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Molecular dynamics simulations of plasma interaction with beryllium-based fusion reactor materials

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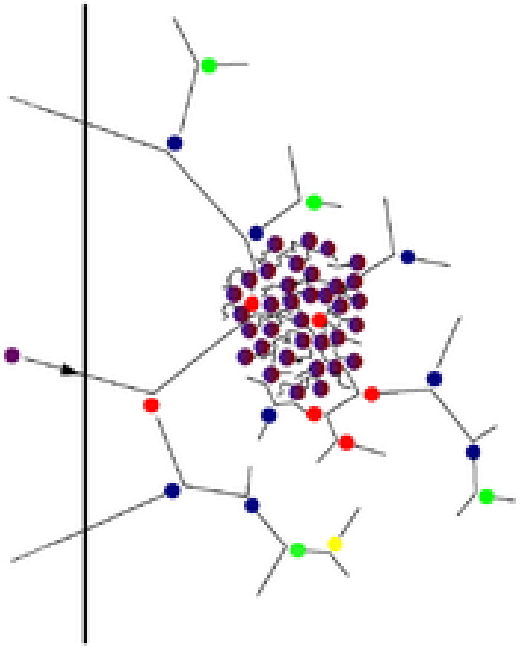
Contents

- The rich materials science of plasma-wall interactions
- Molecular dynamics simulation approach for plasma-wall interactions
- Interlude: a couple of non-Be results
- Interatomic potential for the Be-W-C-H system
- Results for H interactions with Be and its Be-W and Be-C compounds

The rich materials science of plasma-wall interactions

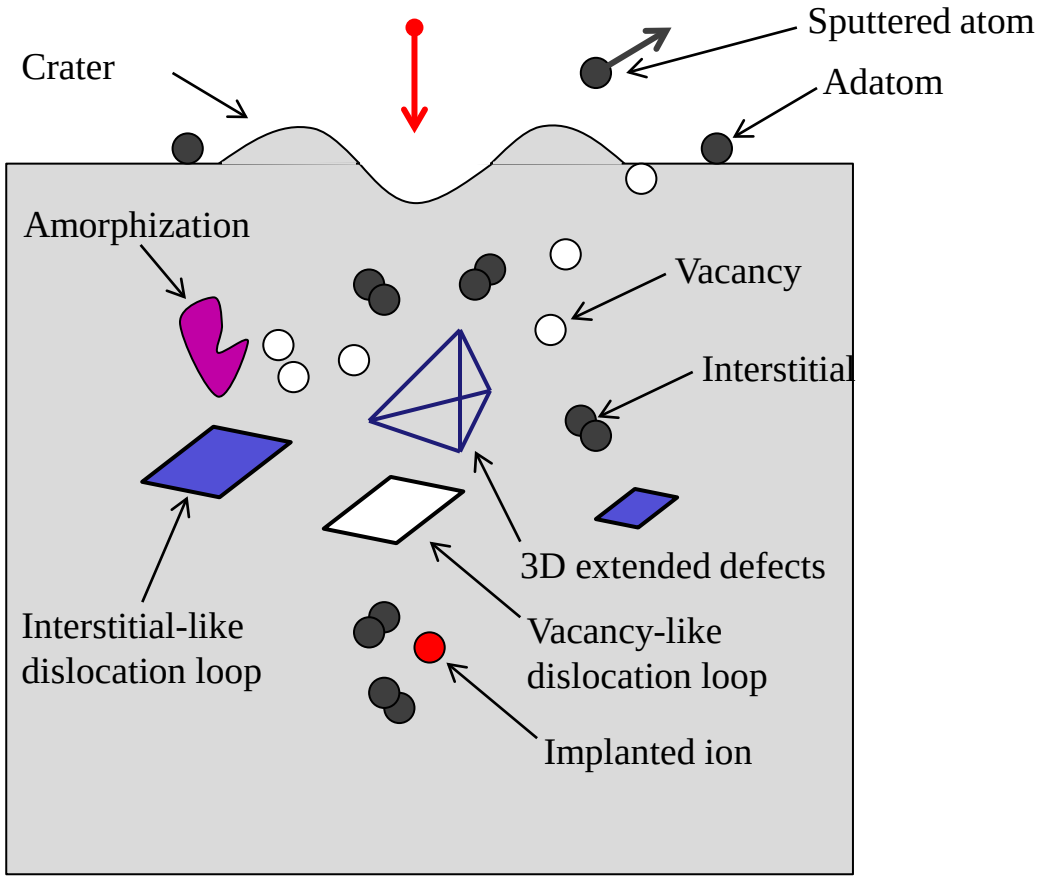
- This is a demanding (and hence fun! J) range of materials physics issues to work on.
- First stage: collision cascade by single incoming ion
- Simplified view:



[Wikipedia by Kai Nordlund]

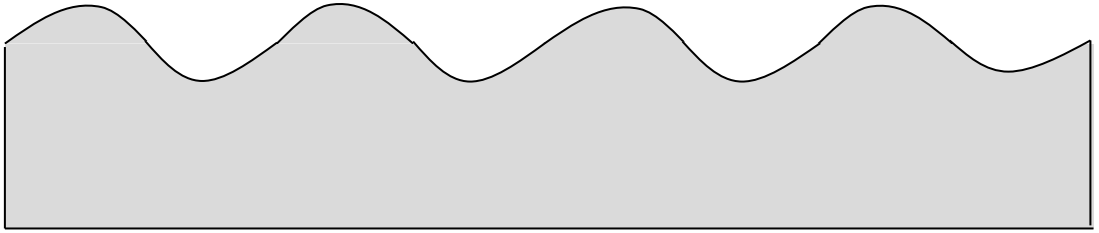
The rich materials science of plasma-wall interactions

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



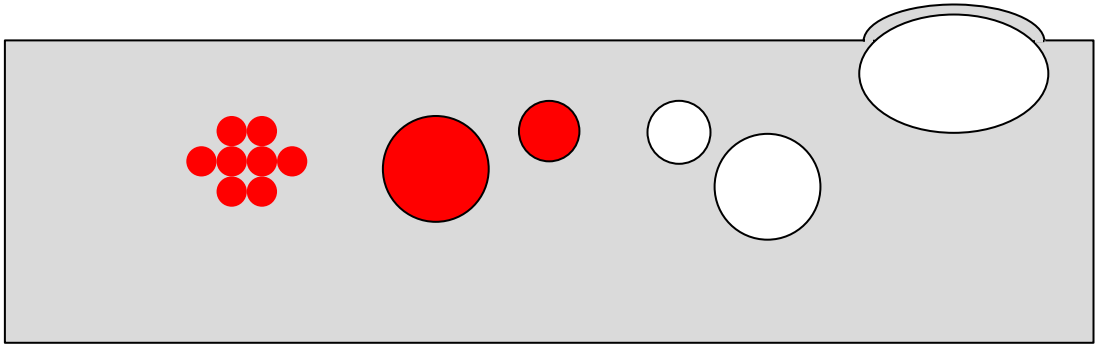
The rich materials science of plasma-wall interactions: high fluences

- 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)]

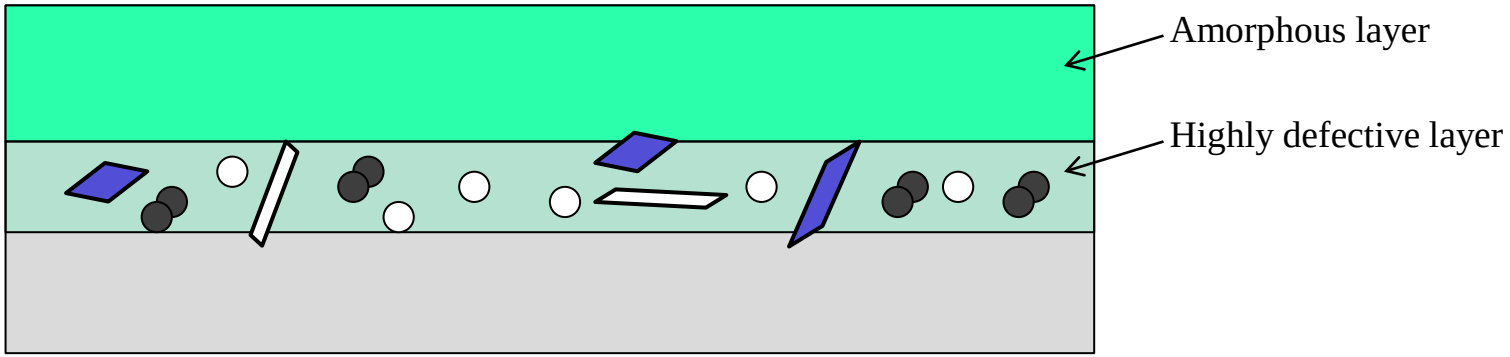
  - Precipitate/nanocluster, bubble, void or blister formation inside solid



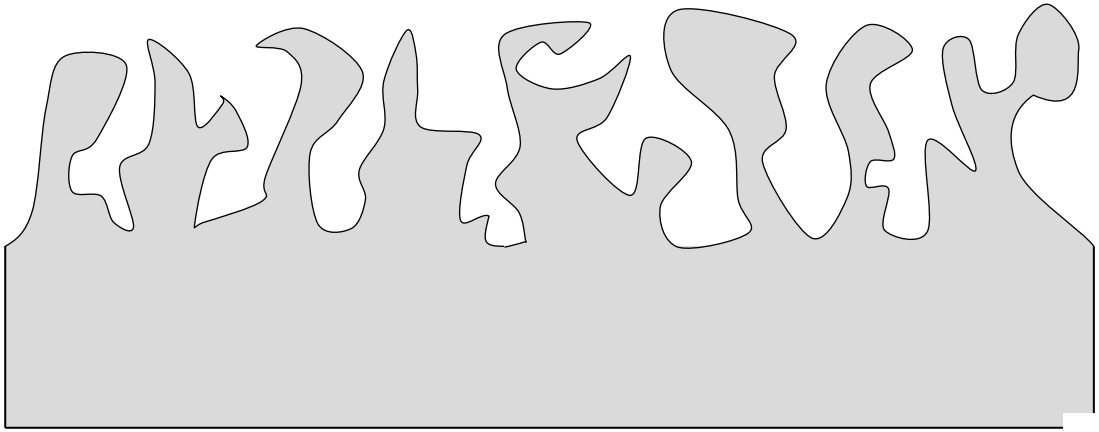
[Bubbles e.g: K. O. E. Henriksson, **K. Nordlund**, J. Keinonen, D, Physica Scripta **T108**, 95 (2004); Nanocrystals e.g. 75S. Dhara, Crit. Rev. Solid State Mater. Sci. 32, 1 [2007)]

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

- Phase changes, e.g. amorphization:

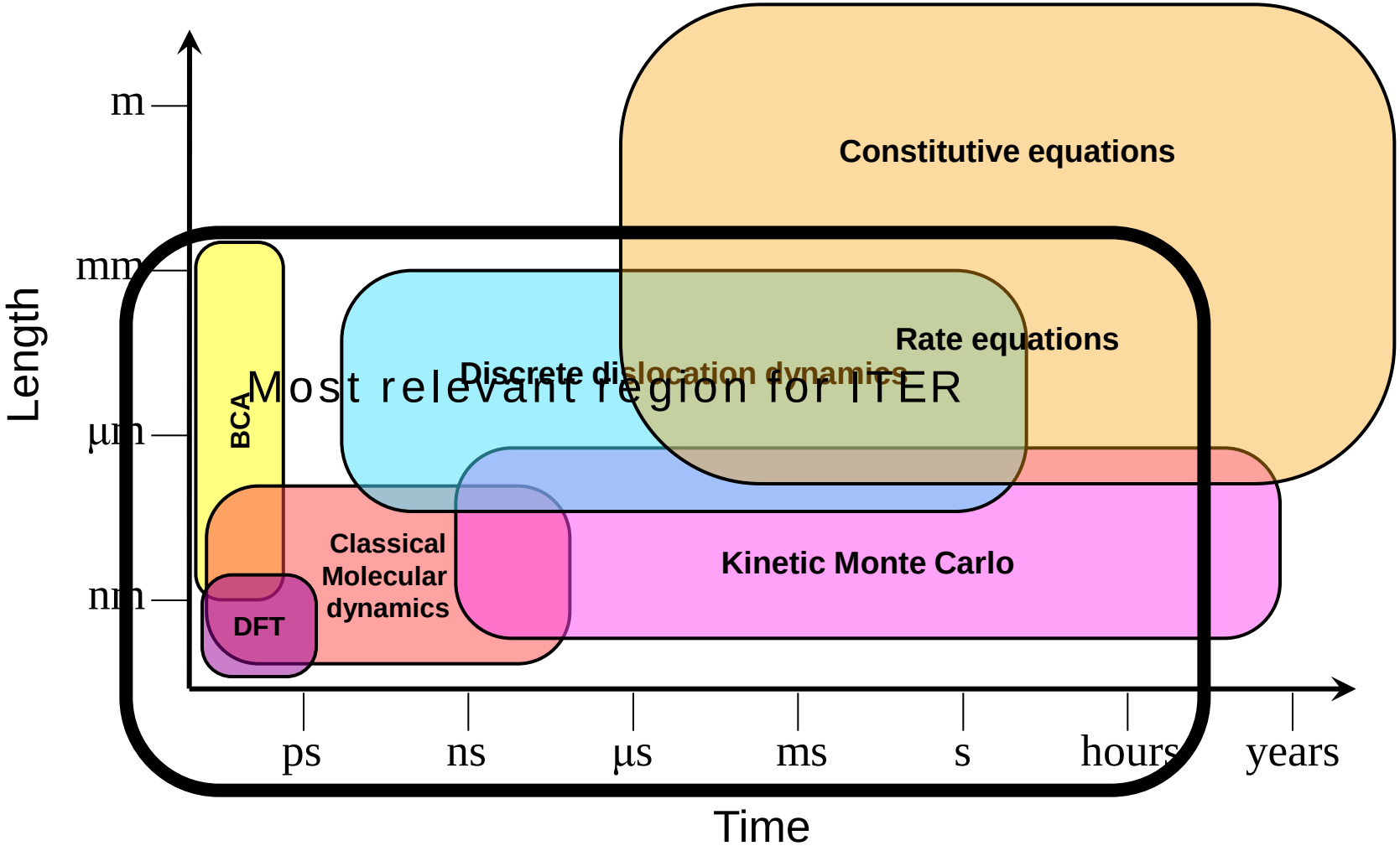


- Spontaneous porousness formation, “fuzz”
  - Highly fusion-relevant now, He -> W does it

