

Computational Materials Science

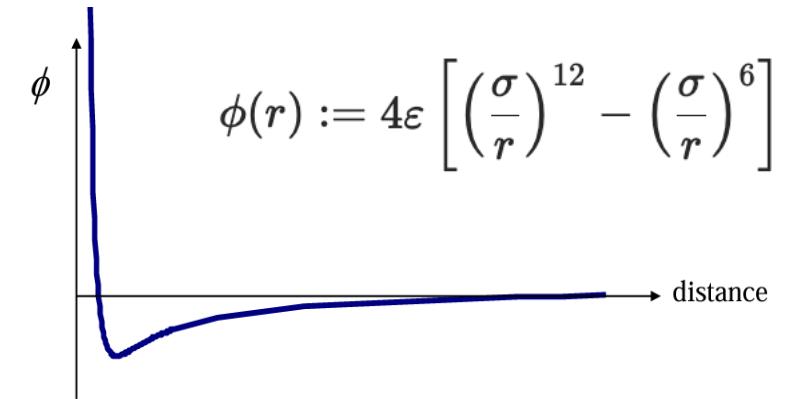
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Molecular Dynamics

Initial hypothesis:

1. Born-Oppenheimer approximation - $\tau_N \ll \tau_e$
2. Electronic problem: *ab initio* QC - $V(r)$ 
3. Nuclei problem treated classically - $\lambda_T \ll a$

Classical MD: assign interatomic potential instead of deriving it



Goal:

study the dynamics of an FCC lattice of 256 silver (Ag) atoms, evaluating *ensemble* averages in the microcanonical (N,V,E) ensemble by computing time averages (ergodic theorem).

Fixed parameters

- 1) $\epsilon = 0.345$ eV
- 2) $\sigma = 2.644$ Å
- 3) Cut-off radius: $R_C = 4.5$ Å
- 4) Thermalization time: $3 \cdot 10^{-12}$

Note on CMS module

`CMS.MolecularDynamics` module consists of 3 main classes that work together to do classical molecular dynamics simulations.

`CrystalStructure`

- Stores the positions of the atoms;
- Finds and stores nearest neighbours.

`CrystalPotential`

Computes the potential energy of the system and the forces acting on each atom.

`CrystalDynamics`

Applies the **velocity Verlet algorithm** to the `CrystalStructure` object using the forces returned by `CrystalPotential`.

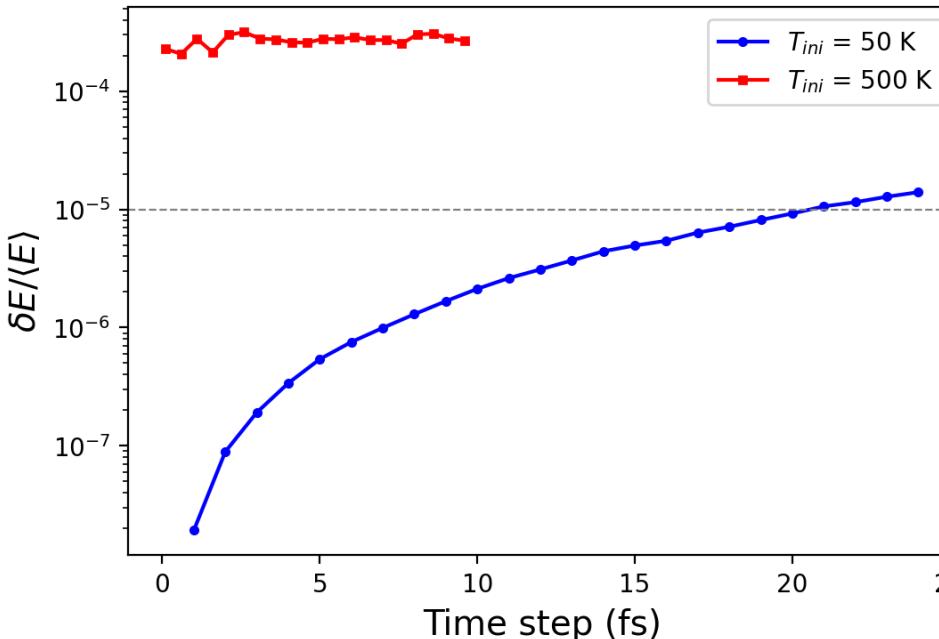
One way to speed up the simulation is to **only consider neighbor atoms** ($r \ll R_C$) when evaluating the potential energy. If so, since the number of neighbors does not scale with system size, potential calculations scale as $\mathcal{O}(N \times N_{neigh})$ instead of $\mathcal{O}(N \times N)$.

1&2 – Sharp cutoff and optimal time-step

Sharp cutoff

Discontinuity in potential leads to energy ‘jumps’ due to thermal agitation.

$$V(r) = \begin{cases} \phi(r), & \text{if } 0 < r < R_C \\ 0, & \text{if } r > R_C \end{cases}$$



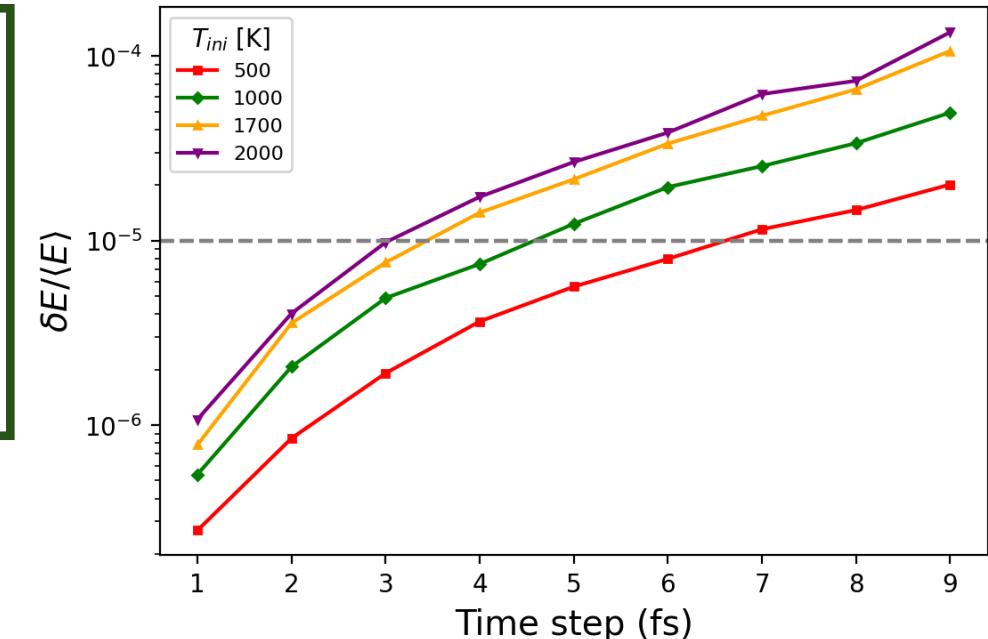
Optimal time-step (fs) at T_{ini} :

