Uniform-acceptance force-biased Monte Carlo: A cheap way to boost MD

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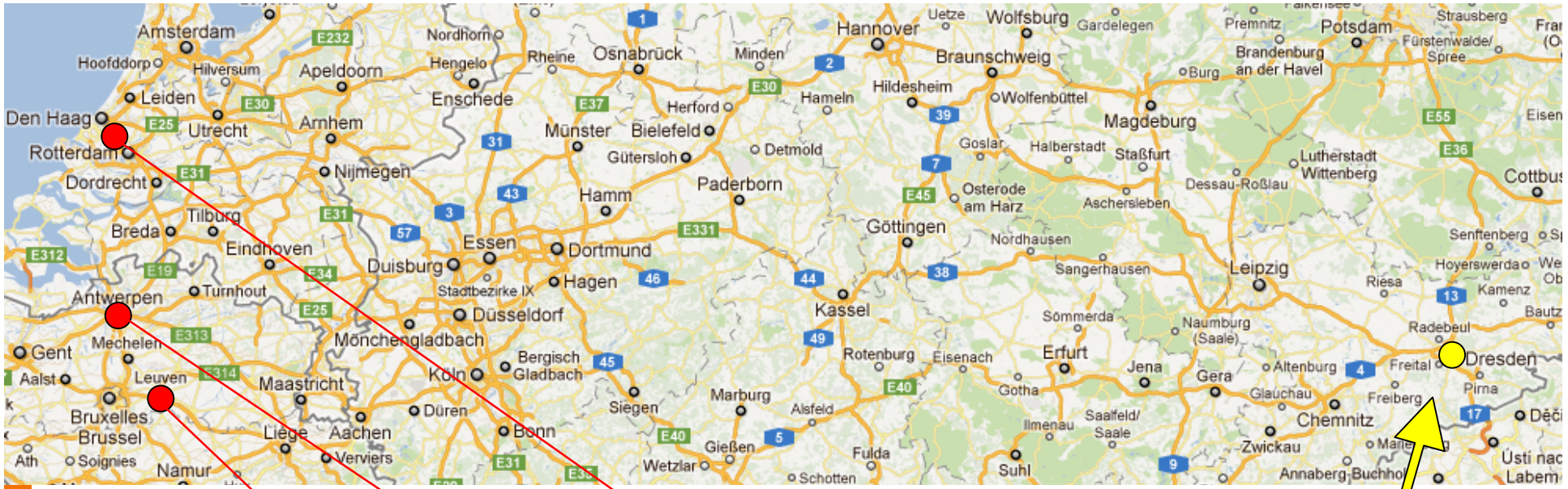

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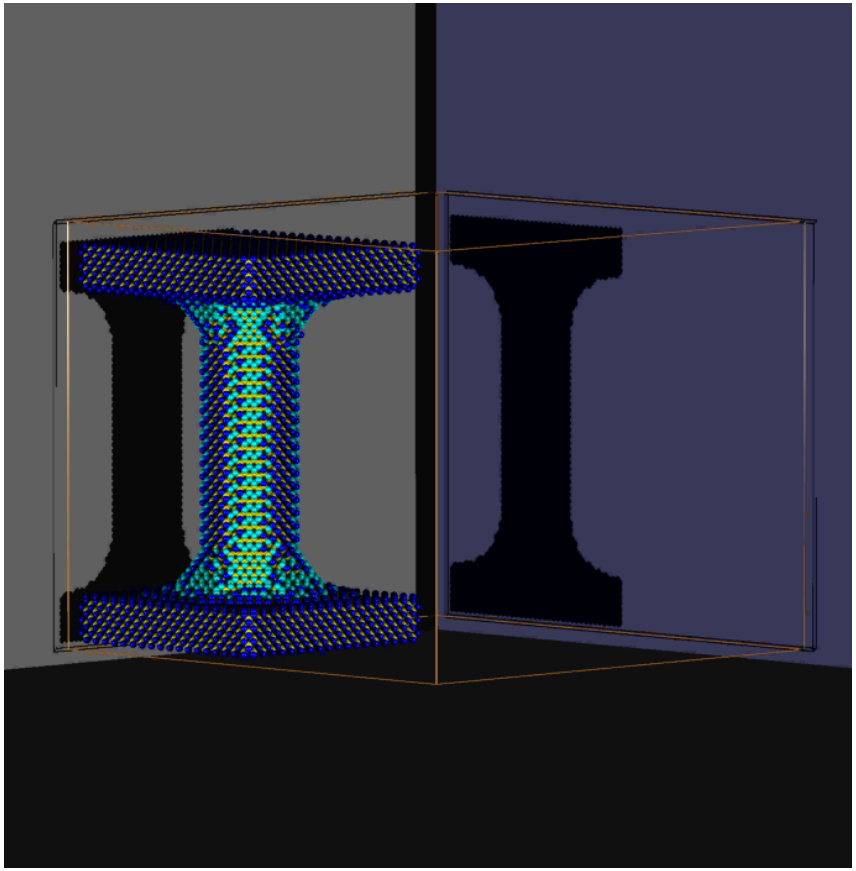
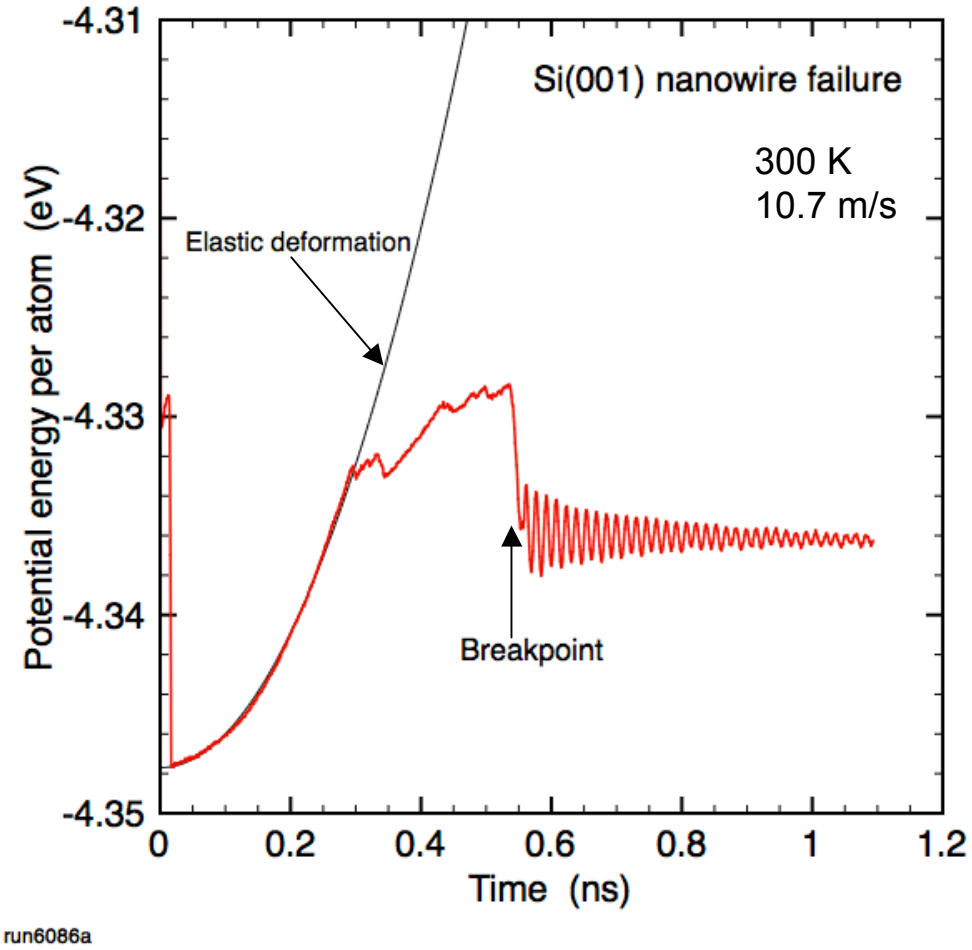
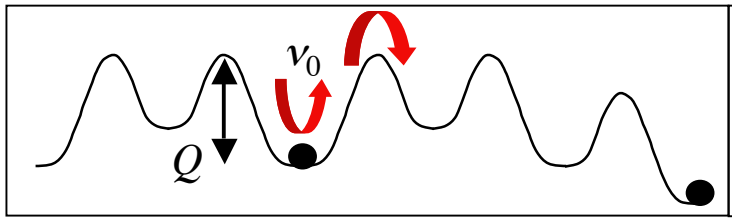
MD: Good for fast mechanics