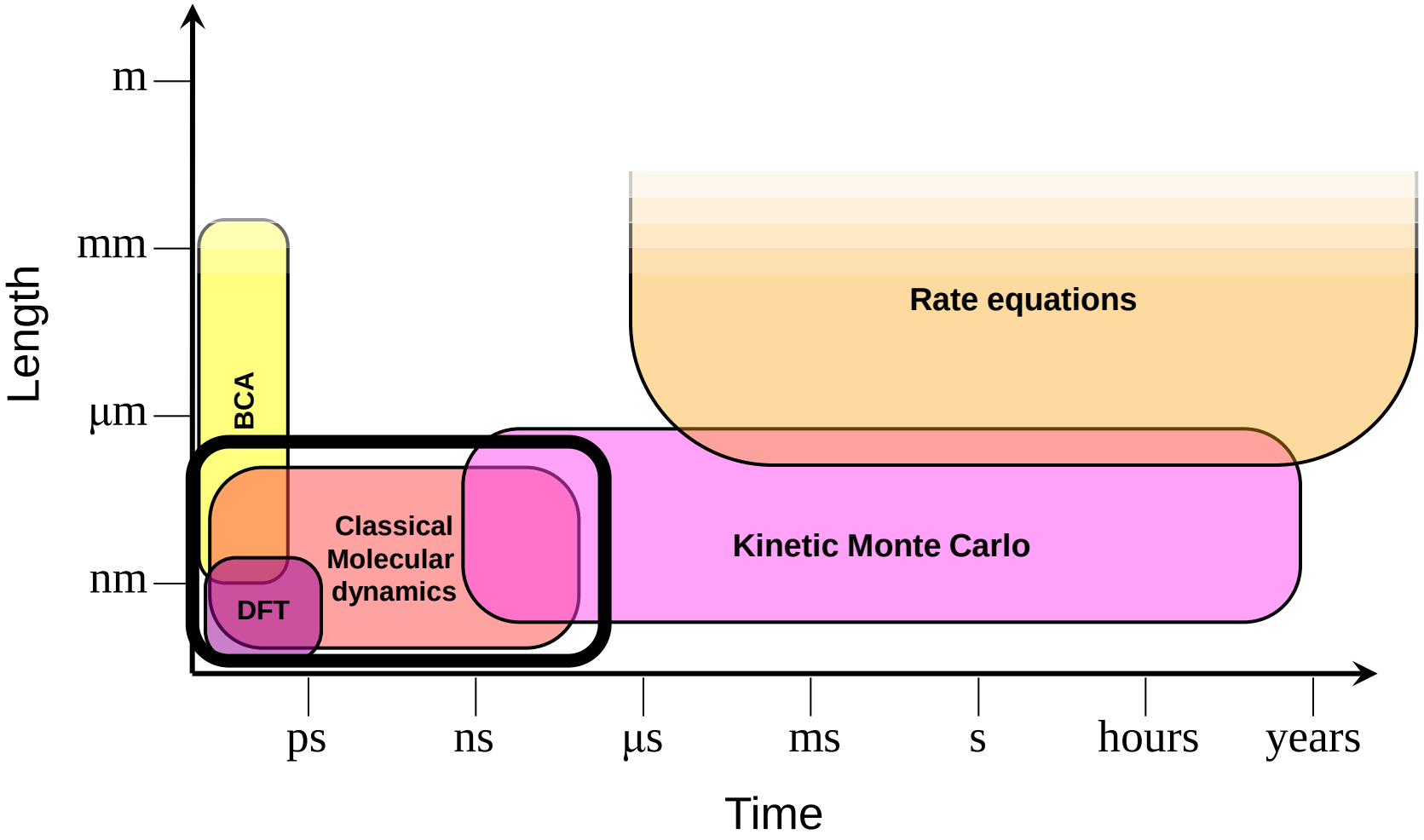


[http://vlt.ornl.gov/research/20110119_highlight_doerner.pdf]