• 50 K:	20
• 500 K:	6
• 1000 K:	4
• 2000 K:	3

Polynomial junction

Smooth potential ‘stabilizes’ energy at high T.

$$V(r) = \begin{cases} \phi(r), & \text{if } 0 < r < R_P \\ P_7(r), & \text{if } R_P < r < R_C \\ 0, & \text{if } r > R_C \end{cases}$$



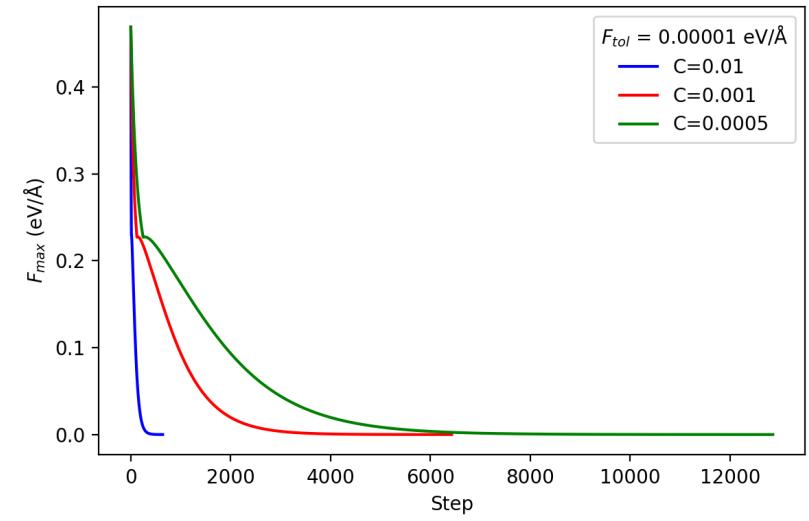
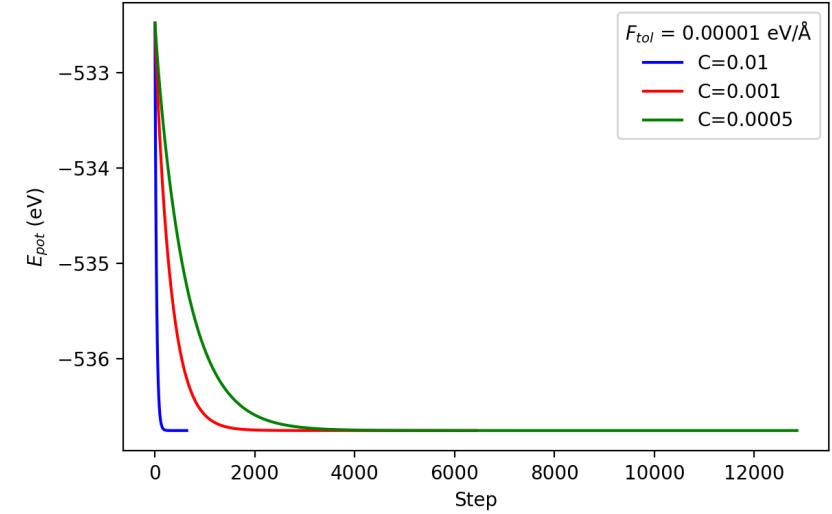
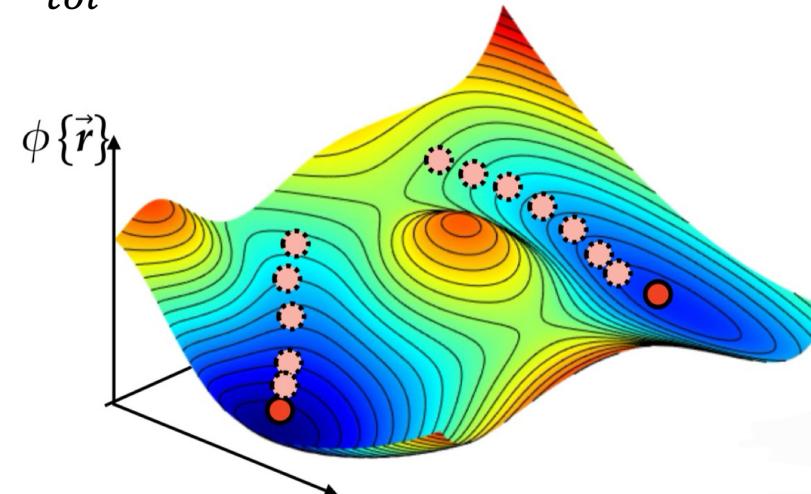
Steepest descent

Objective: to find a local potential energy minimum by moving the system's coordinates in the direction of the most negative gradient of the potential energy surface.