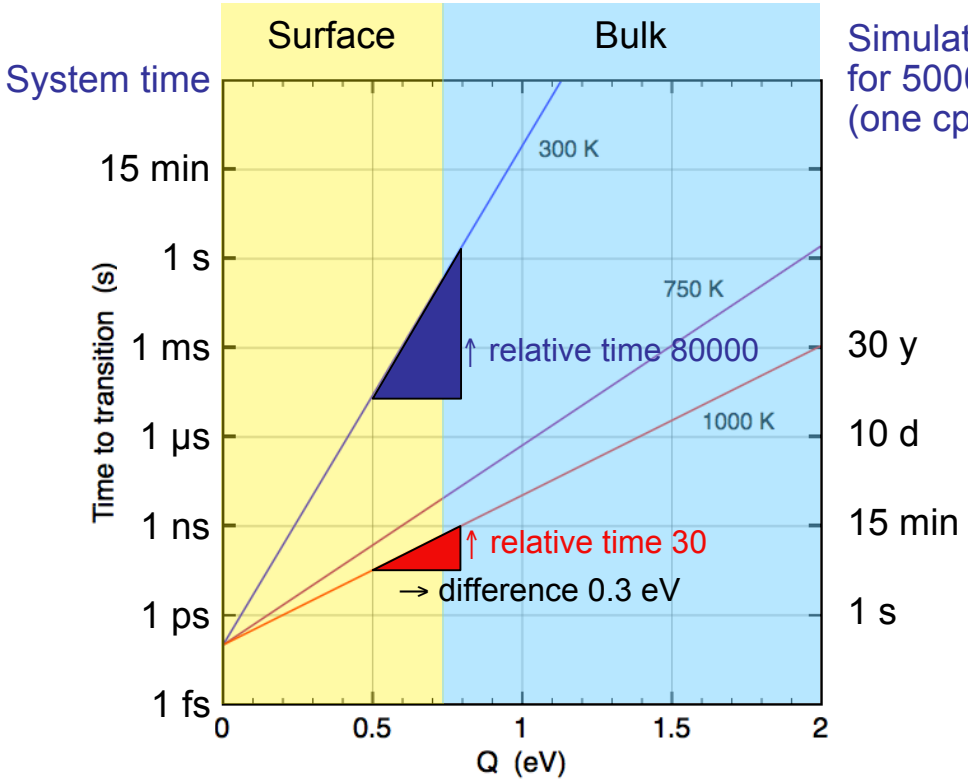
MD: Slow for thermal activation



Transition State Theory

Time to first transition: $\bar{\tau} = \frac{1}{\nu_0} e^{Q/kT}$

10^{13} s^{-1}



Simulation time for 5000 atoms (one cpu)

30 y

10 d

15 min

1 s

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Boosting MD by MC: the simple way

Force-biased Monte Carlo

- No need to detect “events” or “crossings”
- Works for small and big activation barriers
- Simple algorithm, 5 lines of code, no overhead
- No catalogue of transitions needed
- Detailed balance satisfied
- Can be combined with MD, taking turns or in parallel
- Time progress can be measured NEW

Mees, Pourtois, Neyts, Thijsse, Stesmans,
Phys. Rev. B (2012), accepted

Force-biased Monte Carlo: history

- C. Pangali, M. Rao, B.J. Berne, Chem. Phys. Lett. **55** (1978) 413
  - Theory only
- S. Goldman, J. Comput. Phys. **62** (1986) 464
  - H_2O
- G. Dereli, Mol. Simul. **8** (1992) 351
  - Amorphous Si
- C.H. Grein, R. Benedek, and T. de la Rubia, Comput. Mater. Sci. **6** (1996) 123
  - Growth of Ge on Si(100)