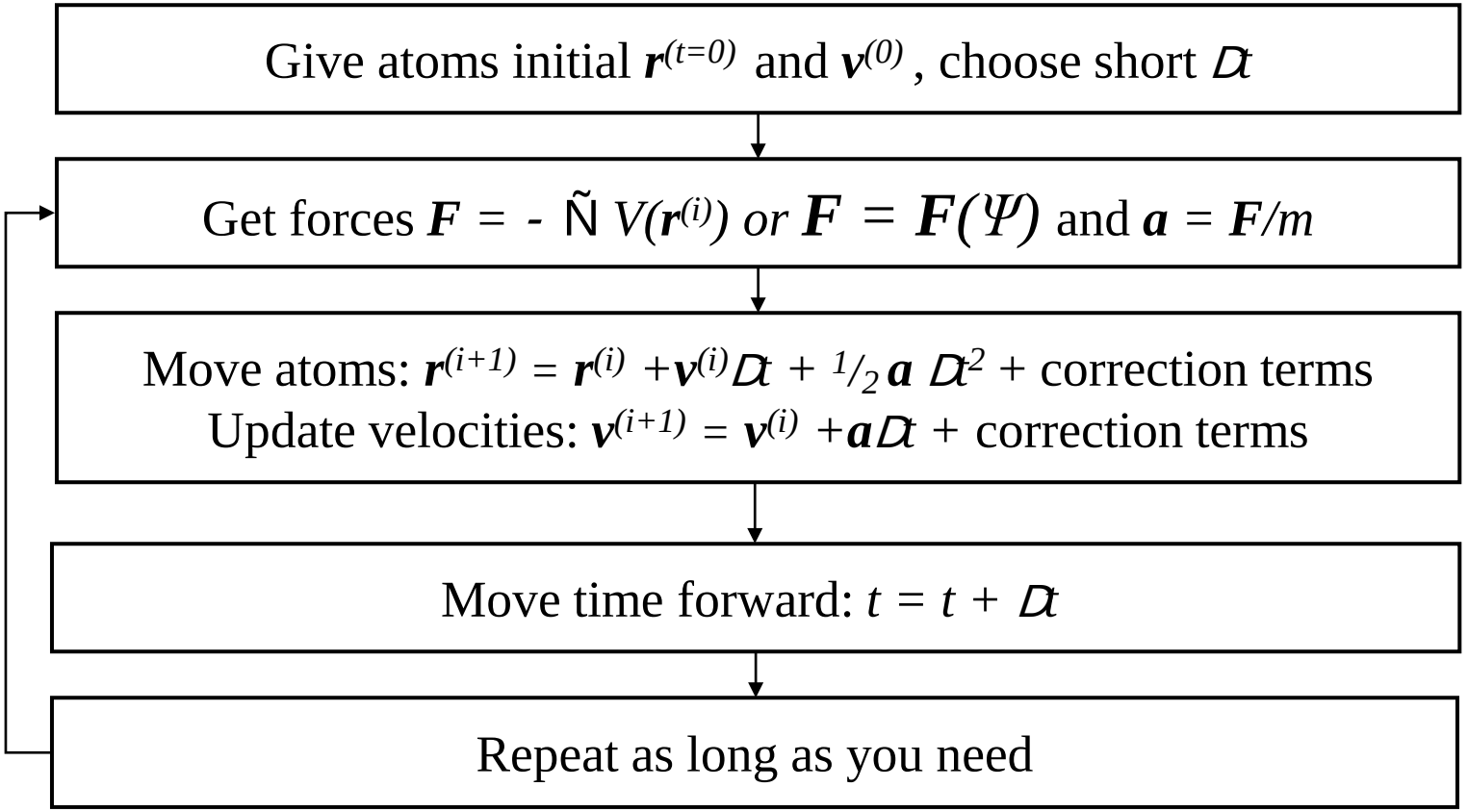
Simulation framework to handle all this



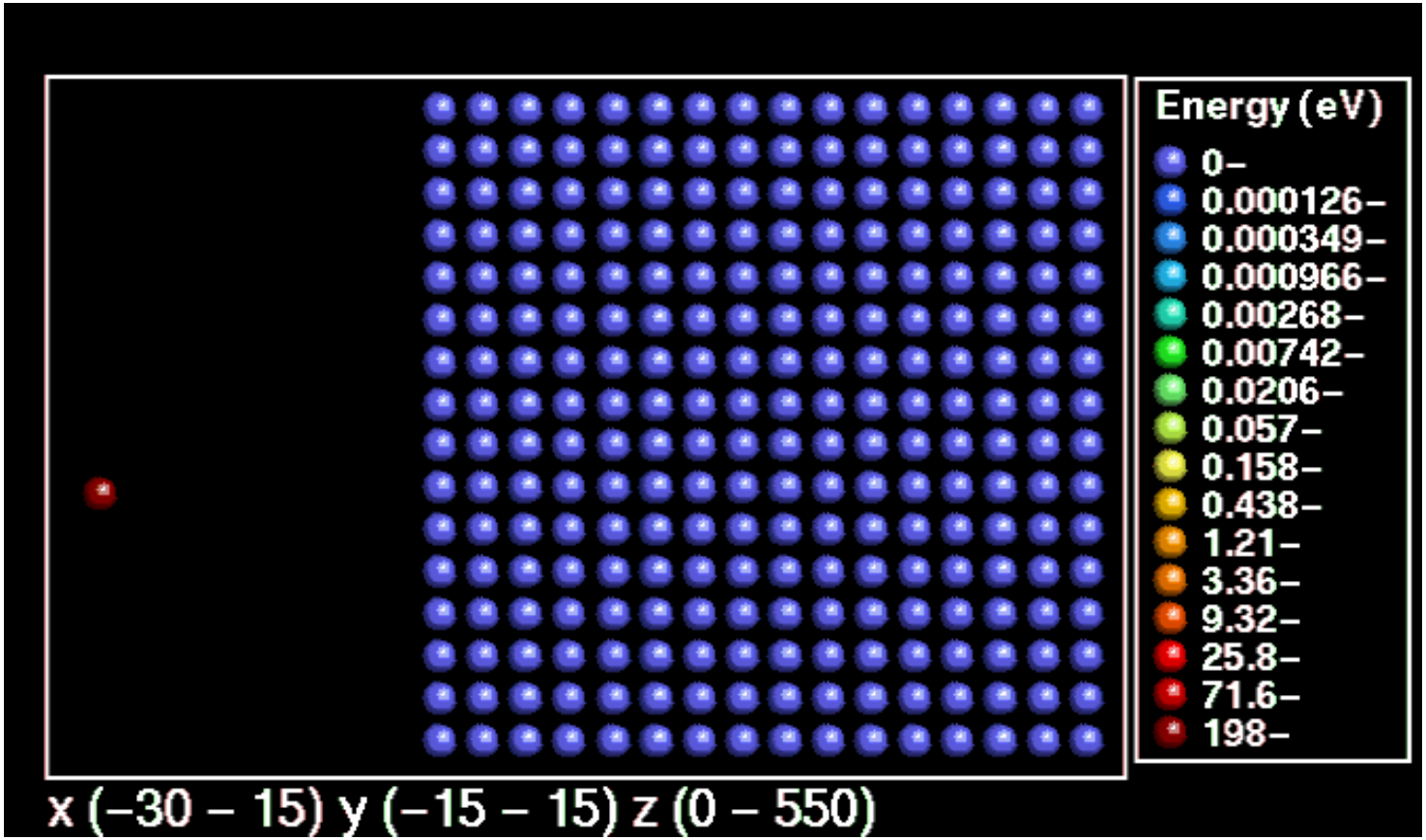
Range of work in our group



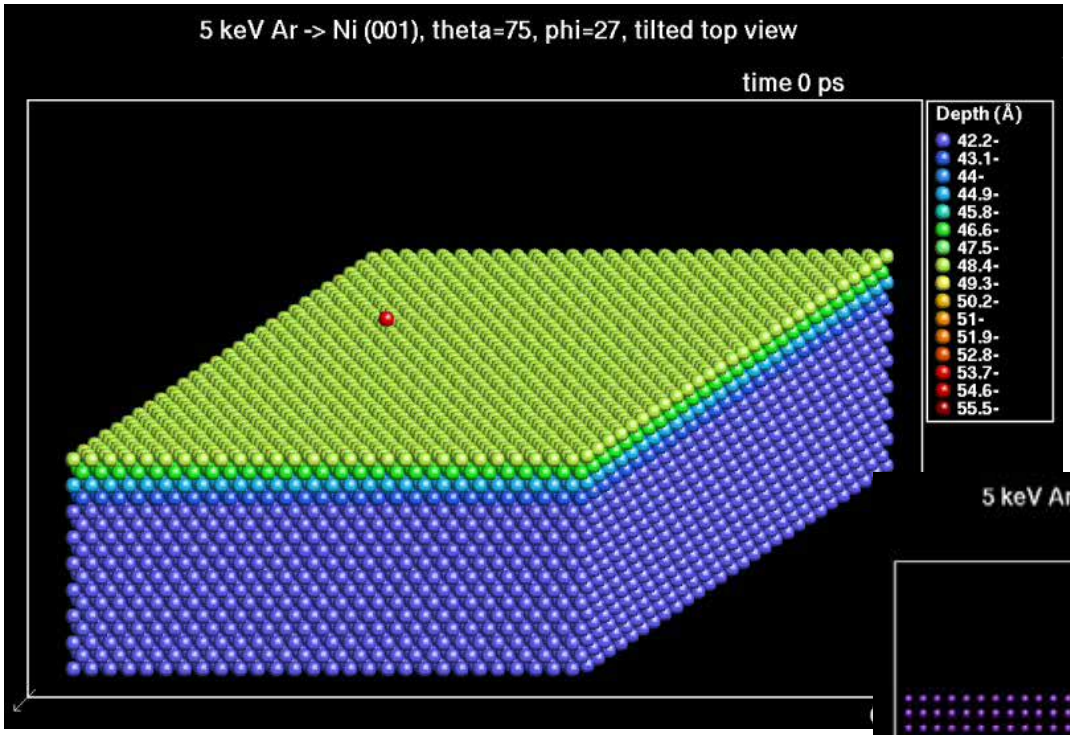
Molecular dynamics algorithm

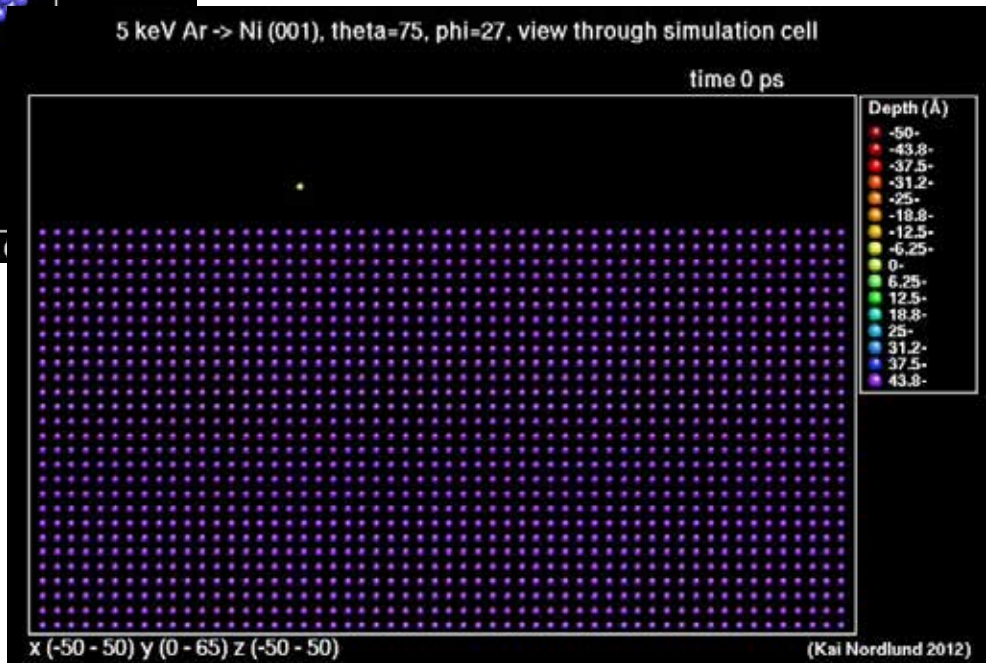


MD example 1: 500 eV Au -> Cu

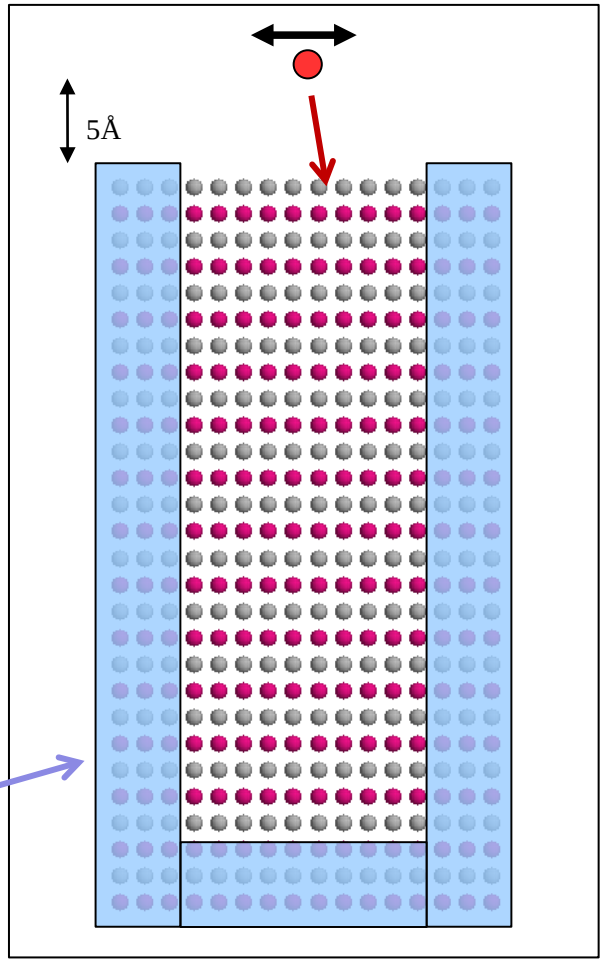


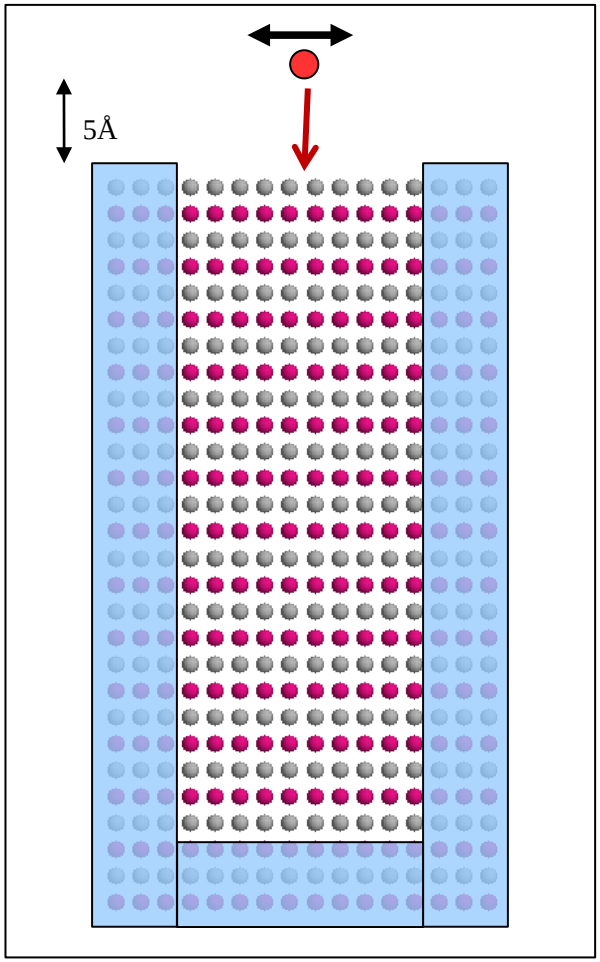
MD example 2: 5 keV Ar -> Ni





Formalism 1: Independent simulations





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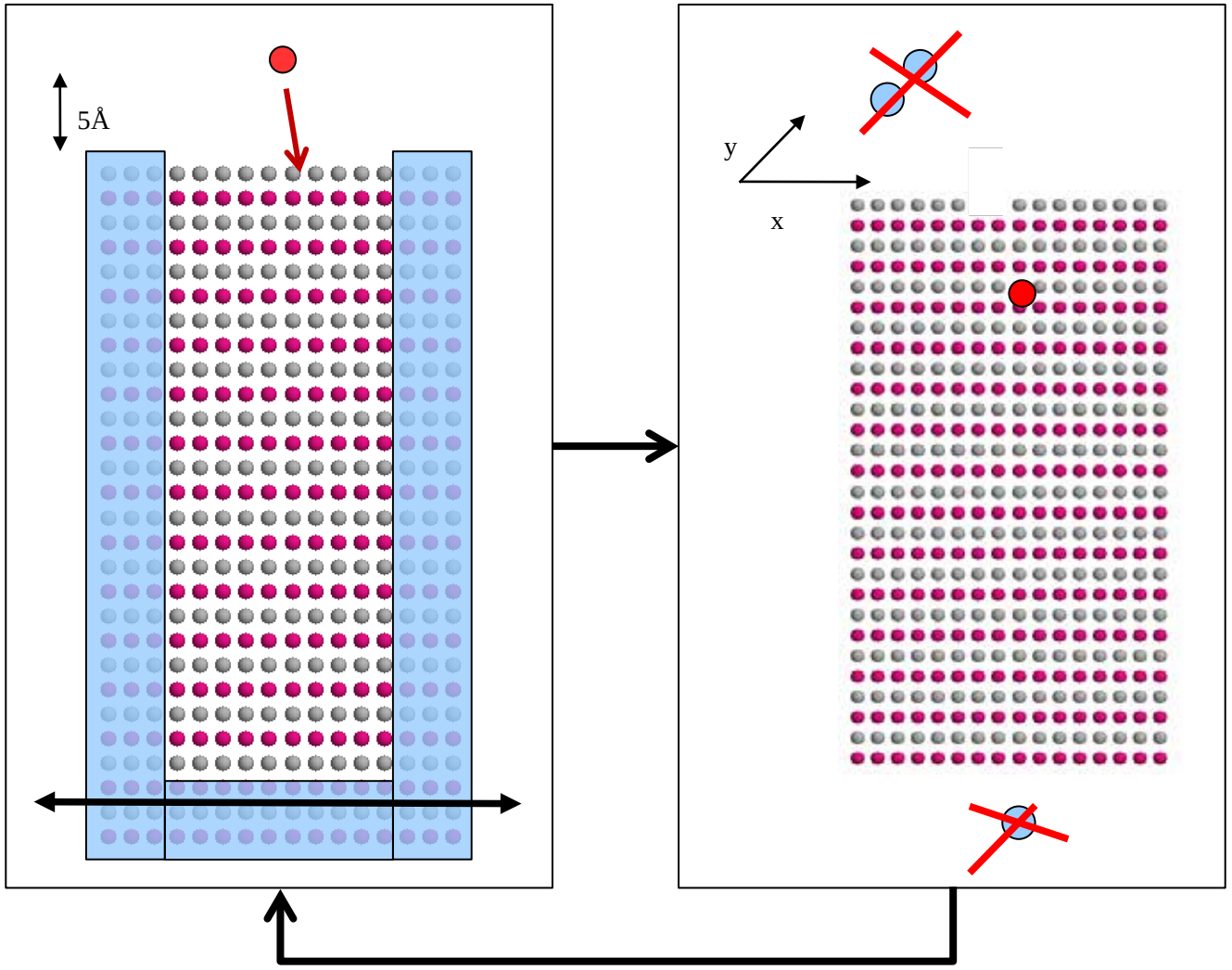
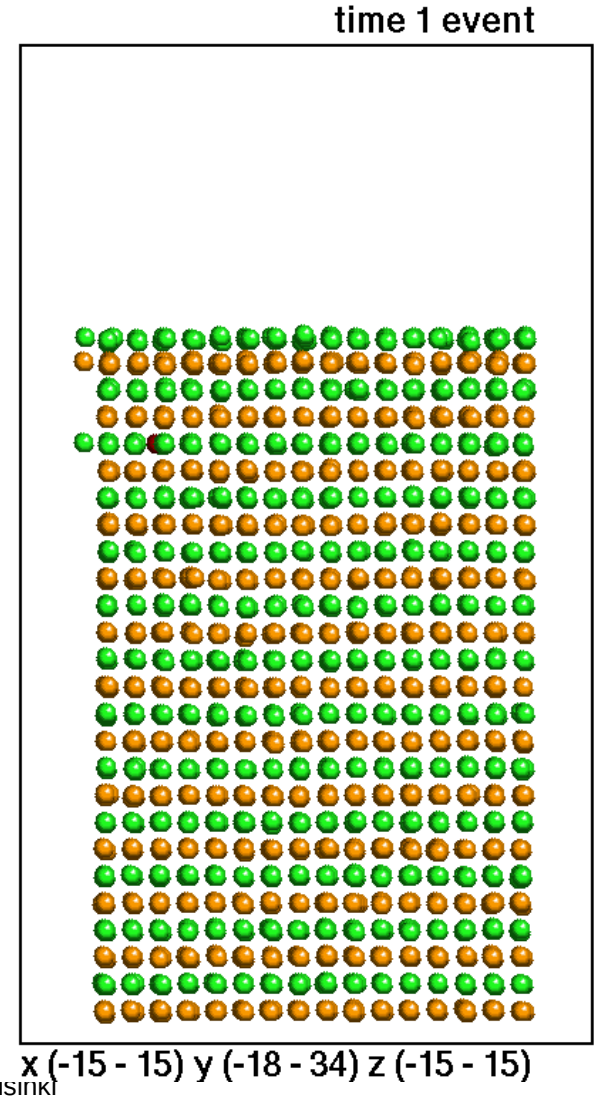
Border cooling

Formalism 2: cumulative simulations



Example from cumulative bombardments

D + 10% He bombardment of C-terminated WC surface



Importance of interatomic potentials

- The key part of any molecular dynamics algorithm is getting the forces acting between atoms (objects):

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

- In many cases this is actually the only physics input (rest is numerical mathematics that is well known)
  - Albeit in irradiation physics: also electronic stopping…
- Hence crucial to get interatomic potential $V(\boldsymbol{r}^{(i)})$ "right"
  - But can this be done?? Atomic world is quantum mechanical!

Tersoff-like potentials

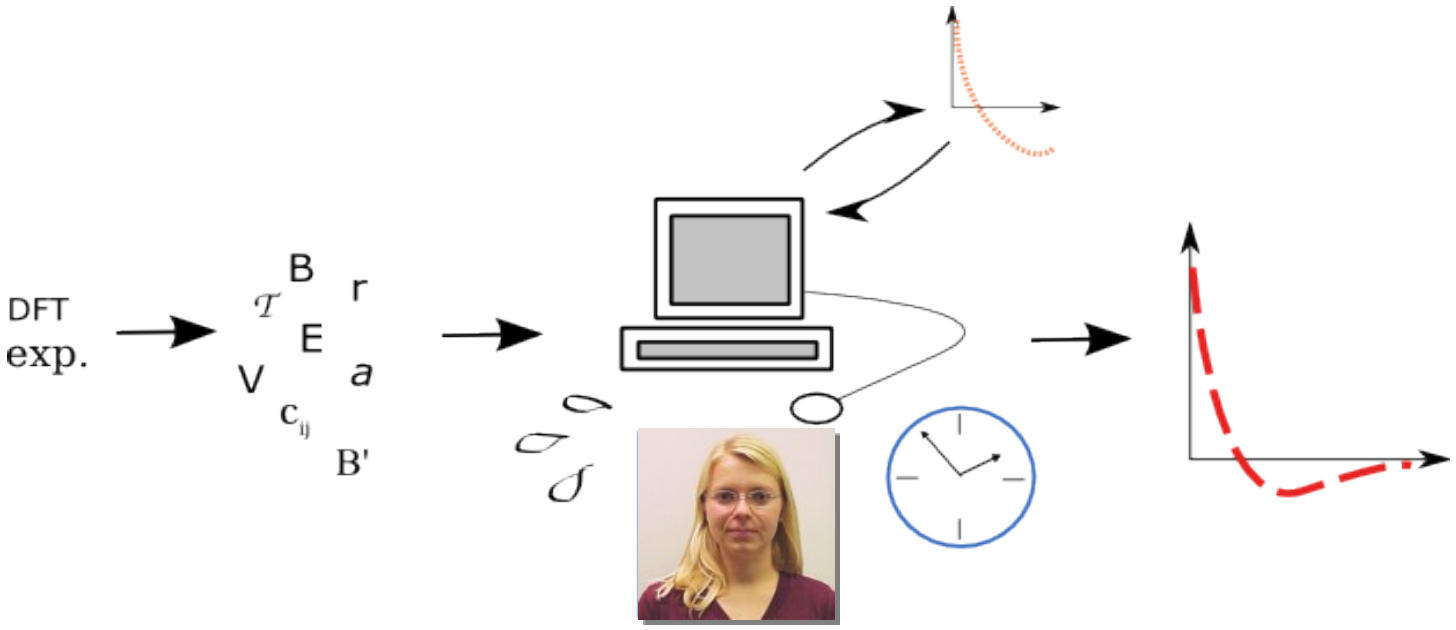
- For mixed systems our favourite type of potentials are the so called Tersoff-like ones
  - A.k.a. Brenner-like or bond-order potential)

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

- Advantages:
  - Without angular term, reduces to Finnis-Sinclair like potential that work well for multitude of metals
  - Works well for carbon in all basic phases (graphene, diamond, nanotube, amorphous carbon)
  - Has physical motivation (Linus Pauling's theory of chemical bonding)
- 8-11 parameters per A-B interaction pair, but 4 of these have direct physical motivation in dimer properties

The really hard part

- Constructing a good potential is the hard part!
- It needs lots of effort, and always leads to compromises
  - Computers cannot compromise – humans needed
  - Some testing (like melting point) cannot be automated

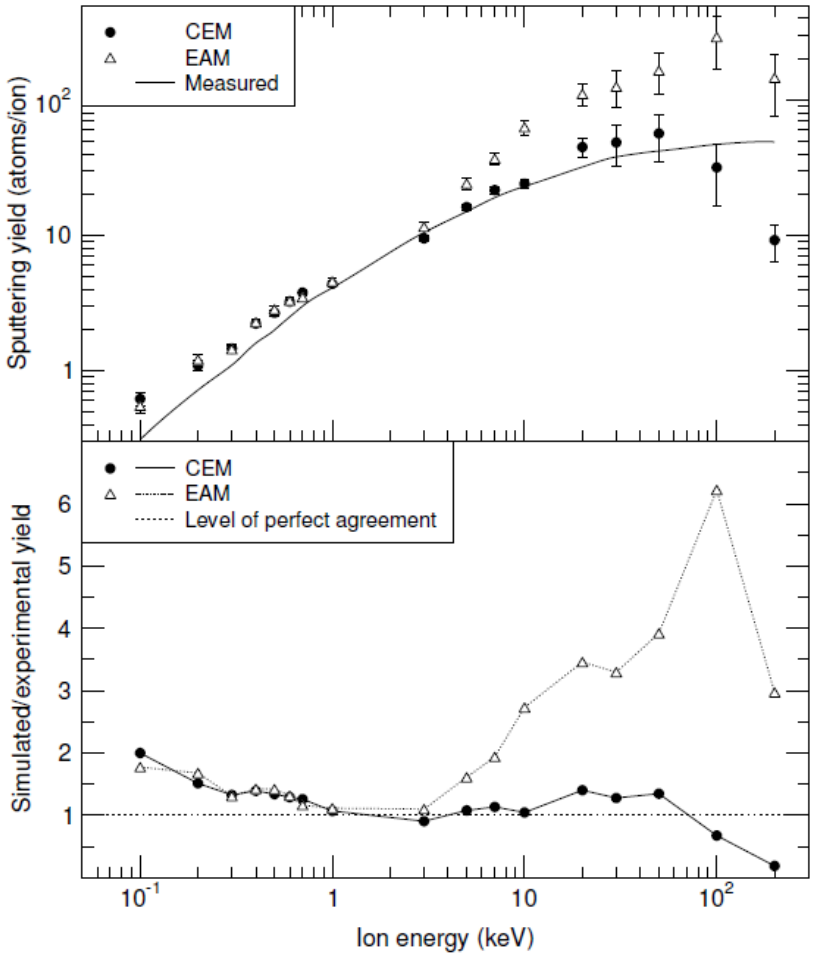


Comparison of potential ”quality”

- There is no unique way to say that one potential is superior to the other
  - Some fits may be outright lousy (e.g. negative elastic constants), many potentials have false (experimentally nonexistent) minima
    - These can be ruled out
  - But how to choose among good-quality fits?
- **Comparison with experiments in application of interest!!**
  - But: then predictive power is lost
  - And experiments not always reliable either…
- **Potential-to-potential comparisons!**
  - If functional forms are independent, can be quite good way!