Mechanism: atoms are moved iteratively of a quantity proportional to the force they are subject to

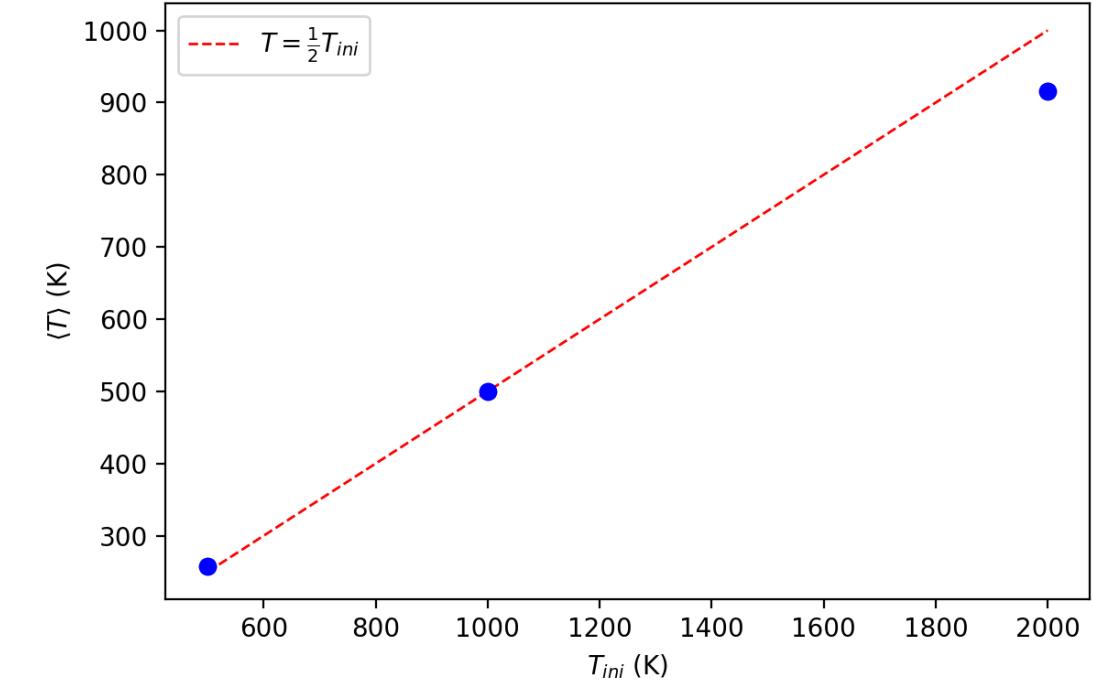
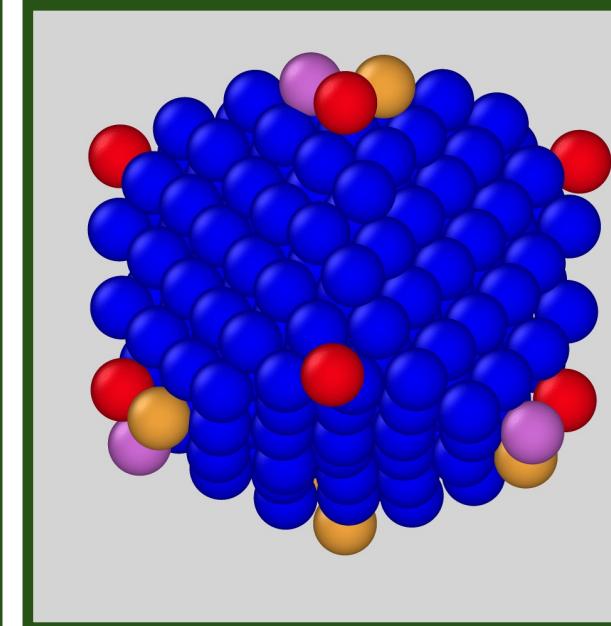
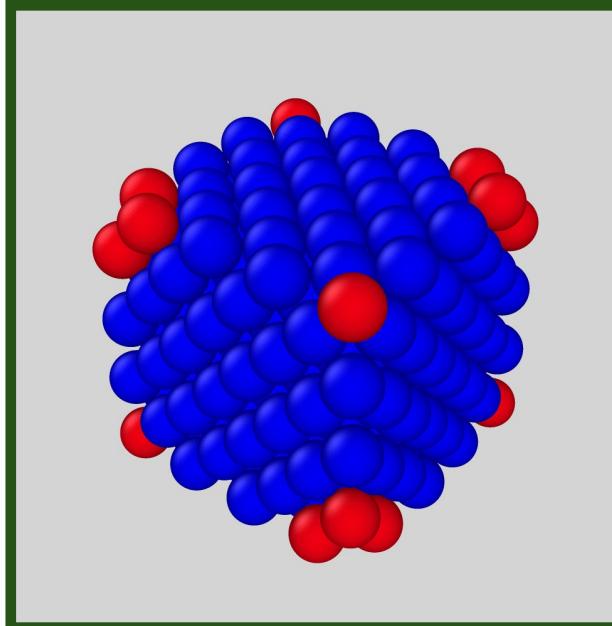
$$\delta \vec{r}_k = C_{steep} \vec{F}_k$$

Convergence is reached if the maximum force is less than an arbitrary value F_{tol} .



3 – Temperature

Simulations starting from $T=500$, 1000 and 2000 K. Average temperature is near to $\frac{1}{2}T_{ini}$. However, as temperature increases, the harmonic approximation becomes less accurate, hence the 2000 K sim deviates more.



500 K (left) and 2000 K (right); atoms on the vertices are highlighted.
Thermal agitation causes atoms to ‘explore’ non-harmonic regions of the LJ potential.

