Defect properties in clusters with **MD**
  - **MD** potential from **DFT** + experiments
- Initial damage profile with **MD** & **BCA** (binary collision approx.):
  - damage profile vs. depth per implanted ion
  - immediate SIA & vacancy clustering: $I_{1-5}$, $V_{1-10}$

# *Multiscale* calculation of hydrogen retention in W: Computational tools

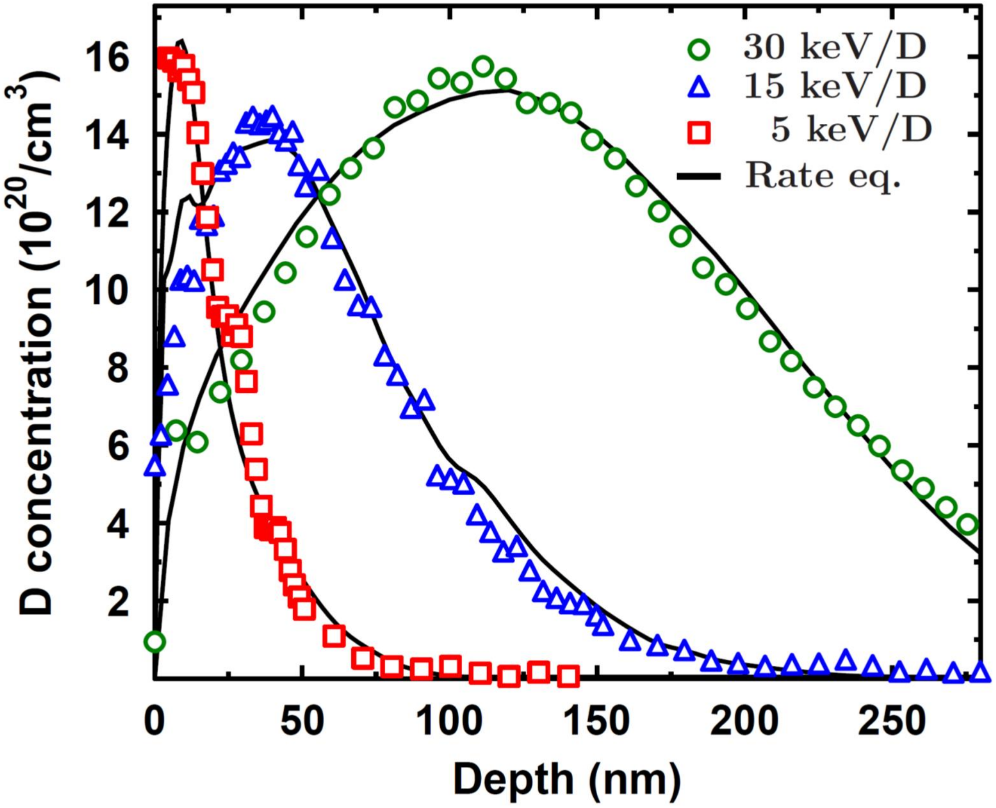
- Energetics from first-principle calculations
  - **DFT** (density functional theory) with VASP 4.6.35
- Defect properties in clusters with **MD**
  - **MD** potential from **DFT** + experiments
- Initial damage profile with **MD** & **BCA** (binary collision approx.):
  - damage profile vs. depth per implanted ion
- Final damage profile with **Rate Equations** $t_{i+1} = t_i + \Delta t$
  - diffusion
  - trapping, detrapping
  - clustering
  - *e.g.* D implantation 30 mins @ RT, annealing for 24 hrs

# Validation of the *Multiscale* method: Rate Equations vs. Implantation experiments

Association Euratom–Tekes

## Rate Equation results:

- Same input parameters as in the experiments:
  5, 15, 30 keV/D
  and
  5.8×$10^{16}$ D/cm$^2$
- D implantation 30 mins @ RT, annealing 24 hrs
- Excellent agreement with the experiments