Examples of reliability studies: Au sputtering

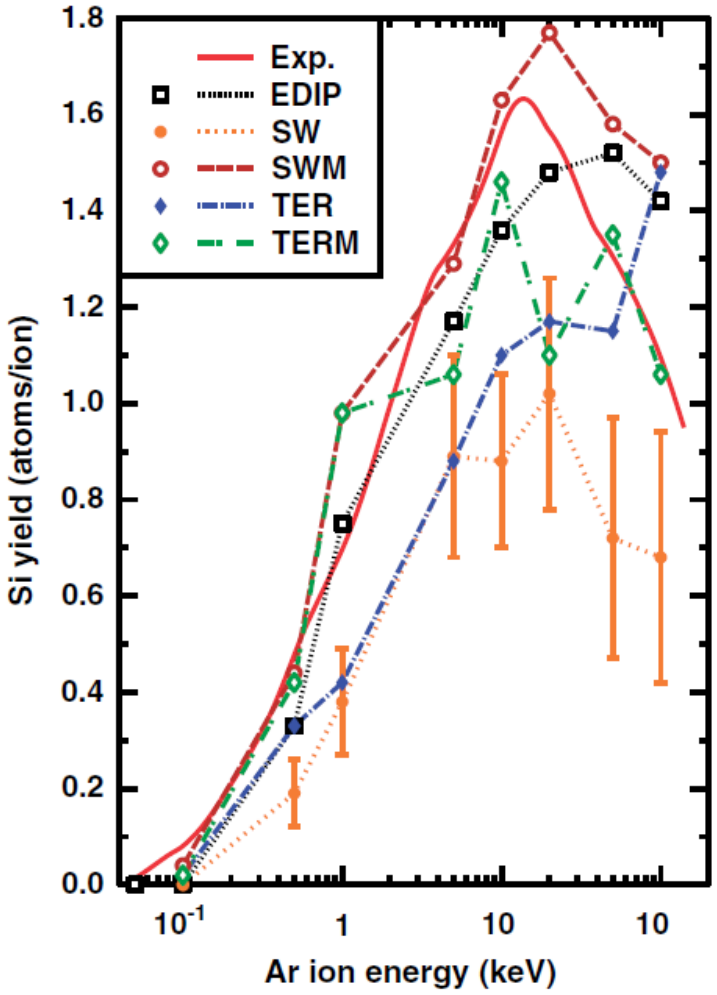
- Au irradiation of Au, EAM vs. CEM potential vs. experiment
- Conclusion obvious: CEM better



[J. Samela et al, Nucl. Instr. Meth. Phys. Res. B **239**, 331 (2005)]

Examples of reliability studies: Si sputtering

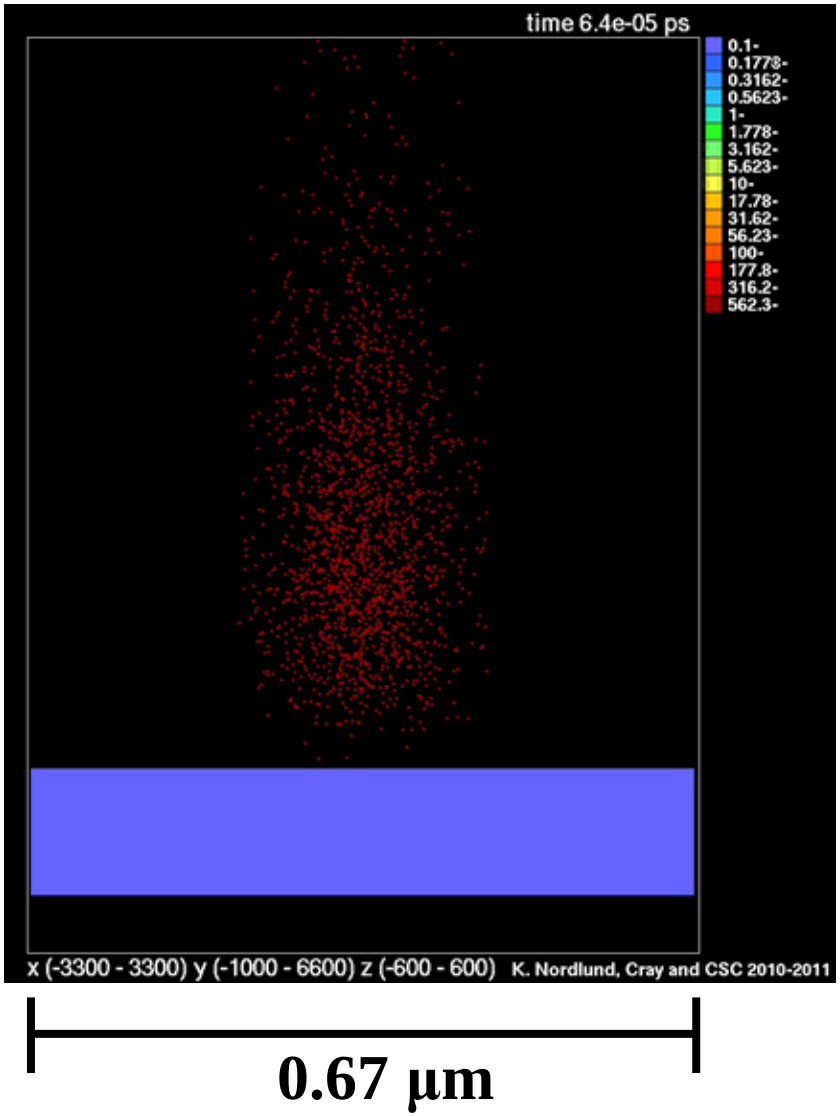
- Ar irradiation of Si
- 6 potentials, none agrees perfectly
  - But SWM, EDIP good



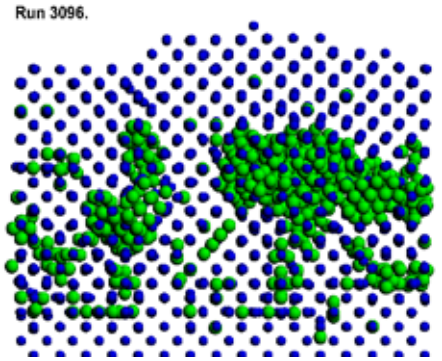
[J. Samela et al, Nucl. Instr. Meth. Phys. Res. B **255**, 253 (2007)]

1. Exascale computing

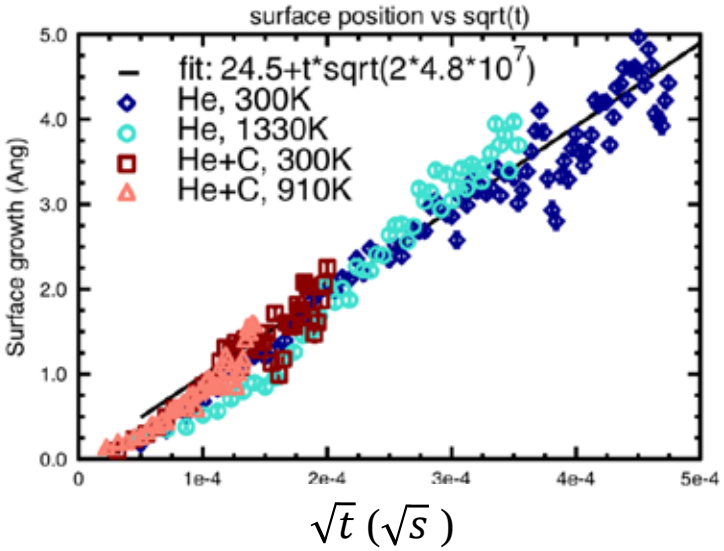
- Our MD code 'PARCAS' has now been rewritten to scale up to at least 100 000 cores
- Enables simulations of multi-billion atom systems



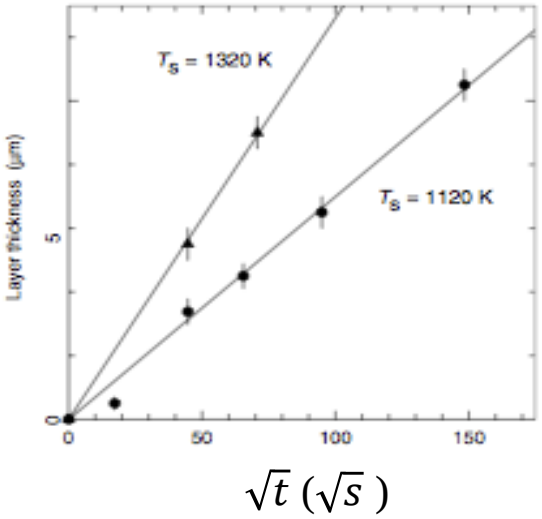
2. He fuzz in W



- We can simulate formation of a nano-scale He fuzz with MD and find that the growth proceeds as $\sqrt{\text{fluence}}$ => excellent qualitative agreement with experiments



$\sqrt{t}$ ($\sqrt{s}$)



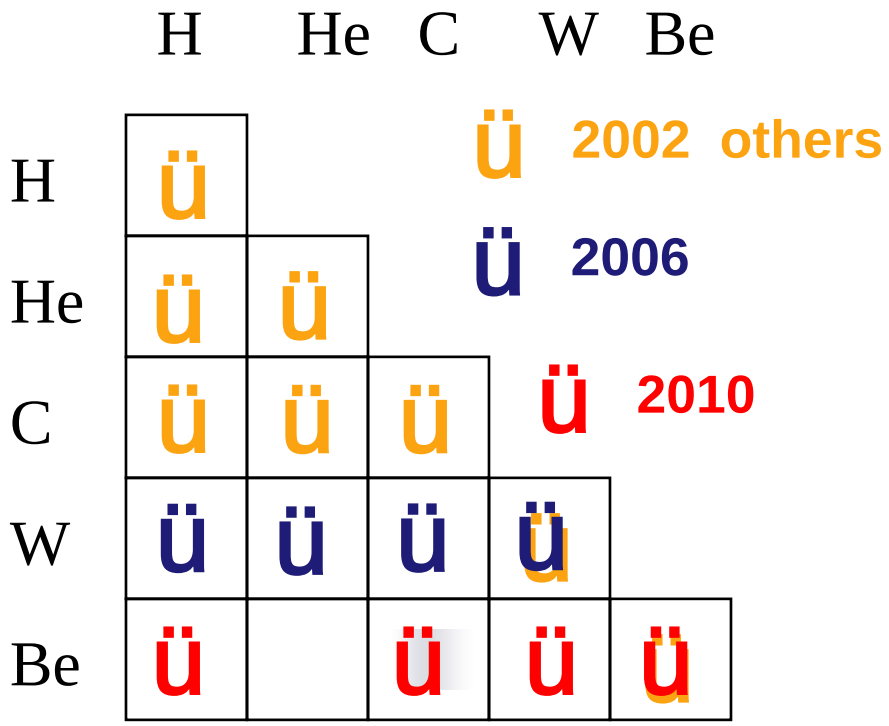
$\sqrt{t}$ ($\sqrt{s}$)

- But prefactor way (1000x) too large
  - We are working on that!

[A. Lasa et al, NIMB (2012) accceptedish]

Set of potentials

- In 2003 – 2010 we made a potential set for the full Be-C-W-H system
  - He as pair potential
- Later Ahlgren in our group made improved potential for W and Guang-Hong Lu's group made improved potential for W-H

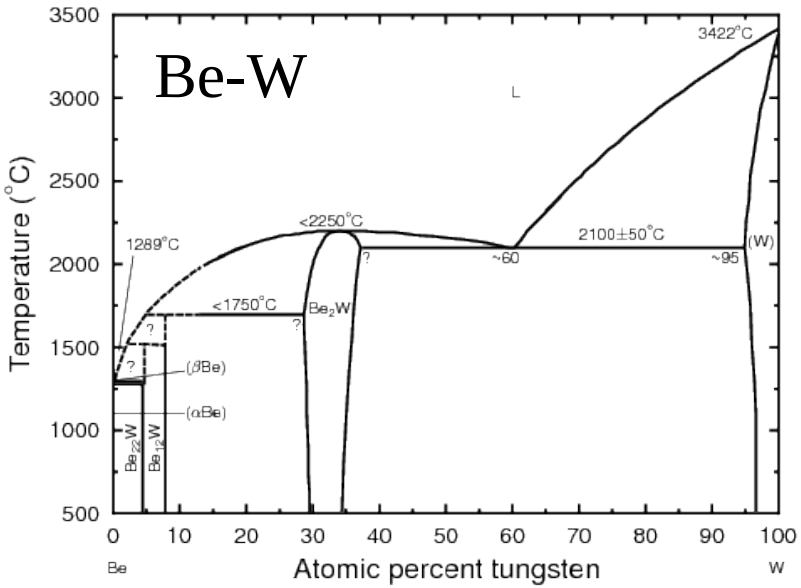


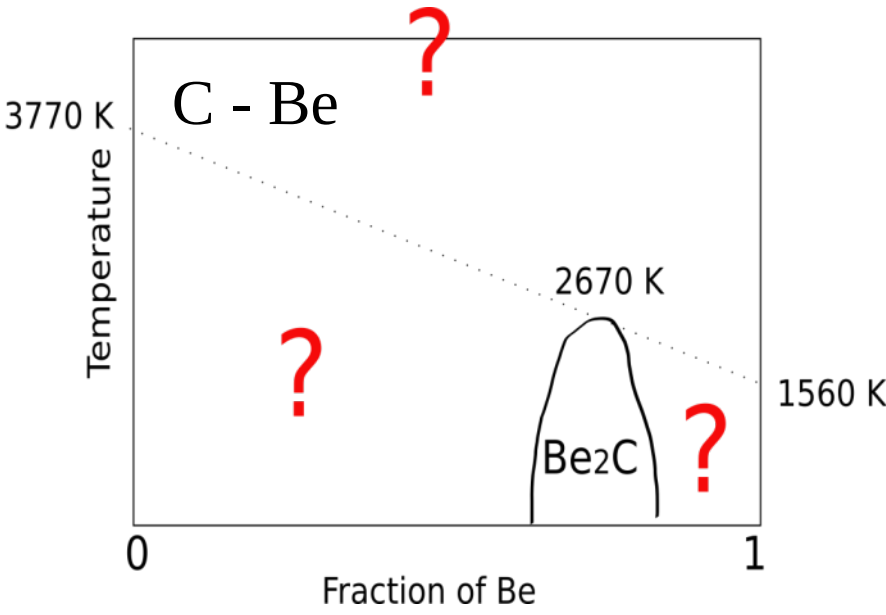
[WCH: Juslin et al, J. Appl. Phys. **98**, 123520 (2005)]

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

Observations of phase formation

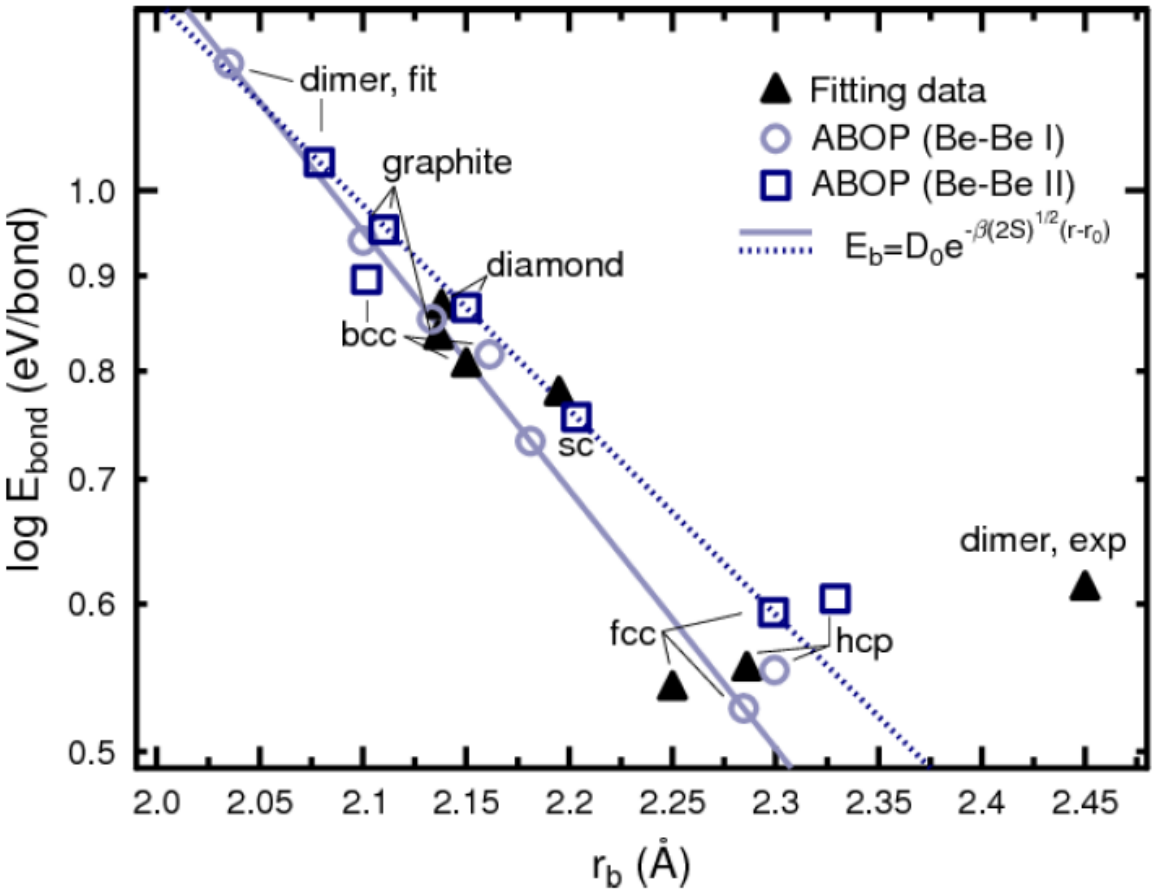
- Our interatomic potentials aim to describe all crucial phases of the materials involved correctly.
- Hence they should be able to reproduce the central part of the phase diagrams – to the extent they are known…