- M. Timonova, J. Groenewegen, and B.J. Thijsse, Phys. Rev. B **81** (2010) 144107
  - Cu surface diffusion, Si phase transitions
- E.C. Neyts, Y. Shibuta, A.C.T. van Duin, A. Bogaerts, ACS Nano **4** (2010) 6665
  - C nanotube growth

MD and force-biased Monte Carlo

Choose a reasonable (first) timestep $\Delta t^{(0)}$ for the problem, then:

$$\mathbf{r}_i^{(n+1)} = \mathbf{r}_i^{(n)} + \mathbf{v}_i^{(n)}\Delta t^{(n)} + \frac{1}{2}\frac{\mathbf{F}_i^{(n)}\left(\Delta t^{(n)}\right)^2}{m_i}$$

Compute $\mathbf{F}_i^{(n+1)}$ from all $\mathbf{r}_i^{(n+1)}$

Compute $\Delta t^{(n+1)}$ (optional)

$$\mathbf{v}_i^{(n+1)} = \mathbf{v}_i^{(n)} + \frac{1}{2}\frac{\mathbf{F}_i^{(n)}\Delta t^{(n)} + \mathbf{F}_i^{(n+1)}\Delta t^{(n+1)}}{m_i}$$

Choose a maximum atomic displacement $\Delta/2$ for the problem, then:

In x-direction (y and z analogously), for each atom i:

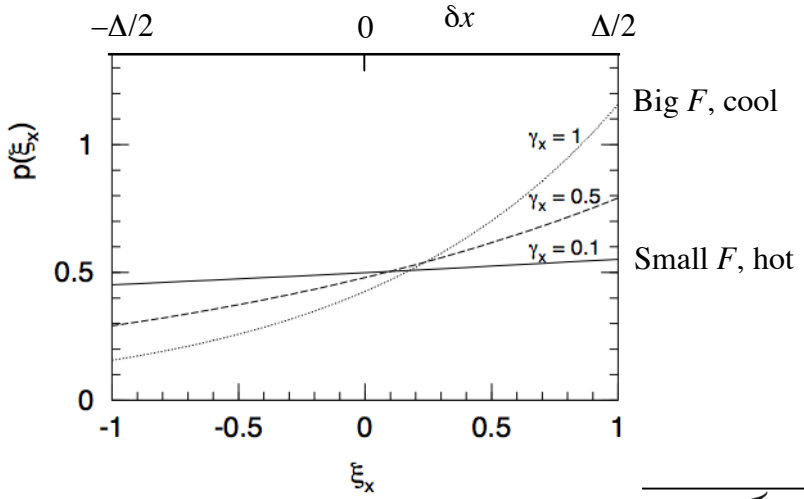
$$\gamma_{x,i} \equiv \frac{F_{x,i}^{(n)}\Delta/2}{2kT} \qquad \text{(“effective force”)}$$

Choose uniform random number $R_{x,i}$ on [0,1]

$$\xi_{x,i} = \gamma_{x,i}^{-1}\ln\left[R_{x,i}(e^{|\gamma_{x,i}|} - e^{-|\gamma_{x,i}|}) + e^{-|\gamma_{x,i}|}\right]$$

$$r_{x,i}^{(n+1)} = r_{x,i}^{(n)} + \xi_{x,i}\Delta/2 \qquad \text{(always accept)}$$

Compute $\mathbf{F}_i^{(n+1)}$ from all $\mathbf{r}_i^{(n+1)}$

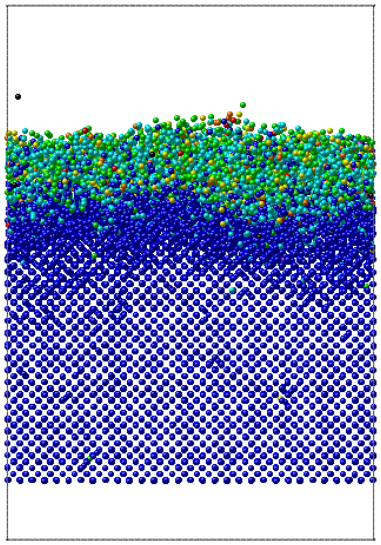


Big F, cool

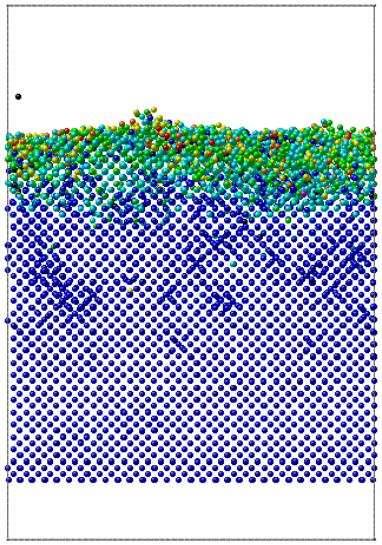
Small F, hot

Early success

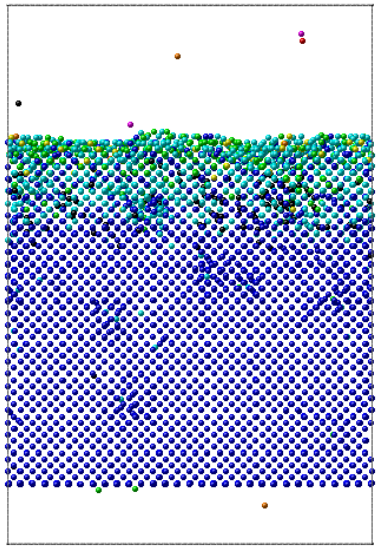
Recrystallization of ion-beam bombarded Si(100)