Experimental:
*Ahlgren, Heinola, et al., Nucl. Instr. Meth. B, **249**, (2006)*
*Heinola, Ahlgren, et al.,Phys. Scripta, **T128** (2007)*

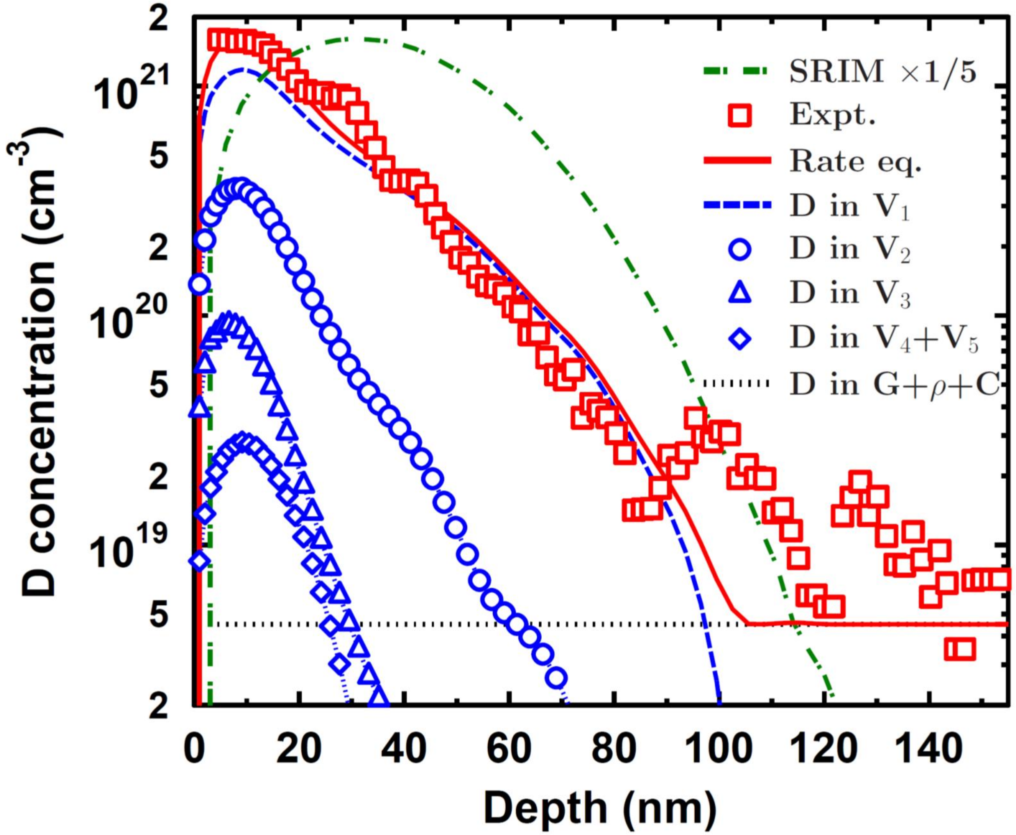
Theory:
*Ahlgren, Heinola, et al. Phys. Rev. B (2010), submitted*

# Validation of the *Multiscale* method: Rate Equations vs. Implantation experiments

**Rate Equation results:**

- Specification of each defect type
- Hydrogen trapping to each defect
- Majority of hydrogen in mono-vacancies ($V_1$) with all implantation energies
- High implantation energy
  → number of larger defects increase

5 keV D in W



- G+ρ is the ***only*** adjustable parameter
  (G+ρ is dislocation and grain boundary sinks)
- C is the inherent C impurity concentration [Plansee]