The pure Be potential

- Fit quality to different phases

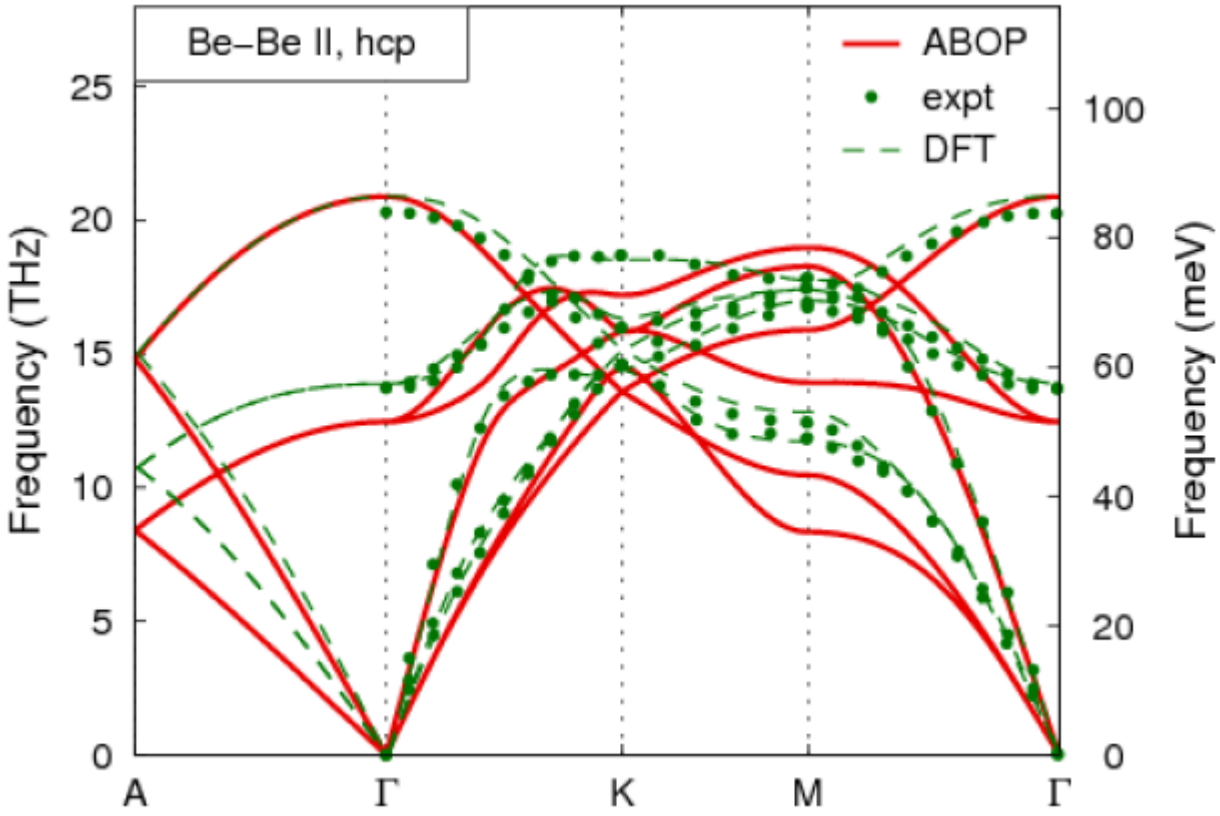


- Pot I better for HCP ground state
- Pot II better for low-coordinated states

=> Maybe better for rough surfaces?

The pure Be potential

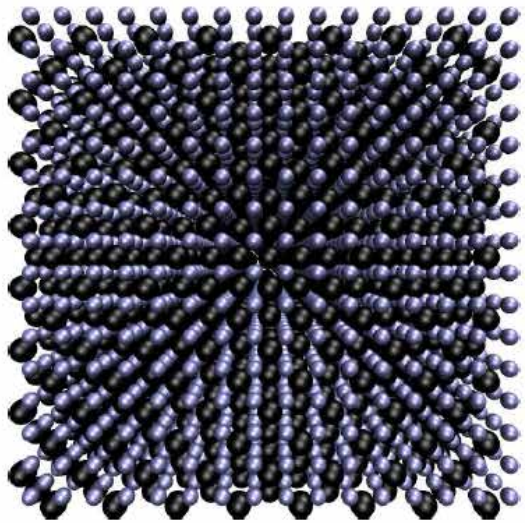
- Phonon dispersion properties well reproduced



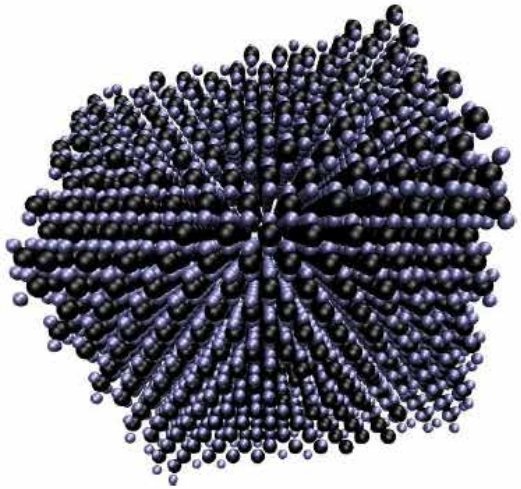
The Be-C potential

- The most important feature of our Be-C potential is that it keeps the (only known) Be_2C intermetallic phase stable

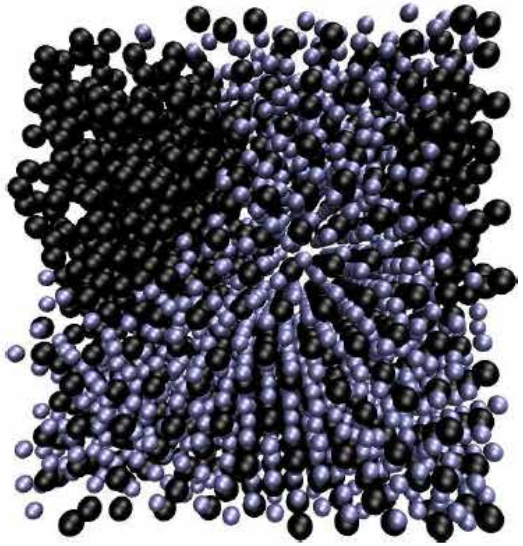
Ideal Be_2C antifluorite structure



Same structure obtained from random melt of Be_2C_1 composition



Segregated BeC obtained from Be_1C_1 random melt



The Be-H potential

- Defects and molecules well reproduced

Molecules

	ABOP		DFT [44]
	Be-H I	Be-H II	
Be-H			
E_c/atom	-1.30	-1.30	-1.30
r_b	1.34	1.34	1.34
Be-H_2 linear			
E_c/atom	-1.65	-1.61	-2.13
r_b	1.35	1.35	1.33
Be-H_3 D3h			
E_c/atom	-1.31	-1.46	-1.35
r_b	1.41	1.40	1.47
Be-H_3 C2v			
E_c/atom	-	-	-1.65
r_b	-	-	1.47
angle	-	-	53^o

Defects

	ABOP		DFT	
	Be-H I	Be-H II	Ref. [57]	Ref. [43]
Interstitials				
E_f^{BT}	1.22	1.35	0.8	1.58
E_f^O	1.46	1.71	unstable	1.79
Ground state	1.04	1.17	0.8	1.58
BT to O migration barrier				
E_m	0.43	0.45		0.38

The Be-W potential

The ground state

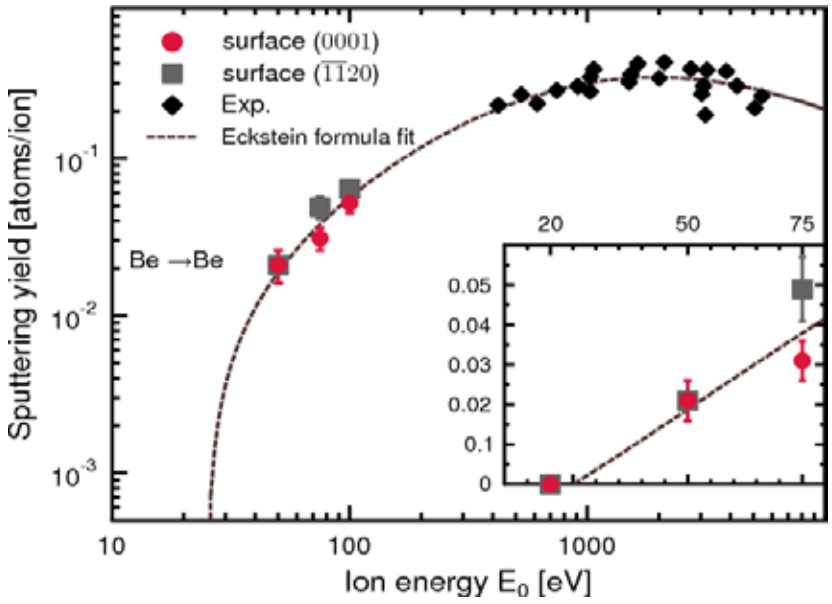
Be_2W ($MgZn_2$, C14, $P6_3/mmc$, no. 194)			
a (Å)	4.46[a]	4.46	4.60
c/a	1.63[a]	1.645	1.63
x_1		-0.169884	-0.174
z_2		0.0668	0.0598
E_c (eV/f.u.)		-21.11	-20.88
ΔH_f (eV/f.u.)		-0.61	-4.8
B (GPa)		224.6	167.3
B'		4.34	3.88
C_{11} (GPa)		451	259
C_{12} (GPa)		98	125
C_{13} (GPa)		107	118
C_{33} (GPa)		436	265
C_{44} (GPa)		170	61
T_{melt} (K)	2523[a]		2100±100
$Be_{12}W$ ($Mn_{12}Th$, $D2_b$, no. 139)			
a (Å)	7.362[a]	7.260[b]	7.55
c/a	0.573[a]	0.566[b]	0.53
x_1			0.365
x_2			0.280
E_c (eV/f.u.)		-40.56[b]	-63.05
ΔH_f (eV/f.u.)			-10.7

Molecules (together with M. Probst)

molecule	DFT [22]	DFT This work	ABOP
BeW			
r_{Be-W} (Å)	2.11	2.062	2.12
E (eV)	-3.78	-1.71	-3.74
ω (cm^{-1})	480	570	454
BeW_2 linear			
r_{Be-W} (Å)		–	2.11
E (eV)		unstable	-6.96
BeW_2 non-linear			
r_{Be-W} (Å)		2.229	2.21
E (eV)		-10.97	-10.58
θ (°)		58.0	61.8
BeW_3			
r_{W-W} (Å)		2.333	2.33
r_{Be-W} I (Å)		2.242	2.36
r_{Be-W} II (Å)		2.339	3.84
E (eV)		-16.06	-17.84
BeW_4			
r_{Be-W} (Å)		1.871	1.93
E (eV)		-17.68	-20.70
Be_2W linear			
r_{Be-W} (Å)		2.132	2.11
E (eV)		-3.94	-6.96
Be_2W non-linear			
r_{Be-W} (Å)		2.115	2.12
E (eV)		-3.94	-7.61
θ (°)		63.7	59.3
Be_3W			
r_{Be-Be} (Å)		2.355	2.12
r_{Be-W} I (Å)		2.127	2.17
r_{Be-W} II (Å)		2.098	2.20
E (eV)		-6.04	-11.12
Be_4W			
r_{Be-W} (Å)		2.172	2.17
E (eV)		-7.24	-12.31

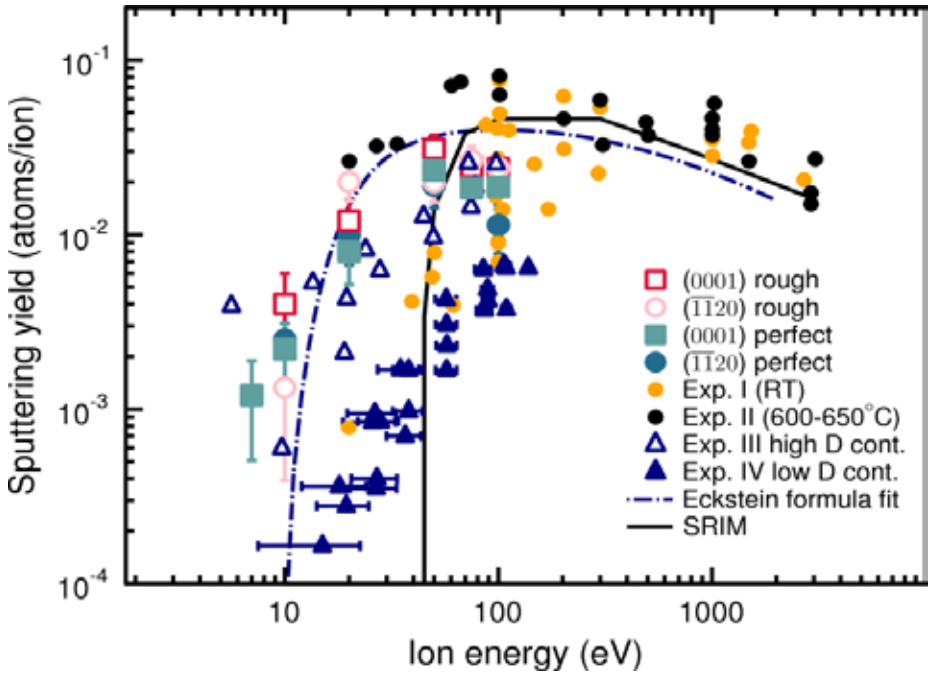
Self-sputtering of pure Be

- 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



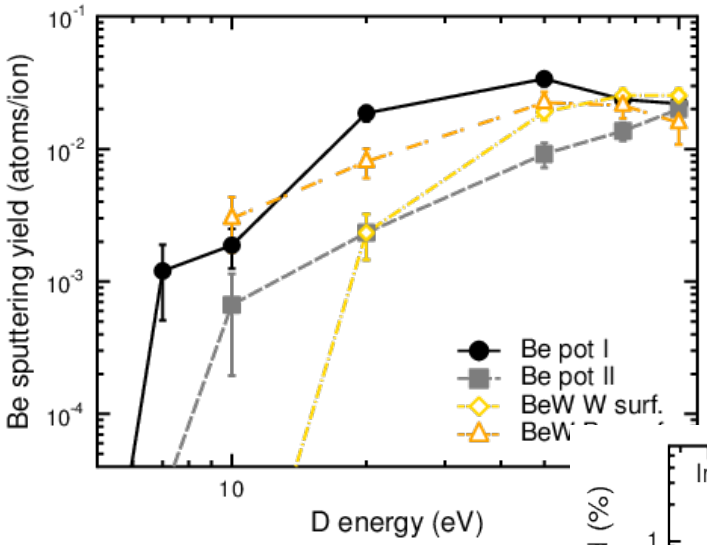
Sputtering of initially pure Be by D

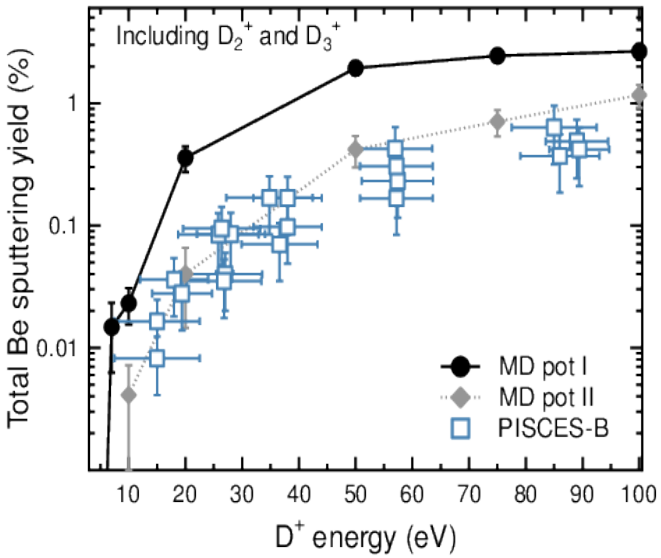
- Our simulations agree with plasma experiments done at the PISCES-B facility at low energies
  - At higher energies with the rest
- Sputtering is seen at 7 eV!