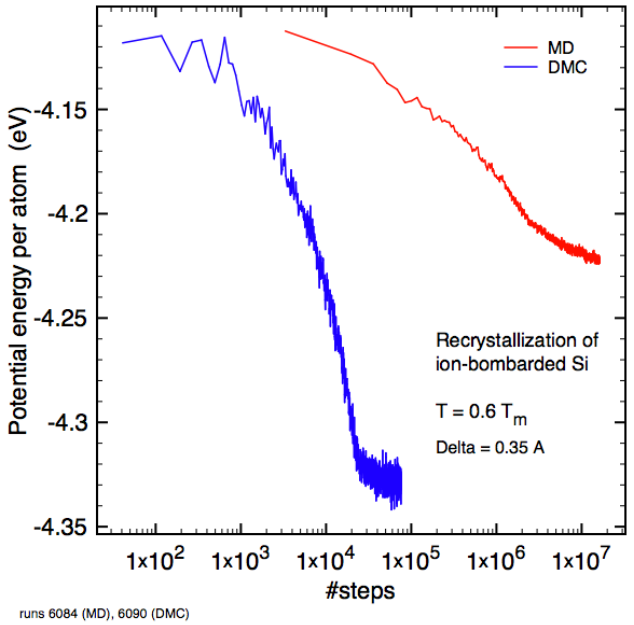
Start



Molecular Dynamics



Force-biased Monte Carlo
$\Delta/2 = 0.075$ Å



Monte Carlo is more than 100 times faster

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Uphill motion, detailed balance

Probability density of a displacement $p(\delta x) = K^{-1} e^{\frac{F_x \delta x}{2kT}} \approx K^{-1} e^{-\frac{\delta U}{2kT}}$

Why this factor 2 here?

Probability of an uphill move $P(\text{uphill}) = \frac{1}{2} - \frac{1}{4}\frac{|F_x|\Delta/2}{2kT}$

RMS displacement in a move $\delta x_{\text{RMS}} = \frac{\Delta/2}{\sqrt{3}}\left(1 + \frac{1}{15}\left[\frac{|F_x|\Delta/2}{2kT}\right]^2\right)$ (more agitation with greater $\Delta/2$ and smaller T)

Detailed balance $W(\mathbf{r}'|\mathbf{r})P(\mathbf{r}) = W(\mathbf{r}|\mathbf{r}')P(\mathbf{r}')$

Erik Neyts

Canonical $W(\mathbf{r}'|\mathbf{r})e^{-U(\mathbf{r})/kT} = W(\mathbf{r}|\mathbf{r}')e^{-U(\mathbf{r}')/kT}$

Transition probability (W) = Displacement (D) × acceptance (A) probabilities:

$$D(\mathbf{r}'|\mathbf{r})A(\mathbf{r}'|\mathbf{r})e^{-U(\mathbf{r})/kT} = D(\mathbf{r}|\mathbf{r}')A(\mathbf{r}|\mathbf{r}')e^{-U(\mathbf{r}')/kT}$$

$$A(\mathbf{r}'|\mathbf{r}) = \min\left[1, \frac{D(\mathbf{r}|\mathbf{r}')}{D(\mathbf{r}'|\mathbf{r})}e^{-(U(\mathbf{r}')-U(\mathbf{r}))/kT}\right] = \min\left[1, \frac{D(\mathbf{r}|\mathbf{r}')}{D(\mathbf{r}'|\mathbf{r})}e^{-\delta U/kT}\right]$$

Detailed balance, uniform acceptance

$$A(\mathbf{r}'|\mathbf{r}) = \min\left[1, \frac{D(\mathbf{r}|\mathbf{r}')}{D(\mathbf{r}'|\mathbf{r})} e^{-\delta U/kT}\right]$$

Metropolis: Trial move is uniformly sampled in its domain: $D(\mathbf{r}'|\mathbf{r}) = D(\mathbf{r}|\mathbf{r}')$

Therefore acceptance is $A(\mathbf{r}'|\mathbf{r}) = \min\left[1, e^{-\delta U/kT}\right]$

UFMC: $D(x'|x) \approx K^{-1} e^{-\frac{\delta U}{2kT}}$

$D(x|x') \approx K'^{-1} e^{+\frac{\delta U}{2kT}}$

If x and x' are not too far apart: $K = K'$ and $F = F'$

$$A(\mathbf{r}'|\mathbf{r}) = \min\left[1, \frac{e^{+\delta U/2kT}}{e^{-\delta U/2kT}} e^{-\delta U/kT}\right] = 1$$

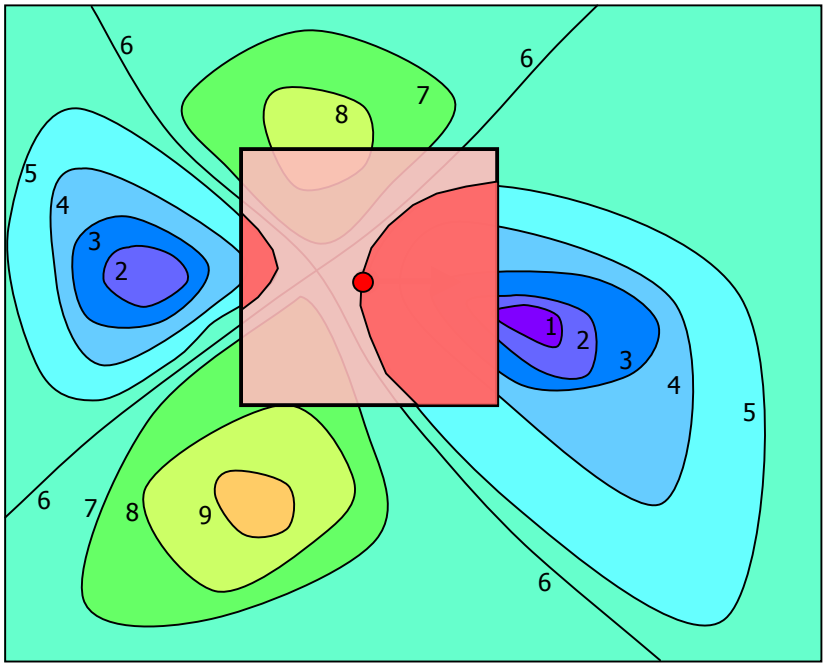
This UFMC is not unique.