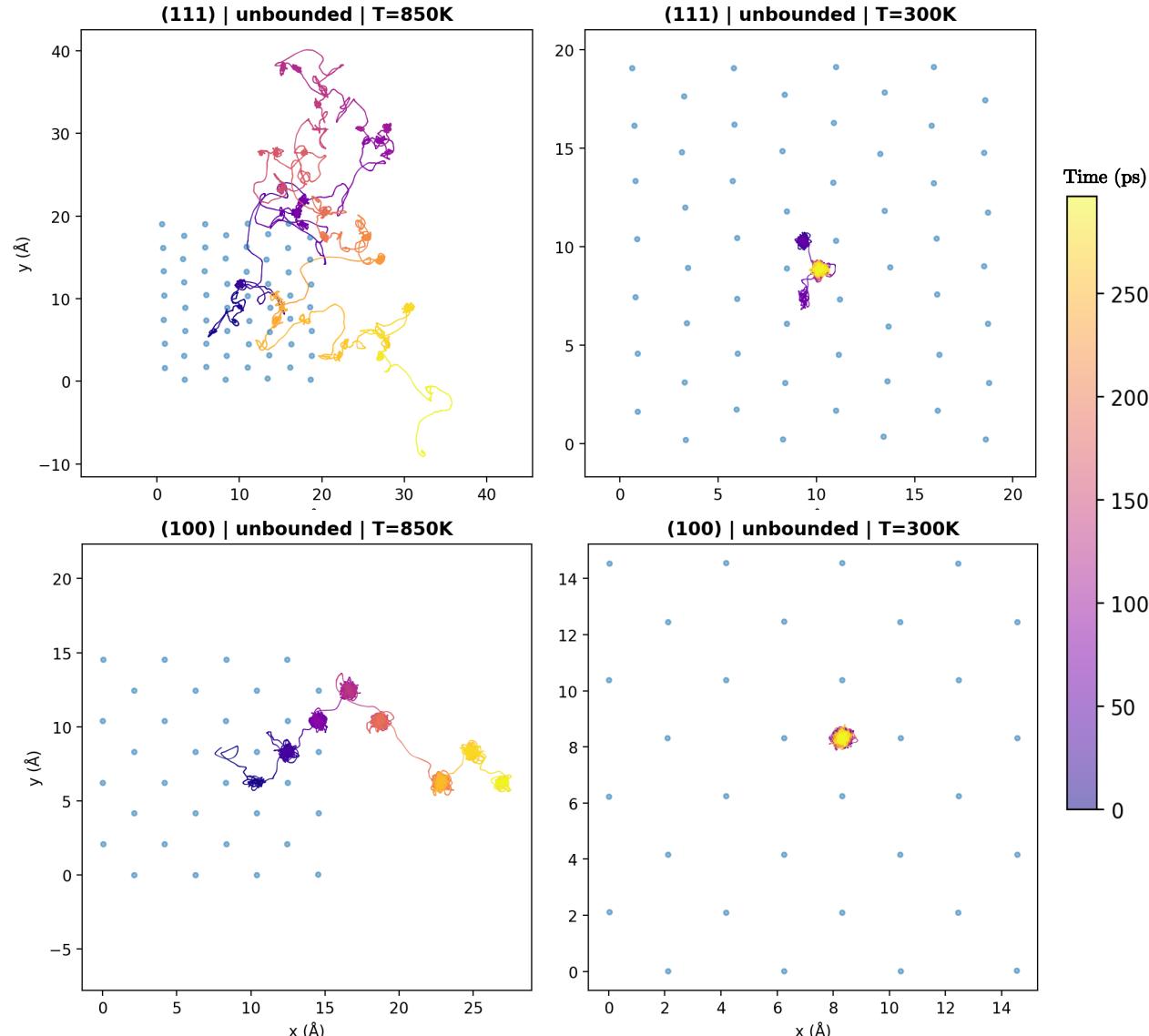
4&5 – Adatom diffusion

Periodic boundary conditions are imposed only on x and y axis, making the crystal an **infinite slab**.

An atom is then placed on top, and its trajectory is traced over time.

This procedure is repeated for (100) and (111) orientations at 300 K and 850 K.

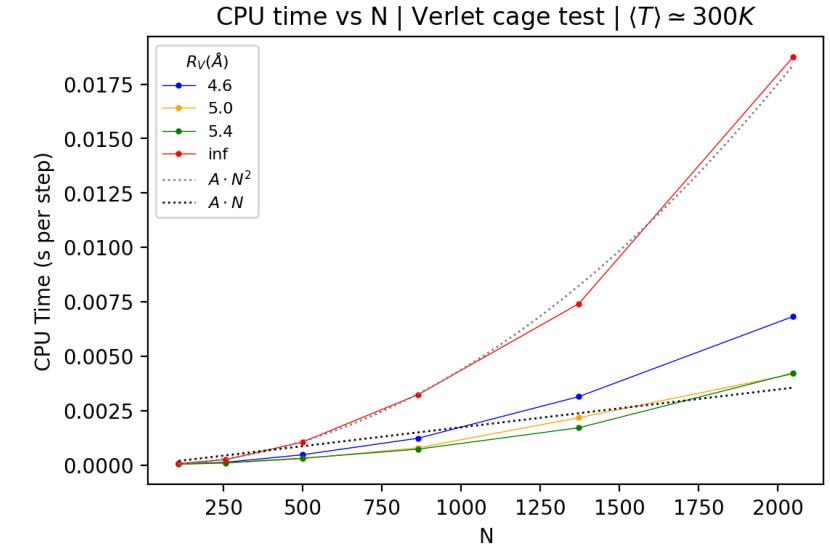
On the surface of the (111) oriented cell atoms are more **densely packed**. Here, the number of first neighbors in the hollow sites is 3, compared to 4 in (100). The adatom is less deeply ‘trapped’ due to a lower energy barrier, making diffusion more frequent.



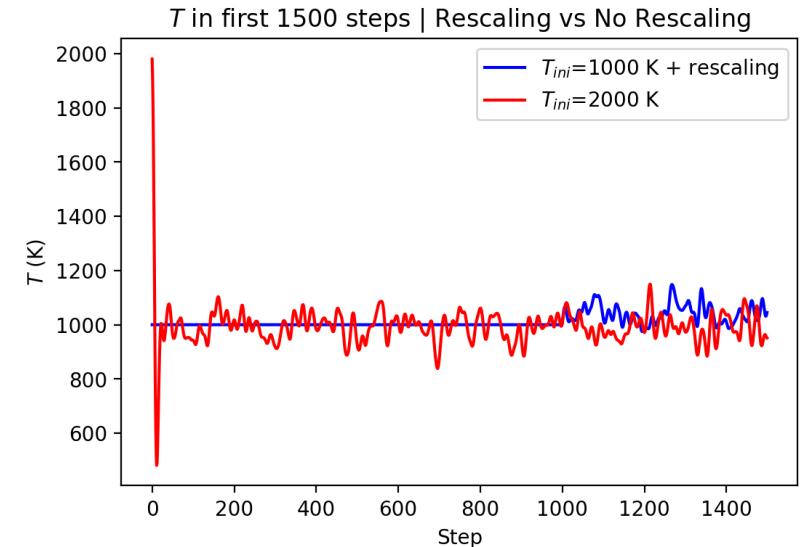
Code optimizations

Verlet cages: recomputing neighbors at each velocity Verlet step is costly. By implementing Verlet cages, this operation is done only when atoms move outside of a ‘control region’. This results in a significant speed up, making the code closer to a $\mathcal{O}(N)$ cost.