Results on Be sputtering
Potential dependence

§ The sputtering yield of pure Be depends on the potential



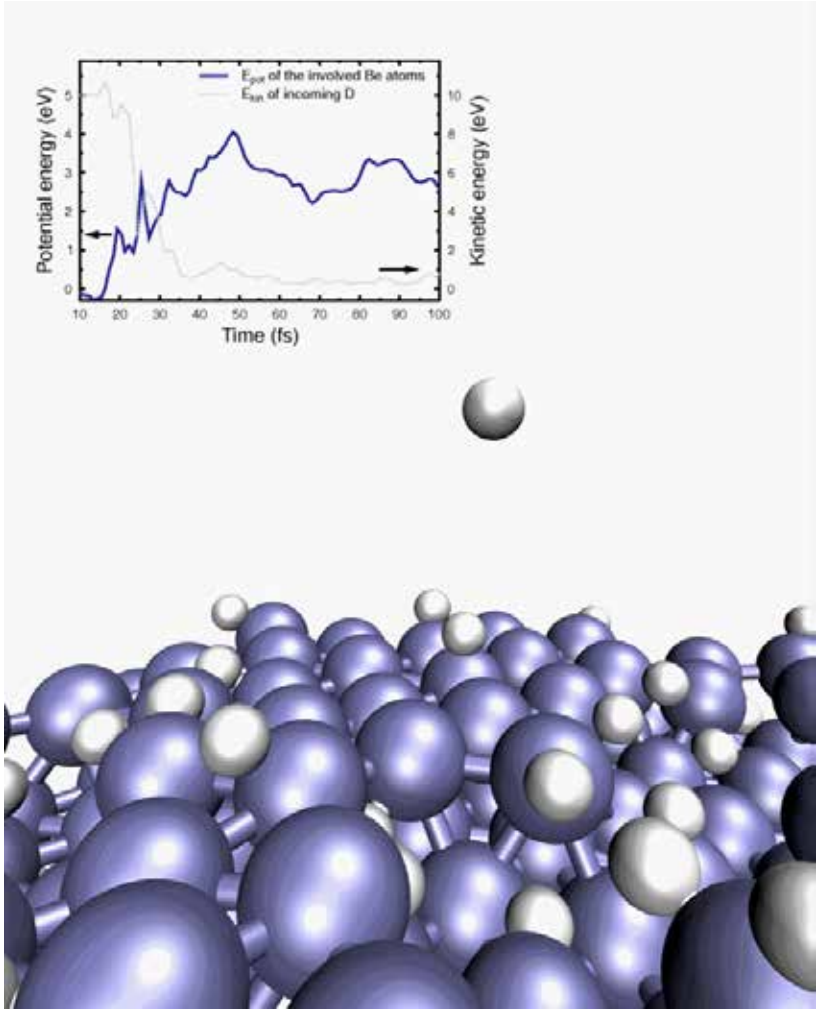


Pot I vs Pot II:
Pot I has:
- Larger cutoff
- Different elastic constants
- Different thermal expansion
- **Lower surface binding energy**

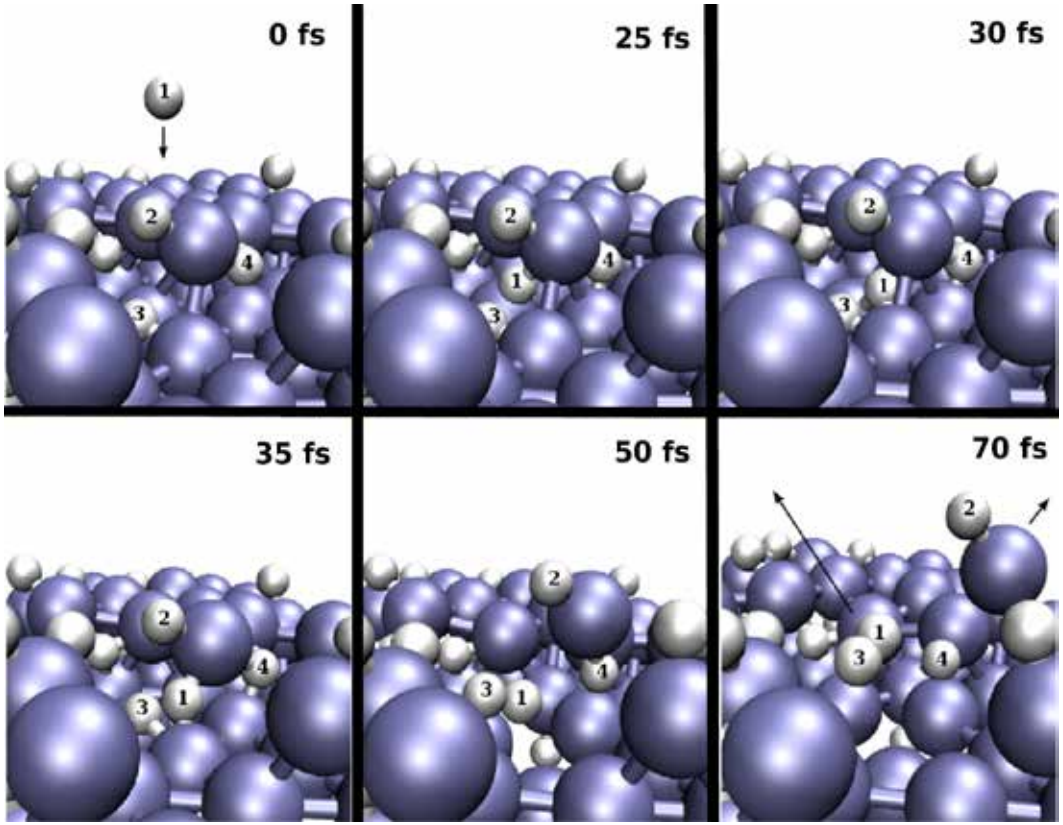
Results on Be sputtering

Sputtering of initially pure Be by D

- The low-E sputtering is explained by swift chemical sputtering



Sputtering of initially pure Be by D

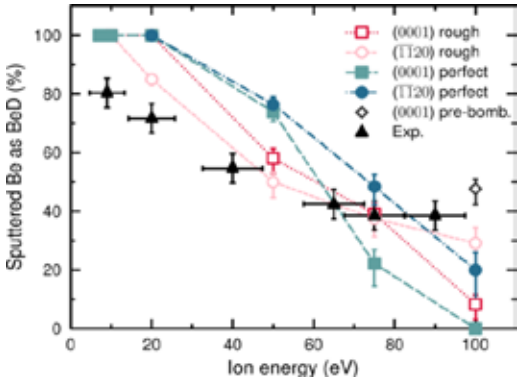


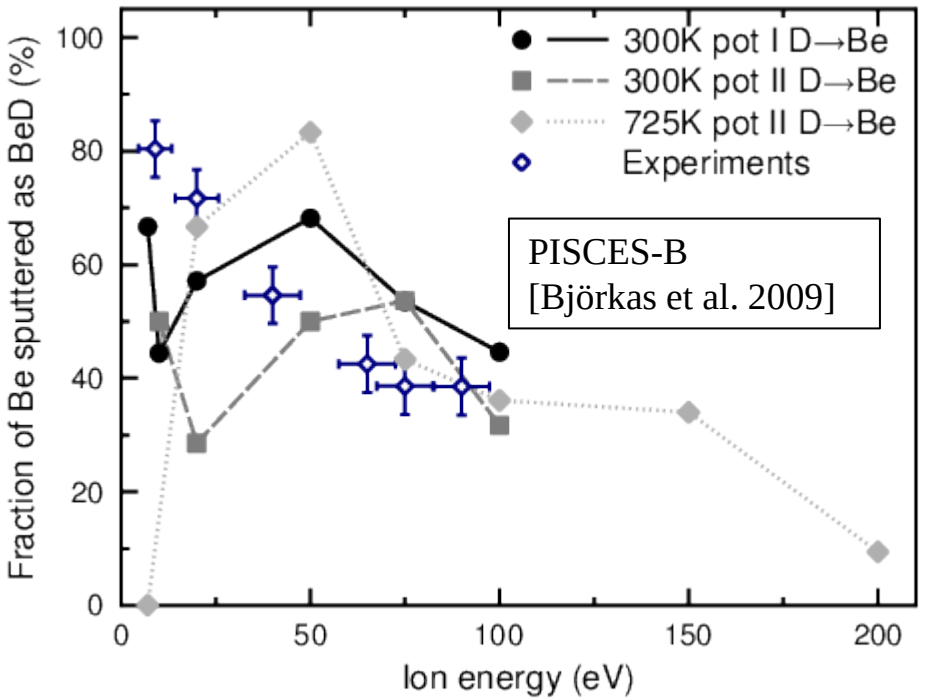
- Snapshots of a similar event
- The D ion breaks all four of the Be-Be bonds
- Ideally a surface Be has nine bonds
- „Roughnening“ of the surface is needed

Results on Be sputtering

D irradiation of initially pure Be

- At low energies a large fraction of Be is eroded as BeD molecules
  - **Chemical sputtering!**
- This fraction decreases with ion energy
- This collaboration came out of a previous IAEA meeting with Doerner!

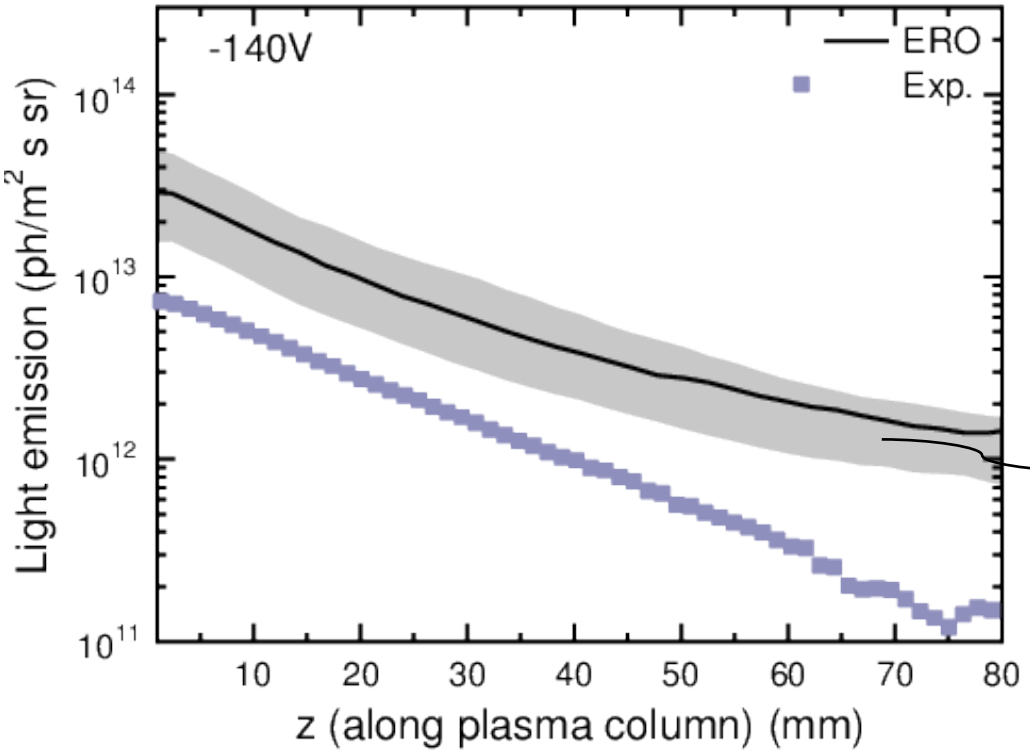




Results on Be sputtering

D irradiation of initially pure Be

- Carolina Björkas has now implemented BeD into ERO, and is able to go from the MD sputtering yields to comparing with PISCES-B experiments



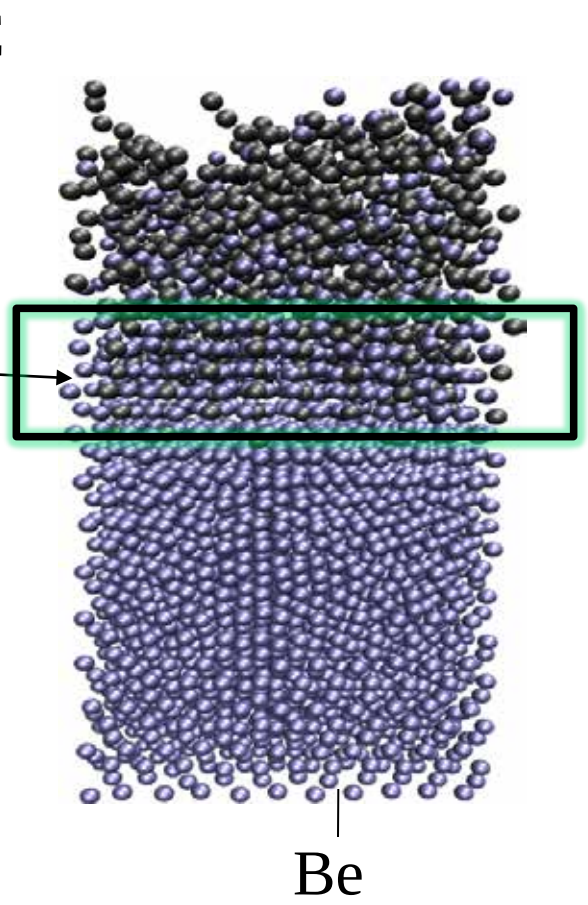
Can be explained by uncertainties in sputtering yields or spectroscopic data?