If $\frac{D(\mathbf{r}|\mathbf{r}')}{D(\mathbf{r}'|\mathbf{r})} = e^{\delta U/kT}$

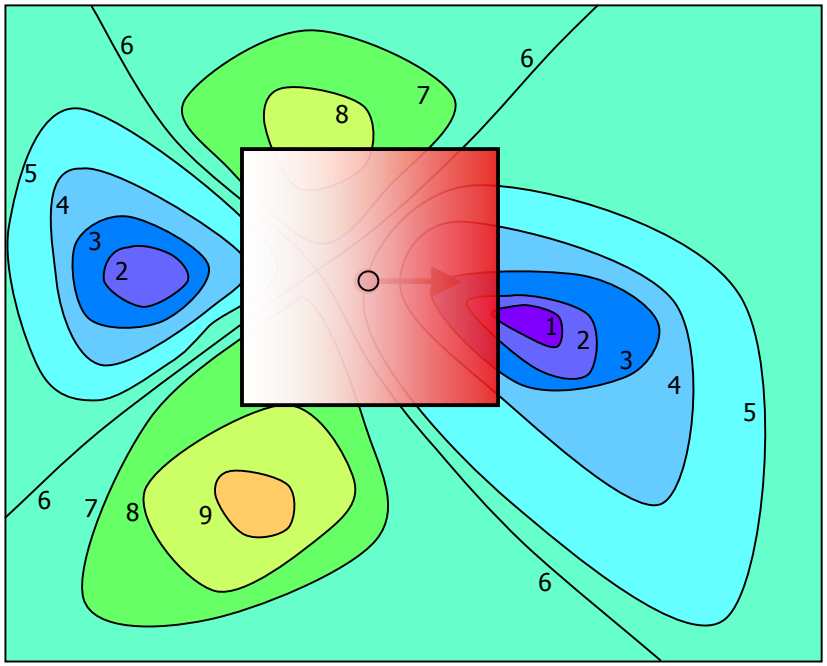
always uniform acceptance.

This explains the factor 2. Therefore: always acceptance *and* detailed balance

Metropolis vs UFMC



Metropolis



UFMC

Time

Maarten Mees

Which time interval Δt can be associated with iteration step n? Define as follows:

$$\Delta t^{(n)} \equiv \frac{\left\langle \left| \delta x^{(n)} \right| \right\rangle}{\left\langle \left| v^{(n)} \right| \right\rangle} \qquad \left\langle \left| \delta x^{(n)} \right| \right\rangle \approx \Delta/6, \text{ a very slow function of the effective force} \qquad \Delta t \approx \frac{\Delta / 6}{\sqrt{2kT / \pi m}}$$

Next, Δ should be made mass-dependent to allow for several atomic masses being present and have the same time interval for each species,

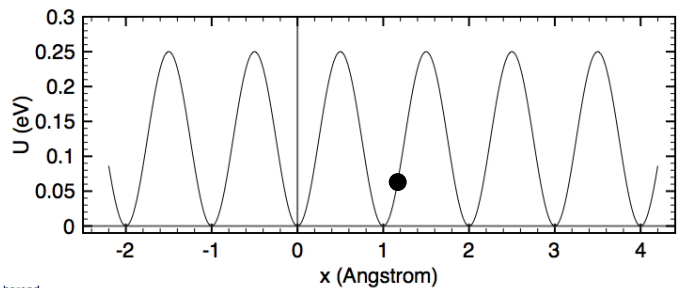
$$\Delta \quad \rightarrow \quad \Delta_i \equiv \Delta \sqrt{m_{\min} / m_i}$$

$$\Delta t \approx \frac{\Delta / 6}{\sqrt{2kT / \pi m_{\min}}}$$

Larger $\Delta \rightarrow$ more boost but more deviation from $F = F'$

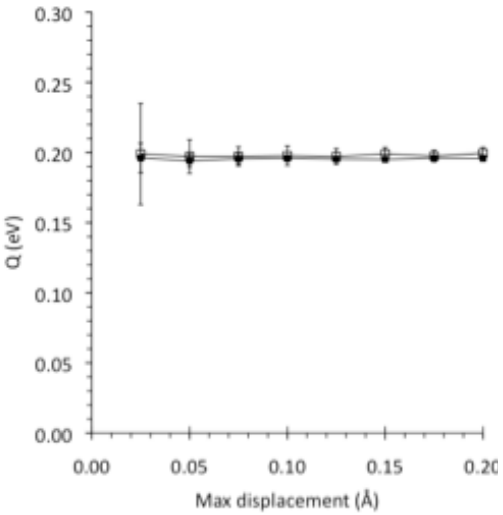
Δt in fs for several $m_{\min}$ and $\Delta/2 = 0.1\ R_{\text{nnb}}$				
$m_{\min}$	300 K	800 K	1300 K	1800 K
H	2.0	1.2	1.0	0.8
Si	33	20	16	13
Cu	54	33	26	22
W	98	60	47	40

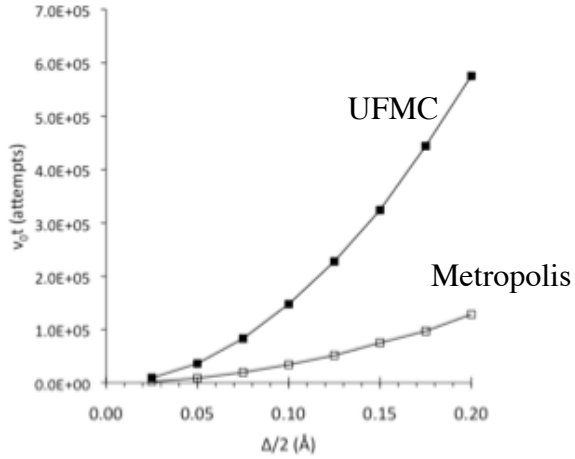
One particle in cosine potential

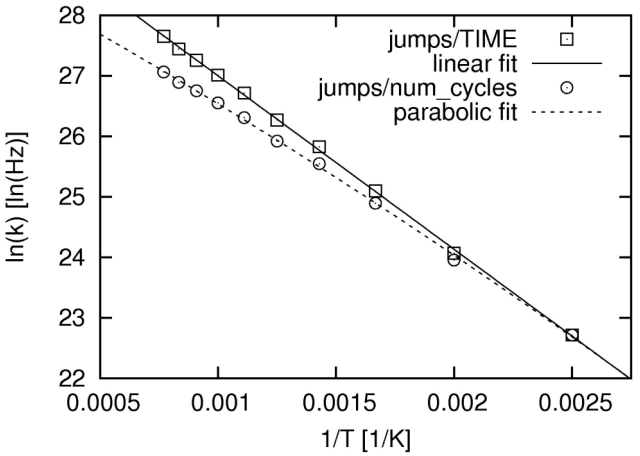


$$U = \frac{Q_0}{2}\left(1 - \cos\frac{2\pi x}{L}\right) \qquad Q_0 = 0.25 \text{ eV}, L = 1 \text{ Å}$$