$$\vec{v}_i(t) \rightarrow \vec{v}_i(t) \sqrt{\frac{T_{\text{want}}}{T(t)}}$$



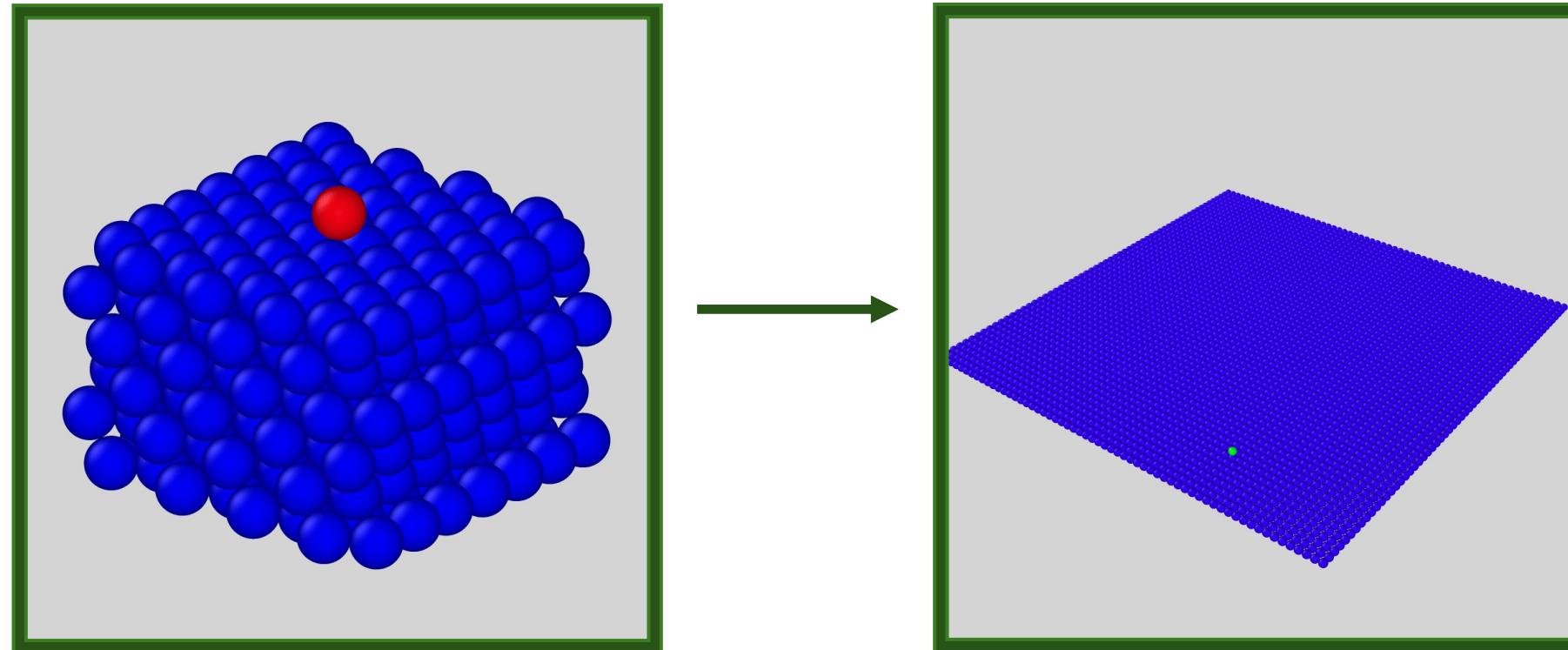
Velocity rescaling: due to the halving of temperature, simulating high T can become impractical. The desired T can be enforced by rescaling velocity at every thermalization step of velocity Verlet.



Kinetic Monte Carlo

Problem: diffusions are interesting yet rare events. MD simulations have the adatom vibrate in place most of the time.

Solution: if **neat time-scale separation** between vibrations (ps) and diffusions (ns), continuum MD trajectory can be replaced with **Markov chain of discrete jumps**.



1 – Stick-where-you-hit

Diffusion rates:

$$k_{\text{diff}} \approx \nu e^{-\frac{E_b}{k_B T}} \xrightarrow{T \rightarrow 0} 0$$

Deposition rate:

$$k_{\text{depo}} = \phi L_x L_y$$

Since $T=0\text{K}$, diffusions are suppressed.
Atoms stay exactly where they are placed.

Random escape times (distance between events) in poissonian process:

$$p(\tau) = k e^{-k\tau}$$

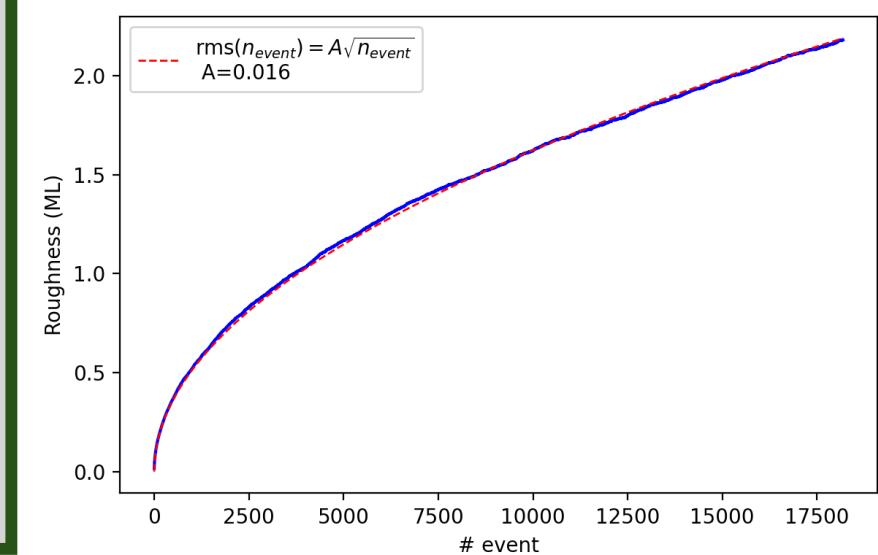
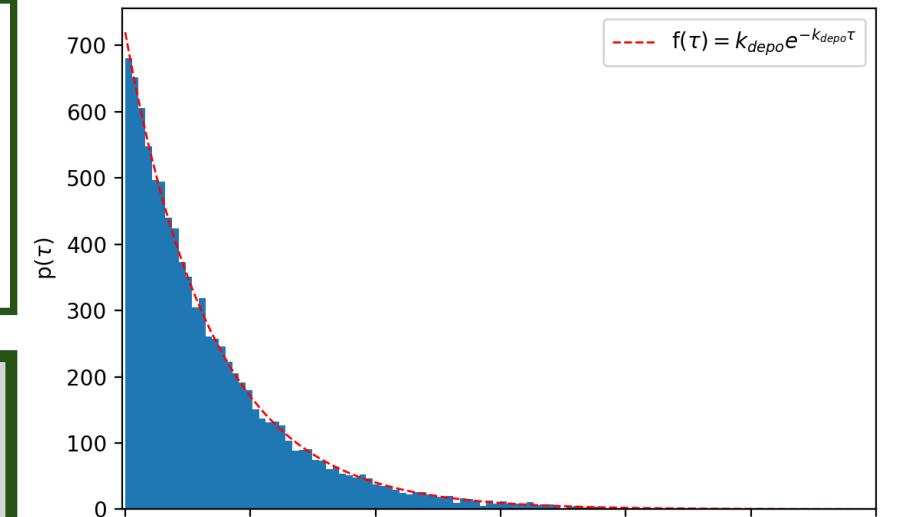
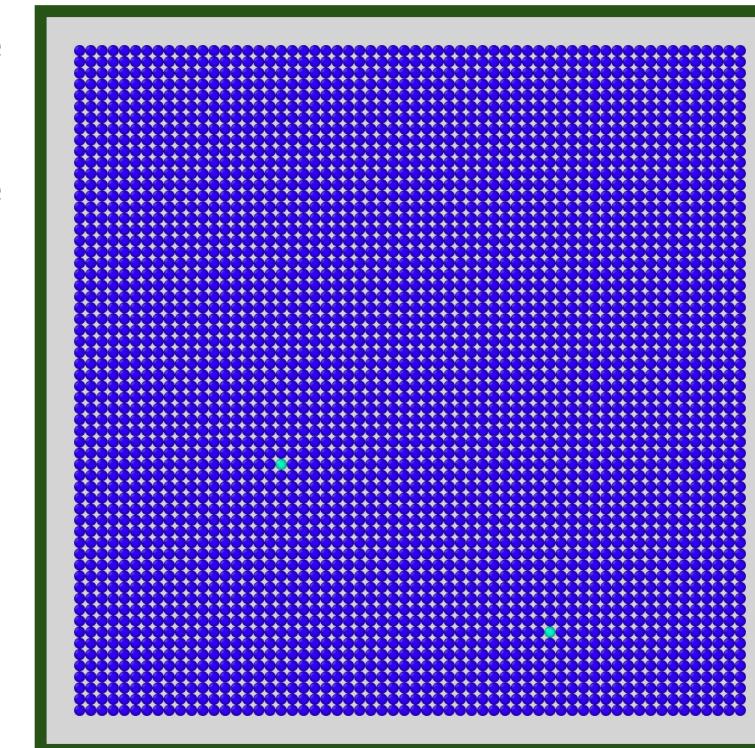
$$\bar{\tau} \simeq 0.00137, \quad \frac{1}{k_{\text{depo}}} \equiv \langle \tau \rangle \simeq 0.00139$$

Disordered growth $\xrightarrow{k_{\text{depo}}} \text{error}$ is poissonian.

$$\langle h \rangle = \frac{n}{L_x L_y} := \lambda, \quad \sigma_h = \sqrt{\lambda}$$

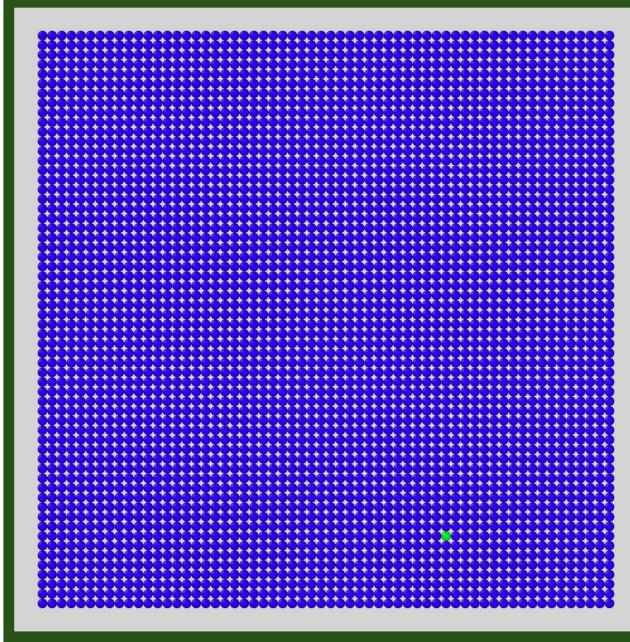
Parameters

- 1) $L_x \times L_y = 60 \times 60$
- 2) $\phi = 0.2 \text{ ML/s}$
- 3) $\theta = 5 \text{ ML}$
- 4) $T = 0 \text{ K}$