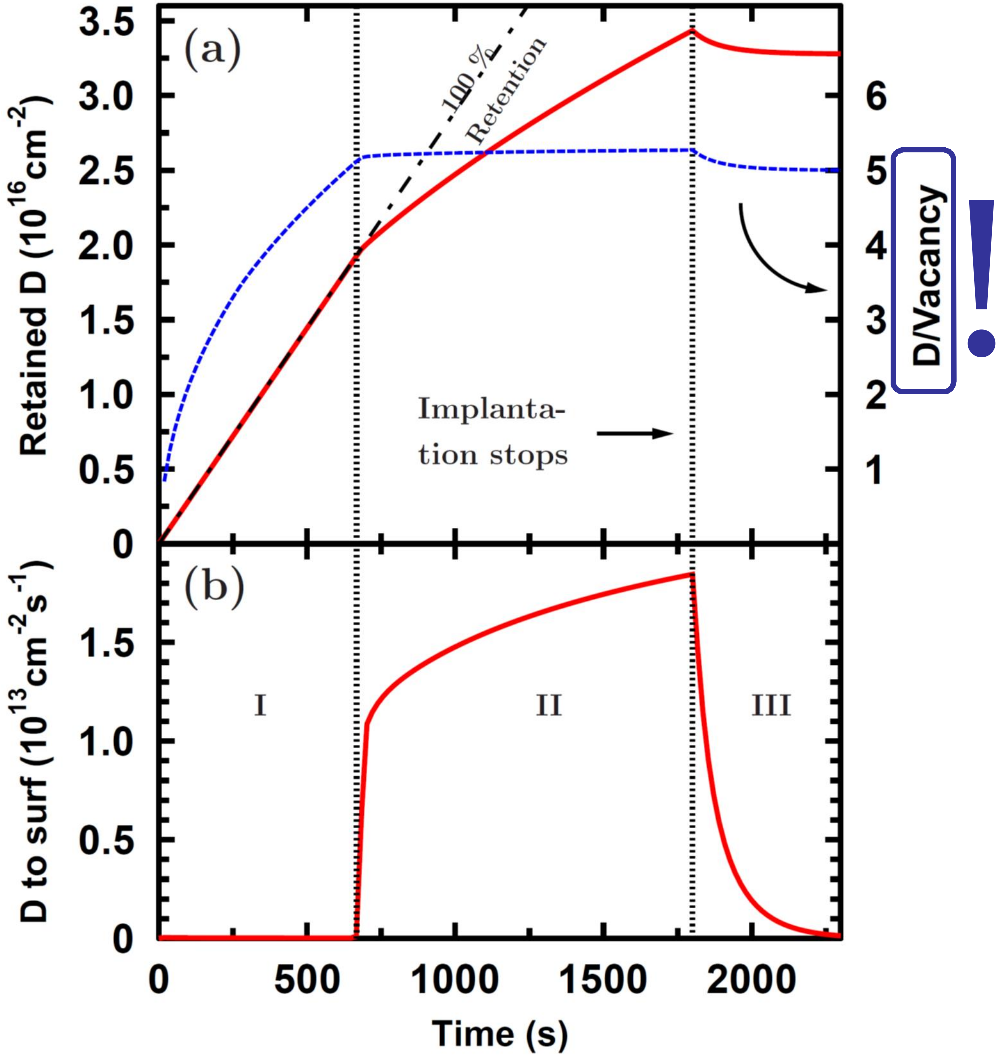
*Ahlgren, Heinola, et al., Phys. Rev. B (2010), submitted*

# *Multiscale* method: Rate Equations

Association Euratom–Tekes

## Retention & recycling

- Accumulation of D to the W surface in the course of implantation
→ Hydrogen recycling



*Ahlgren, Heinola, et al., Phys. Rev. B (2010), submitted*

# Conclusions - W

- Bubble formation and trapping in W by H and He is dramatically different
- Experiments on D trapping can be reproduced by a multiscale modelling scheme
  - Combining results from DFT+MD+BCA/MD with an analytical set of Rate Equations for realistic length and time scales
  - Implantation and diffusion of D in W (@ RT) and grain boundaries and impurities included in the system
  - Model and experiments on 5, 15 and 30 keV/D implantations and with 5.8x$10^{16}$ D/cm$^2$ were shown to be in excellent agreement