TST: Number of jumps in time t: $n_j = \nu_0 t\, e^{-Q/kT}$





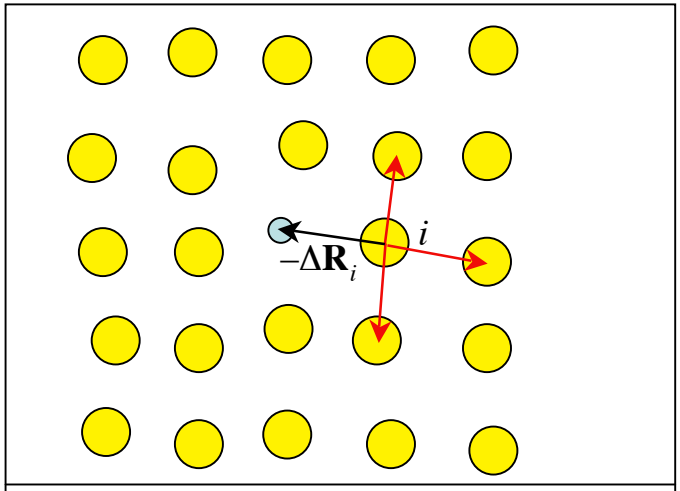


Counting arrivals in 5% region around a new minimum

Somewhat different UFMC version
$\Delta/2 = 0.10$ Å
Q from straight line = 0.247 eV
ν_0 = 0.9e13 Hz
Counting crossings (incl recrossings)

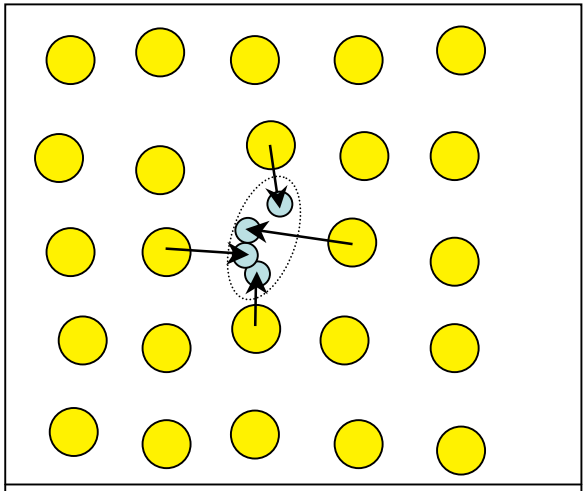
Quasivacancies

Counting “vacancies” in crystals, amorphous, liquids in a consistent way



○ “Missing neighbor” (MN) of atom i:
$\mathbf{r}_{MN} = \mathbf{r}_i - \Delta\mathbf{R}_i$

$\Delta\mathbf{R}_i = \sum_j(\mathbf{r}_j - \mathbf{r}_i)$, should be $> 0.8\ R_{nnb}$

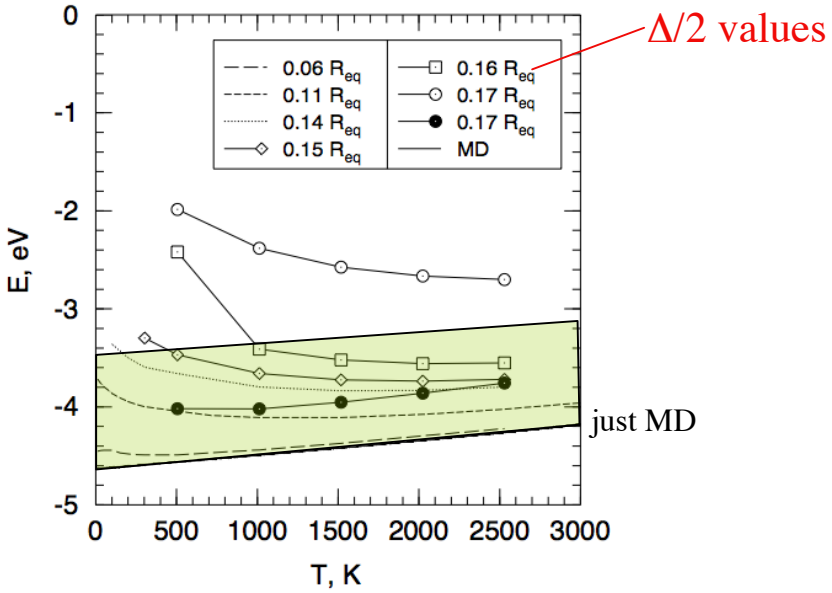


Quasivacancy (QV)