Range including uncertainties in n_e and T_e

Results on Be sputtering

C irradiation of Be

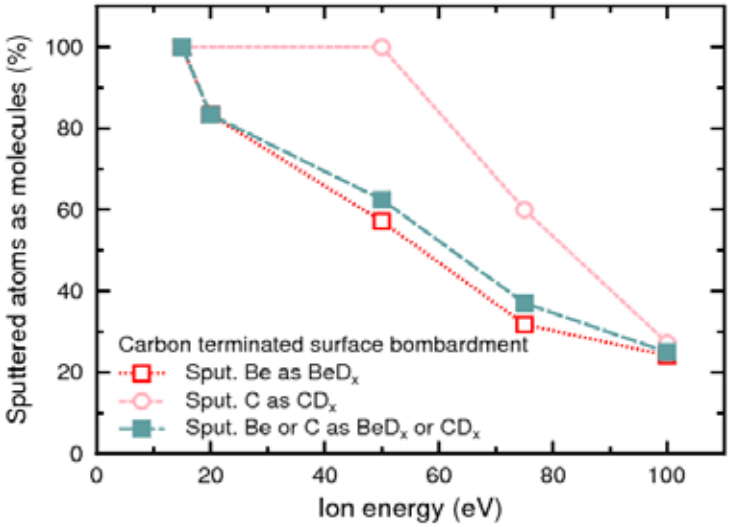
- 20 – 100 eV C ion irradiation
  - flux ~$2 \cdot 10^{25}$ $m^{-2}s^{-1}$
  - @ 1500 K
- Layers of Be_2C are formed!
- Carbide layers will form on beryllium surfaces

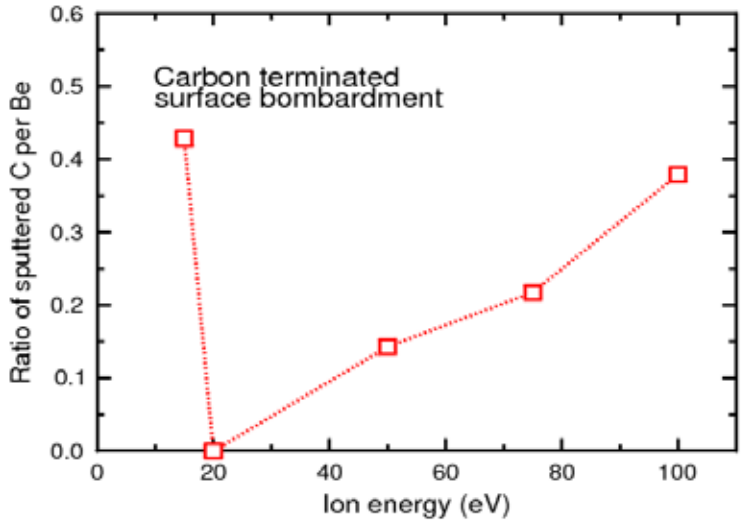


Results on Be sputtering

D irradiation of Be_2C

- 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





Results on Be sputtering

Irradiation of Be_2C

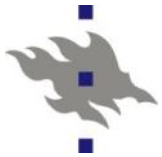
- Molecules sputtered: mostly BeD

	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

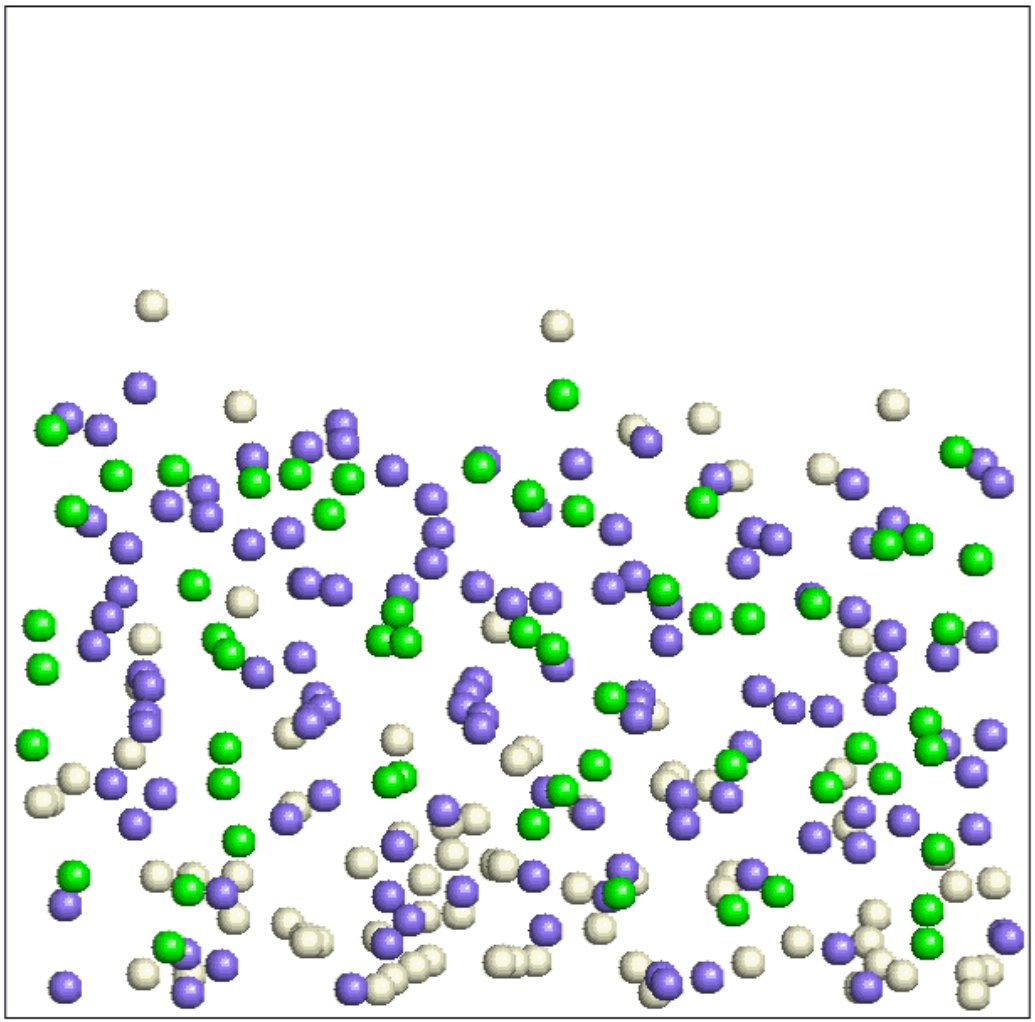
**In fact, a $BeDCD_3$ molecule was sputtered

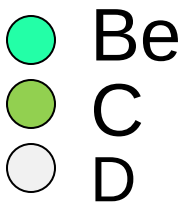
[M. Mehine, C. Björkas, K. Vörtler, K. Nordlund, and M. I. Airila, J. Nucl. Mater. 414, 1 (2011)].



Results on Be sputtering

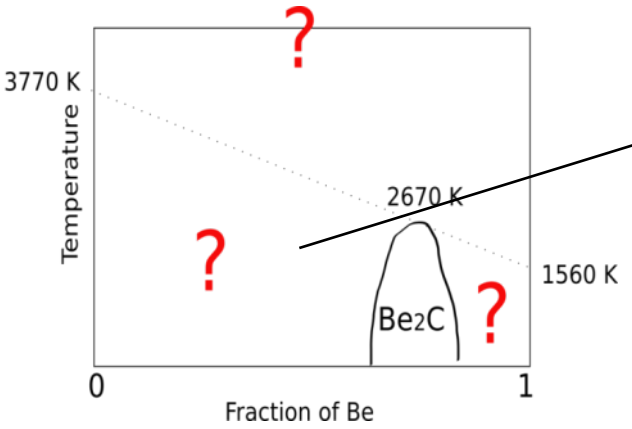
Irradiation of Be_2C

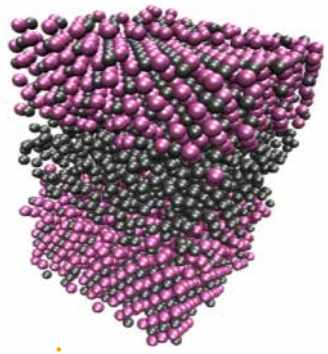




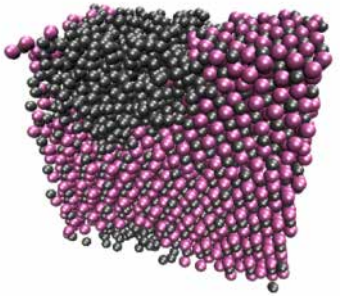
Random mixtures of Be and C

- 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

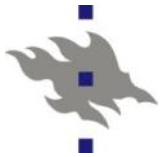




layered BeC



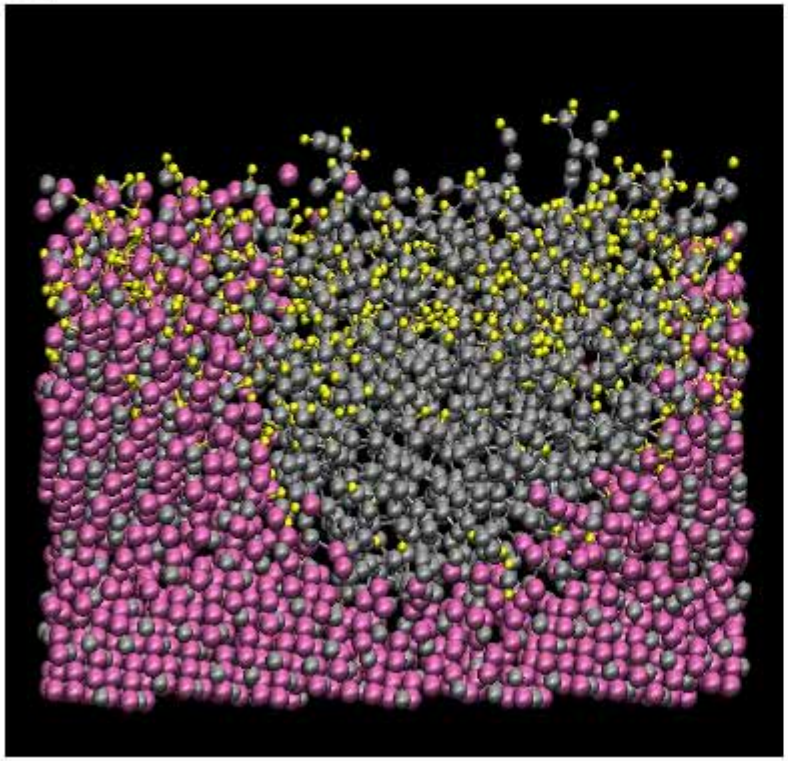
BeC cell, mixed



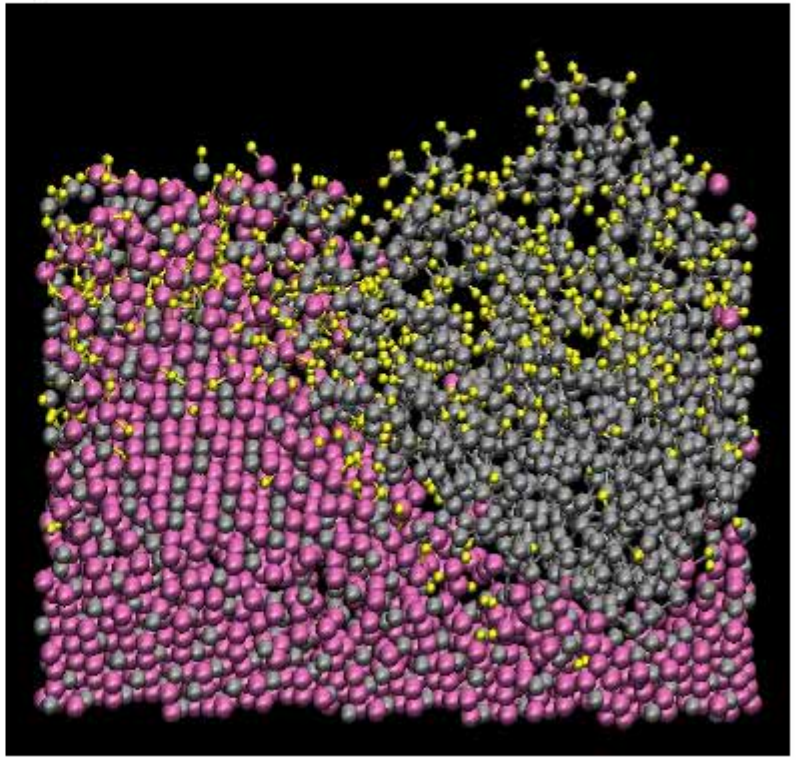
Random mixtures of Be and C

20 eV D → Be_2C / C mixed surface after (a) 2000 impacts and (b) 3000 impacts, pink = Be; gray = C; yellow = D

a)

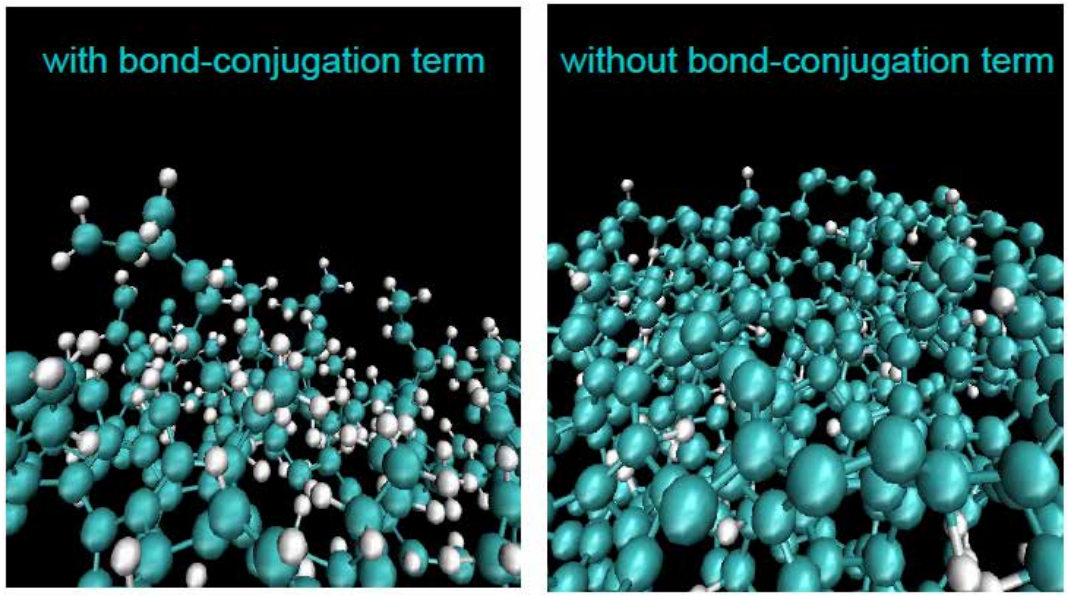


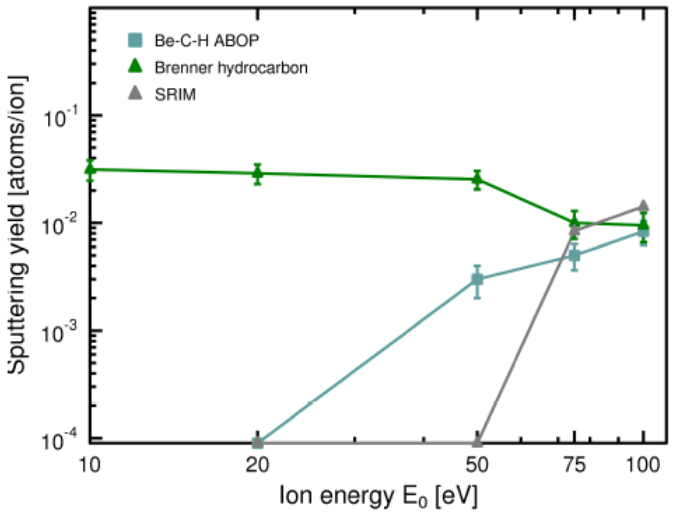
b)



Irradiation of mixed Be-C systems

- We noticed a nontrivial potential dependence, though.
- Without the chemical so called ”bond conjugation” term for C, almost no H sticks to a mixed Be-C surface with high C content, and sputtering yield is almost zero
- With it, higher yields, which is more realistic
- **Morale of the story: surface chemistry really important!**

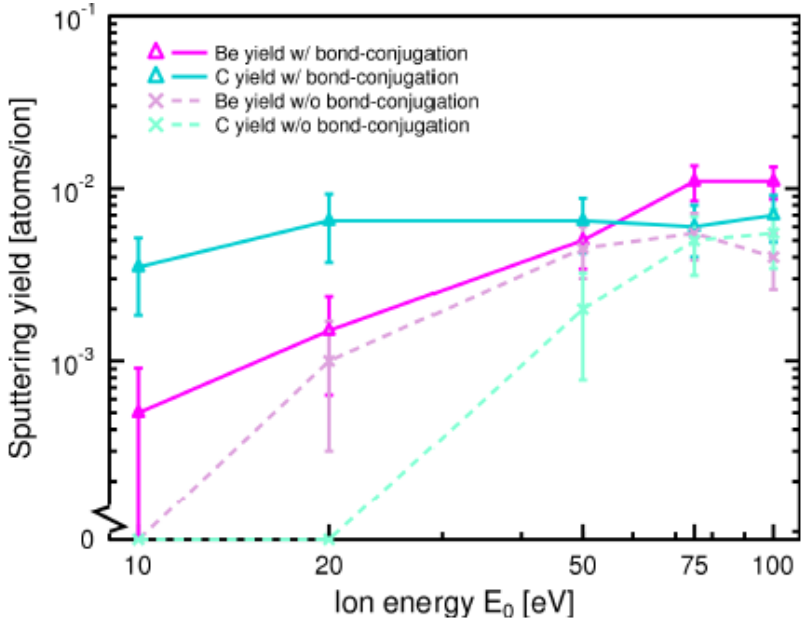


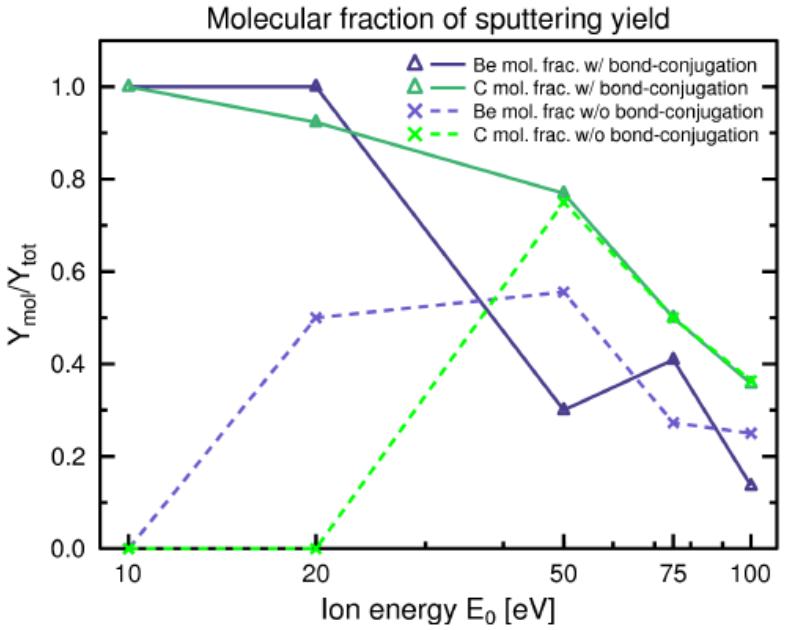


[A. Meinander et al, NIMB (2012) submiited].