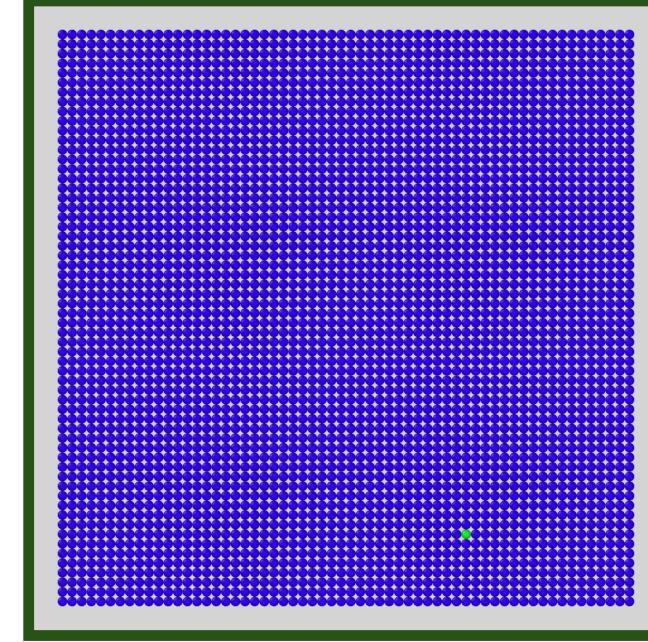


2 – Deposition and diffusion I

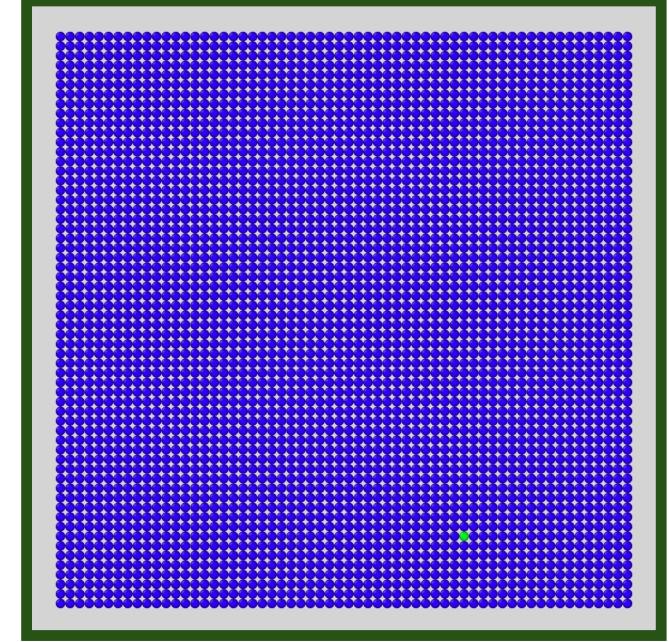
$\phi = 10 \text{ ML/s}$



$\phi = 0.01 \text{ ML/s}$



$\phi = 0.0001 \text{ ML/s}$

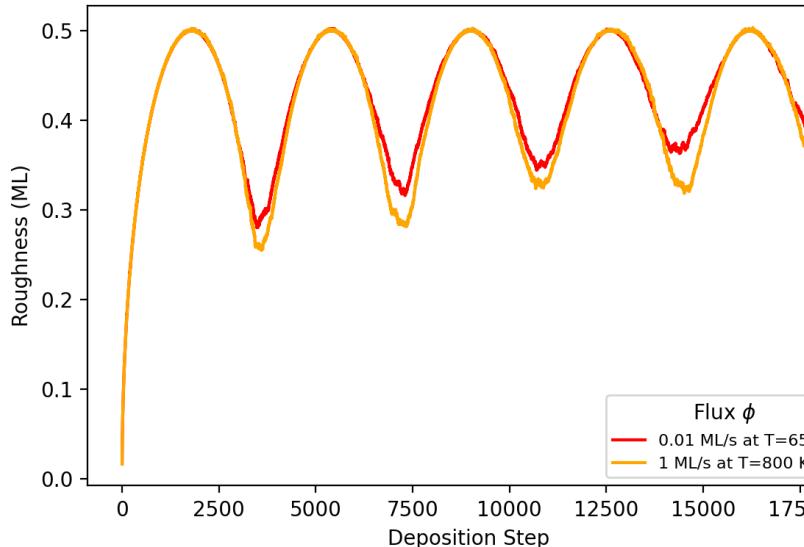
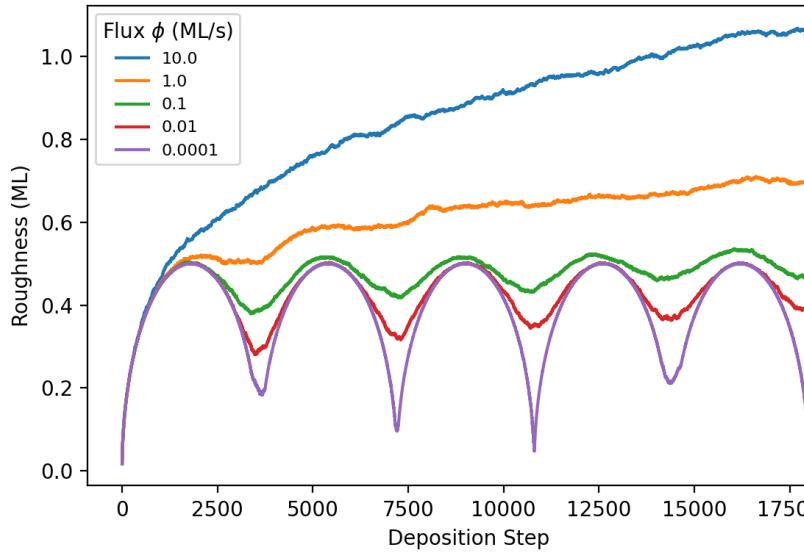