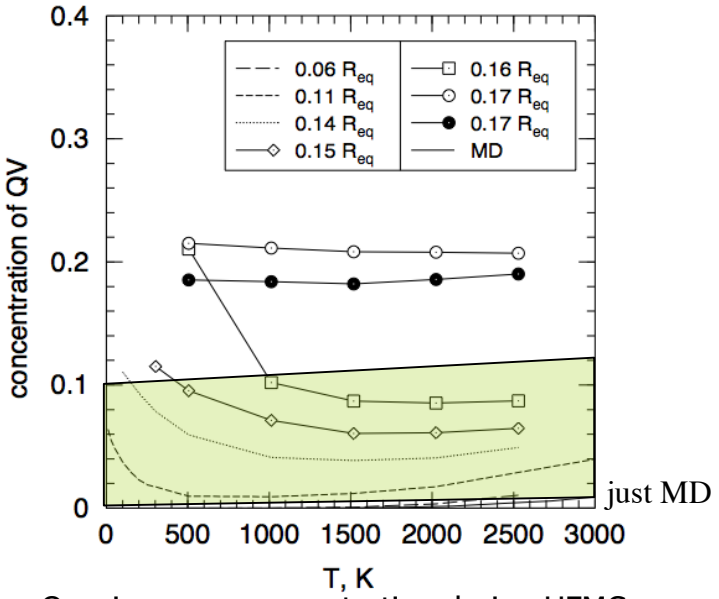
QV concentration =
(MN concentration)/Z

Test: When UFMC should do nothing

Silicon crystal, MEAM-potential (M. Timonova, B.J. Lee, BJT). Quite good, but T_m = 2990 K (too high)



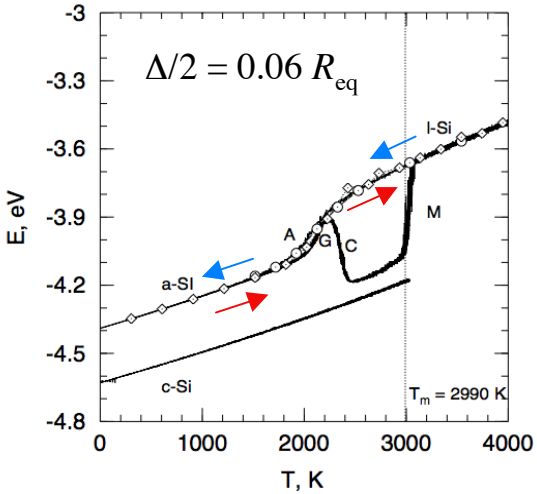
Potential energy during UFMC

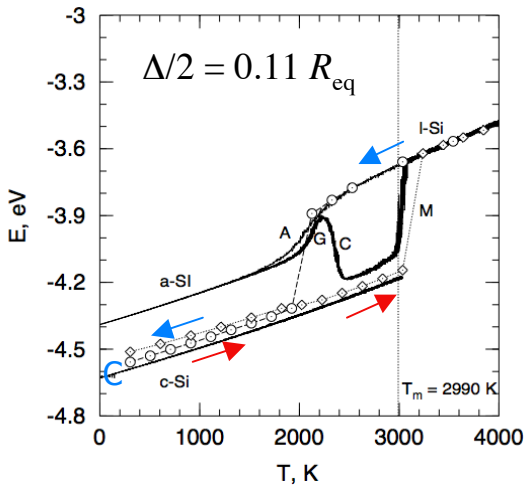


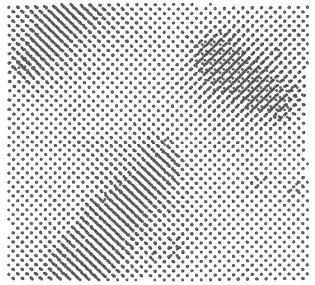
Quasivacancy concentration during UFMC

- As expected: more agitation with greater Δ/2 and smaller (!) T. "Effective forces" are larger.
- Robust: All UFMC results, followed by MD, return to a perfect crystal (except o o o o → ● ● ● ● = violent UFMC, with Δ/2 = 0.17 R_{eq}).
- More robust: **each** atom returns to its own position when UFMC in green area is followed by MD. So: Δ/2 = 0.15 R_{eq} is safe. Also at surface (100), including dimerization.

Si phase transformation where MD fails







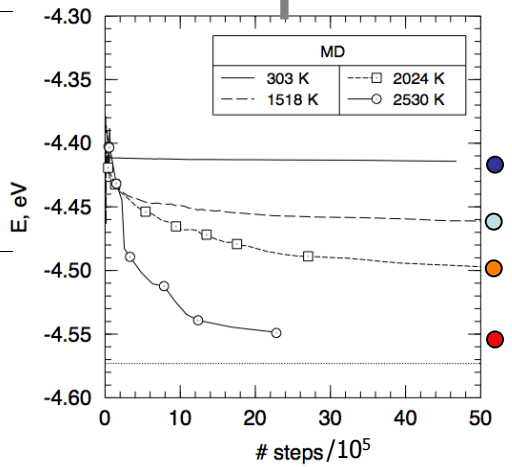
Polycrystal formed at C

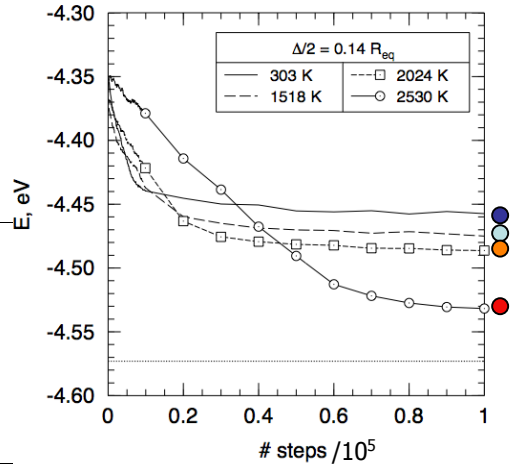
Potential energy during cooling+heating
MD: 1 ps/K (lines) -- much slower than UFMC

- MD: Cooling to amorphous (relaxed), heating to glass transition, xtallization, melting (liq: $Z = 5.6$).
- UFMC with $\Delta/2 = 0.06\ R_{eq}$: Cooling to amorphous (relaxed), heating to liquid ($Z = 5.5$).
- UFMC with $\Delta/2 = 0.11\ R_{eq}$: Cooling to polycrystal, heating to liquid.
  The amorphous phase also crystallizes to a polycrystal at 300 K