D irradiation of mixed Be-C systems

- Results for two versions of potential

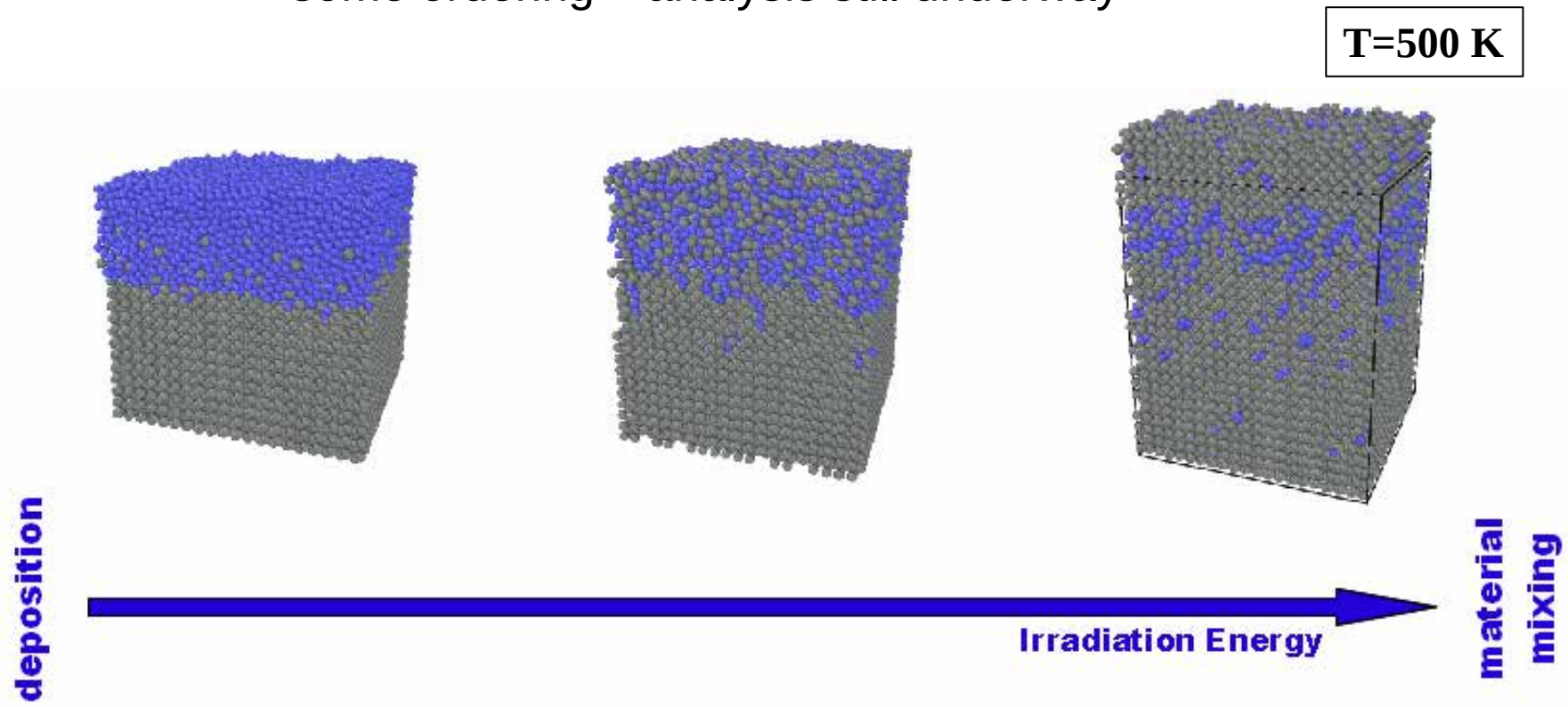




- Sputtering of CxDy-molecules from partial C-surface still increasing between 2000 and 3000 impacts for 10 eV and 20 eV D ions
- Sputtering of Be shows no increase after 2000 impacts, neither from mixed surface nor from carbide surface

Be irradiation of W surfaces

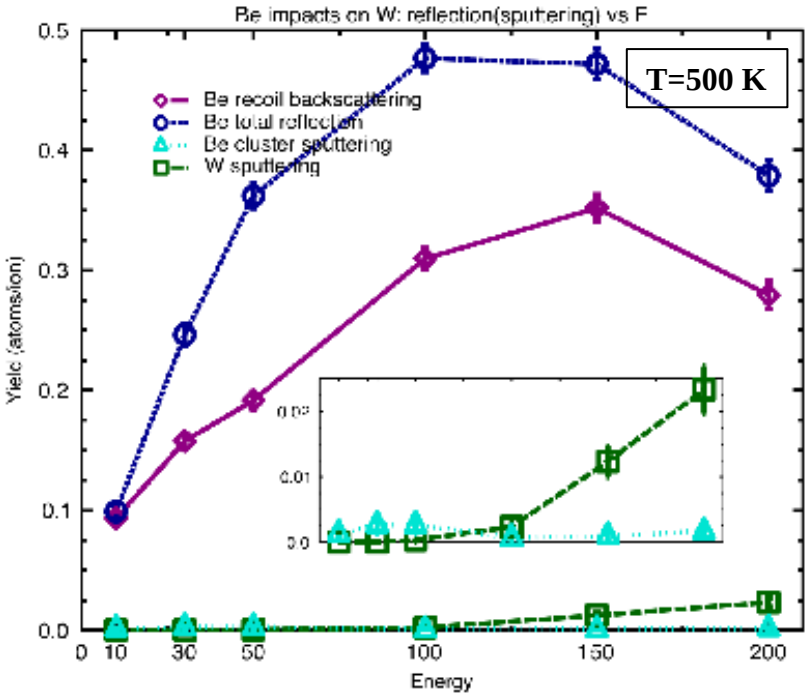
- Be bombardment of W makes for alloying, growth and some ordering – analysis still underway



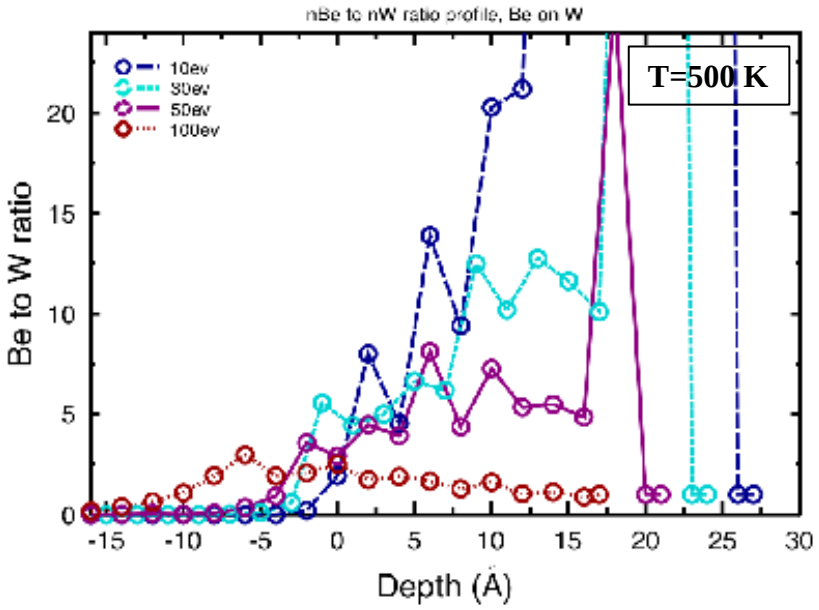
Results on Be sputtering

Be irradiation of W surfaces

Be reflection, W sputtering...



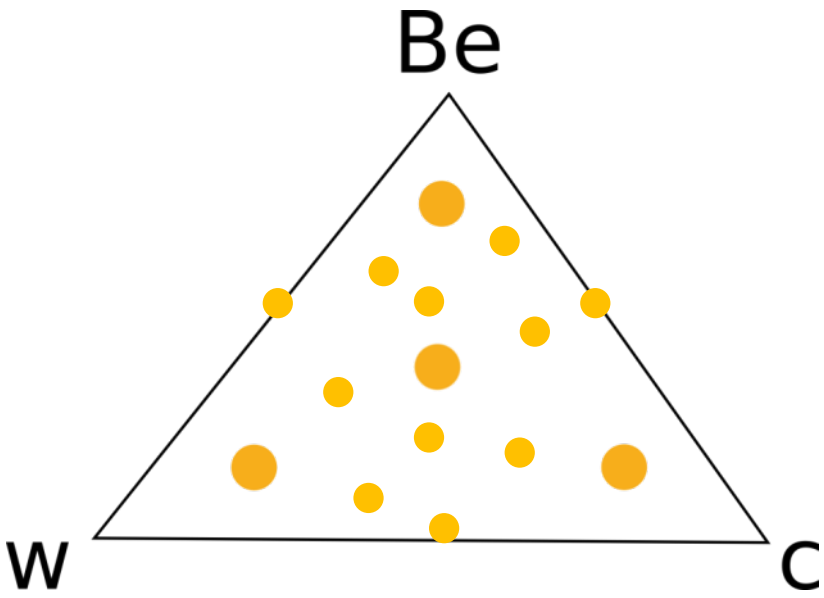
...and alloying



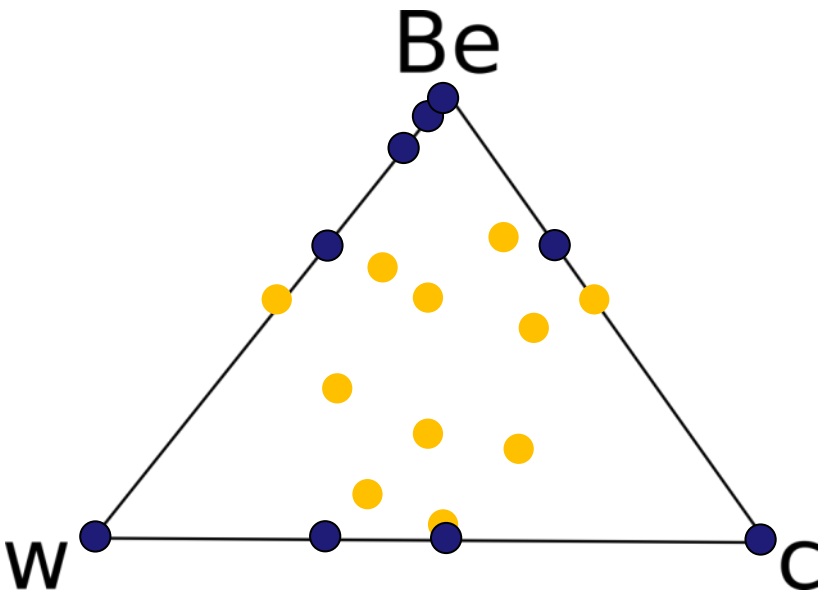
Conclusions on interpolation

- The observation that phase segregation occurs even on MD timescales is actually very encouraging!!

Instead of:



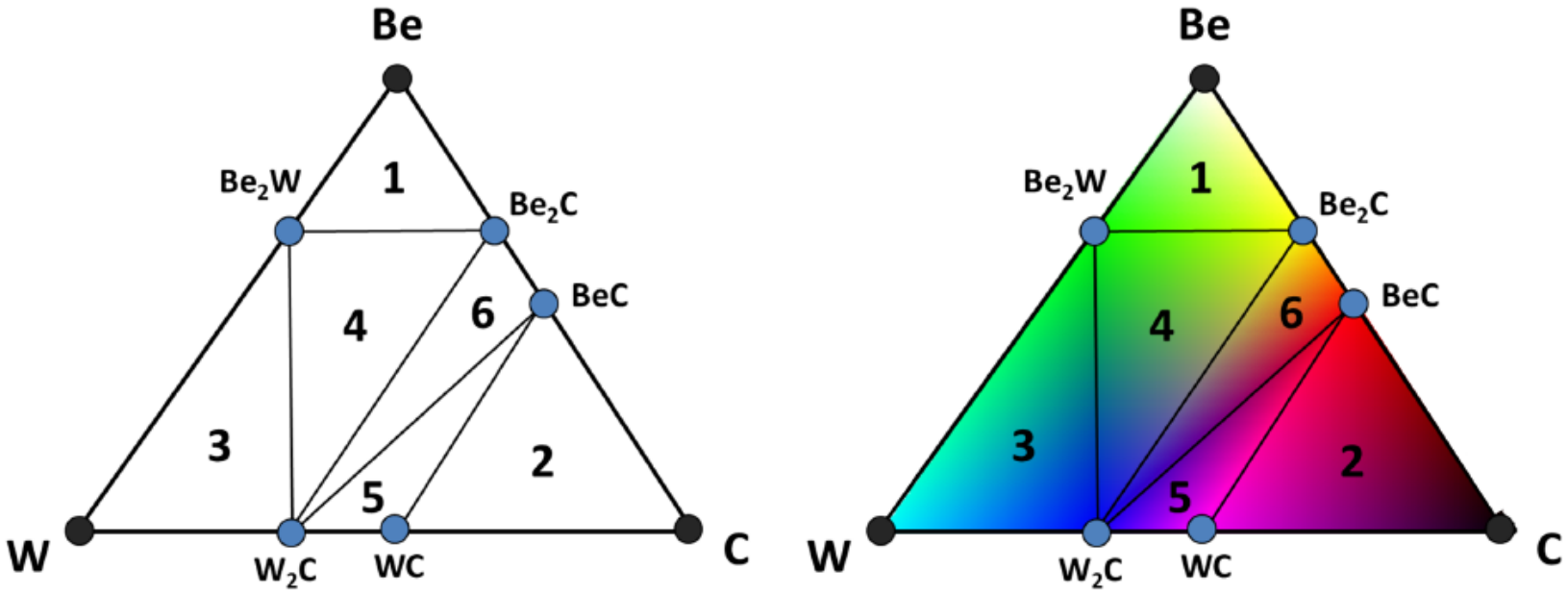
Only existing phases needed*(?):



*** There are no known intermediate ternary phases**

Interpolation scheme

- Linear interpolation scheme between main phases has been devised



[Markus Airila et al, PSI 2012 proceedings, submitted to JNM]

Conclusions

- MD can be extremely useful for obtaining qualitative understanding of what is going on!
  - And this is most important in science!
- But getting quantitative agreement/predictive capacity is challenging due to uncertainties in the potentials
  - Situation is improving, but slowly…
- For the specific case of Be, we have shown that:
  - Be can sputter as BeD molecules
  - BeC mixtures segregate easily into Be, C and Be_2C heterogeneous phases
  - Be bombardment of C or W leads to alloying (even on MD timescales!)

midsummer…

June 30 – July 5 2013
8:30 am- 5:30pm only

Chairmen:
Kai Nordlund, chair
Flyura Djurabekova, chair
Jyrki Räisänen, co-chair
Timo Sajavaara, co-chair

- Fundamental physics
- Beam proc.
- Sputtering
- Oxides ceramics
- Ionic crystals
- Glass
- High Tc oxides
- Polymers
- Nuclear materials
- Applications
- Nanostructures

WELCOME!