Si recrystallization: UFMC faster than MD

	MD	UFMC++		
		$\Delta/2 = 0.06\ R_{eq}$	$\Delta/2 = 0.11\ R_{eq}$	$\Delta/2 = 0.14\ R_{eq}$
303 K	0 % Ar evapor. 17 % QV	0 % Ar evapor. 17 % QV	2.5 % Ar evapor. 2.5 % QV	17 % Ar evapor. 2.5 % QV
1518 K	8.7 % Ar evapor. 16 % QV	3.6 % Ar evapor. 11 % QV	33 % Ar evapor. 2 % QV	15 % Ar evapor. 4 % QV
2024 K	12 % Ar evapor. 8 % QV	8,7 % Ar evapor. 8 % QV	71 % Ar evapor. 1.8 % QV	19 % Ar evapor. 2.5 % QV
2530 K	88 % Ar evapor. 2 % QV	60 % Ar evapor. 1 % QV	78 % Ar evapor. 1 % QV	89 % Ar evapor. 1 % QV





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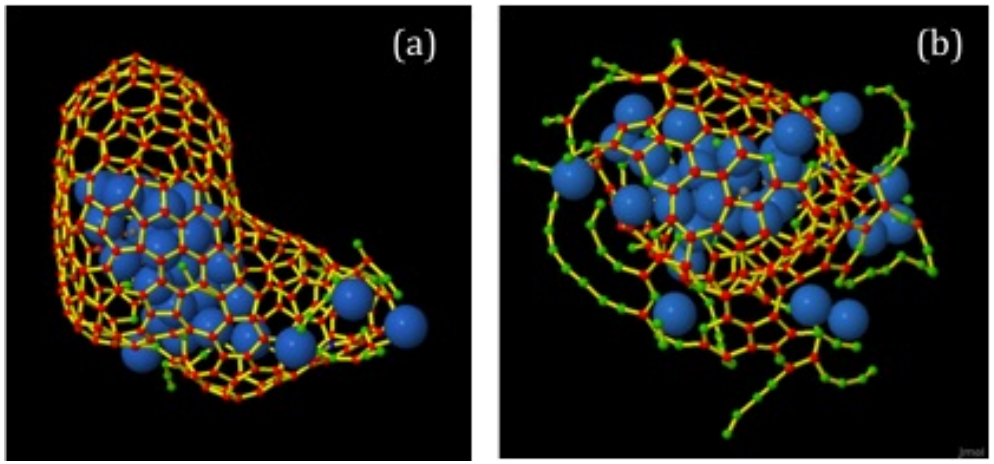
Other successes

E.C. Neyts, Y. Shibuta, A.C.T. van Duin, A. Bogaerts, ACS Nano **4** (2010) 6665



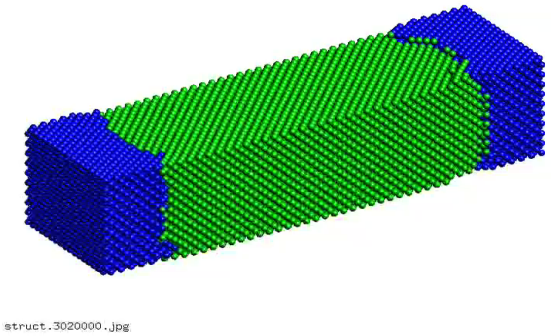
UFMC, well defined chirality MD

Also: Ni nanocluster melting, Neyts/Bogaerts JCP 2009

Surprises

Fe: fcc → bcc transformation

MD



bcc
fcc
bcc

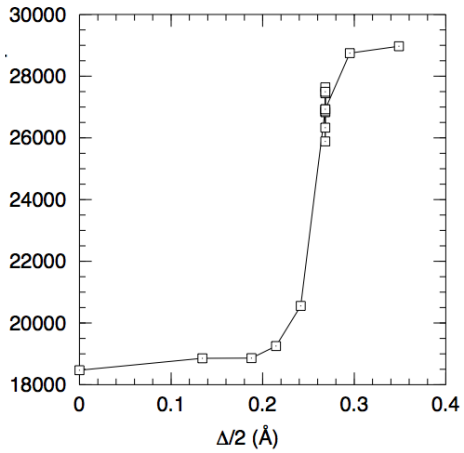
$$w_{(m)}^{(l)}(i) = \left| \sum_{j}^{neighbors} Y_{(m)}^{(l)}(\theta_{ij}, \phi_{ij}) \right|^2$$

Rotationally invariant:

$$w^{(l)}(i) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} w_{(m)}^{(l)}$$

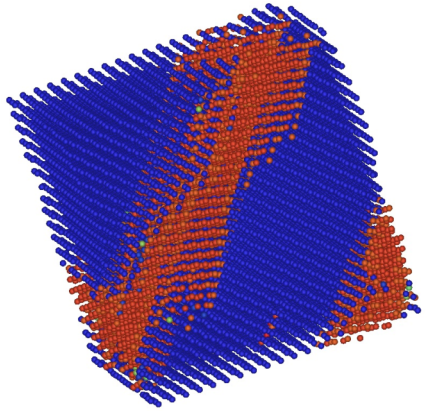
UFMC

Number of fcc atoms after 3×10^5 steps

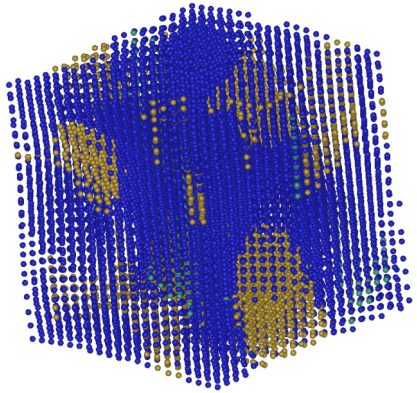


UFMC goes the wrong way!

UFMC: A cheap method to construct a polycrystal? Here bcc Fe



UFMC 1000 K → MD 1000 K → Quench



UFMC 1000 K → Quench

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Conclusions

- UFMC has much potential as MD booster
  - Very easy to handle
  - Only 5 lines of program code
  - No thermostat needed, T is built into the method
  - Solid statistical basis
  - Time can be implemented sensibly
  - Mixture of atomic masses can be handled consistently
  - Dynamic creation and annihilation of QV appears essential
- For further study
  - Boost is not always spectacular
  - Alternative displacement statistics may be better
  - Does not work in close packed systems?
  - Convenient method to generate polycrystals?