Parameters

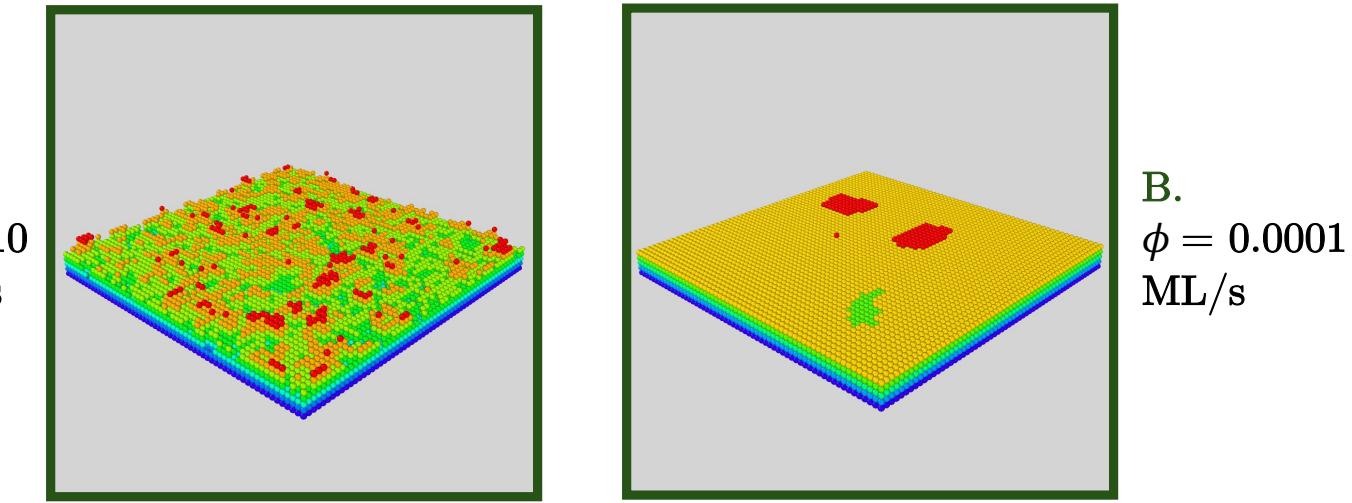
- 1) $L_x \times L_y = 60 \times 60$
- 2) $\phi = 0.0001 - 10 \text{ ML/s}$
- 3) $\theta = 5 \text{ ML}$
- 4) $T = 650 \text{ K}$

High deposition rates give results similar to the *stick-where-you-hit* regime, since deposited atoms have not enough time to diffuse before a new deposition event happens. Low deposition rates give atoms the opportunity to diffuse and arrange in clusters. The slower the deposition, the greater the clusters.

2 – Deposition and diffusion II



- A. **Multi-layer growth:** atoms diffusion is limited, new nuclei form on top of incomplete layers, roughness monotonically increases;
- B. **Layer-by-layer:** atoms migrate to islands before layering, roughness peaks at half the layer, then diminishes until the layer is complete.



Since it's a competition between deposition and diffusion, if the ratio between the two rates is maintained, the behavior of $\phi_1 = 0.01$ ML/s can be reproduced with $\phi_2 = 1$ ML/s at two different temperatures. If $T_1 = 650$ K, then $T_2 \simeq 800$ K:

$$\frac{k_{\text{diff}}(T_1)}{\phi_1} \simeq \frac{k_{\text{diff}}(T_2)}{\phi_2} \iff \frac{1}{T_2} \simeq \frac{1}{T_1} - \frac{k_B}{E_b} \ln \frac{\phi_2}{\phi_1}$$

Metropolis Monte Carlo

Configurational (Metropolis) Monte Carlo is used to inspect the equilibrium in large systems.

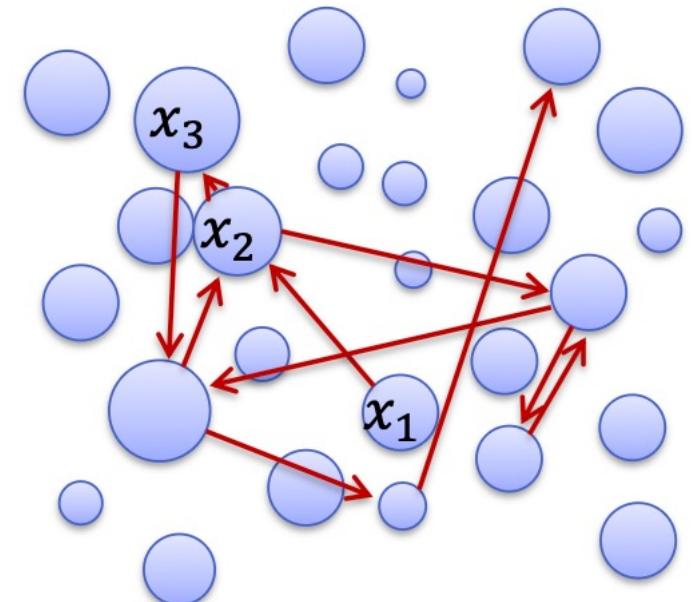
The algorithm generates a sequence of microstates according to their Boltzmann probability. In the context of **importance sampling**, the most probable configurations are found more frequently, as they provide the dominant contributions to the system's thermodynamic averages.

$$\langle A \rangle_{N,V,T} = \frac{\sum_j A_j e^{-H(x_j)/k_b T}}{\sum_j e^{-H(x_j)/k_b T}} \rightarrow \frac{1}{N} \sum_j^* A_j$$

full sum over all configurations
 stochastic sum over configurations generated based on probability

This is made moving atoms between sites with a probability depending on the energy difference and temperature:

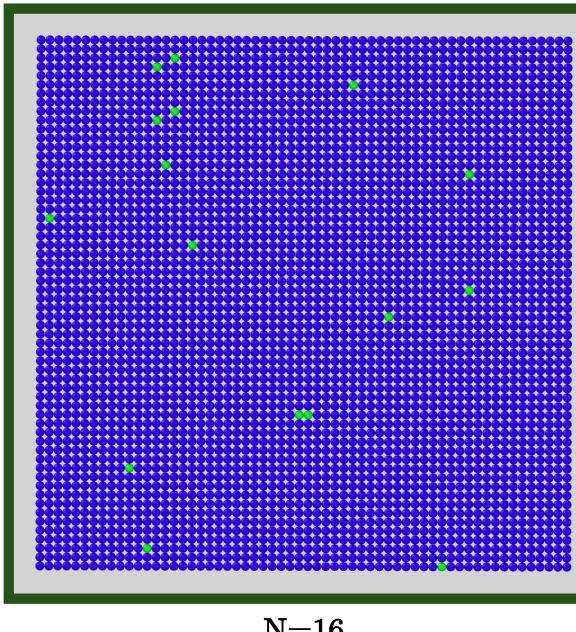
$$P_{x_i \rightarrow x_j}^{\text{acc}} \equiv \begin{cases} 1 & \text{if } E_j \leq E_i \\ e^{-\frac{E_j - E_i}{k_B T}} & \text{if } E_j \geq E_i \end{cases}$$



1 – Minimum energy configuration

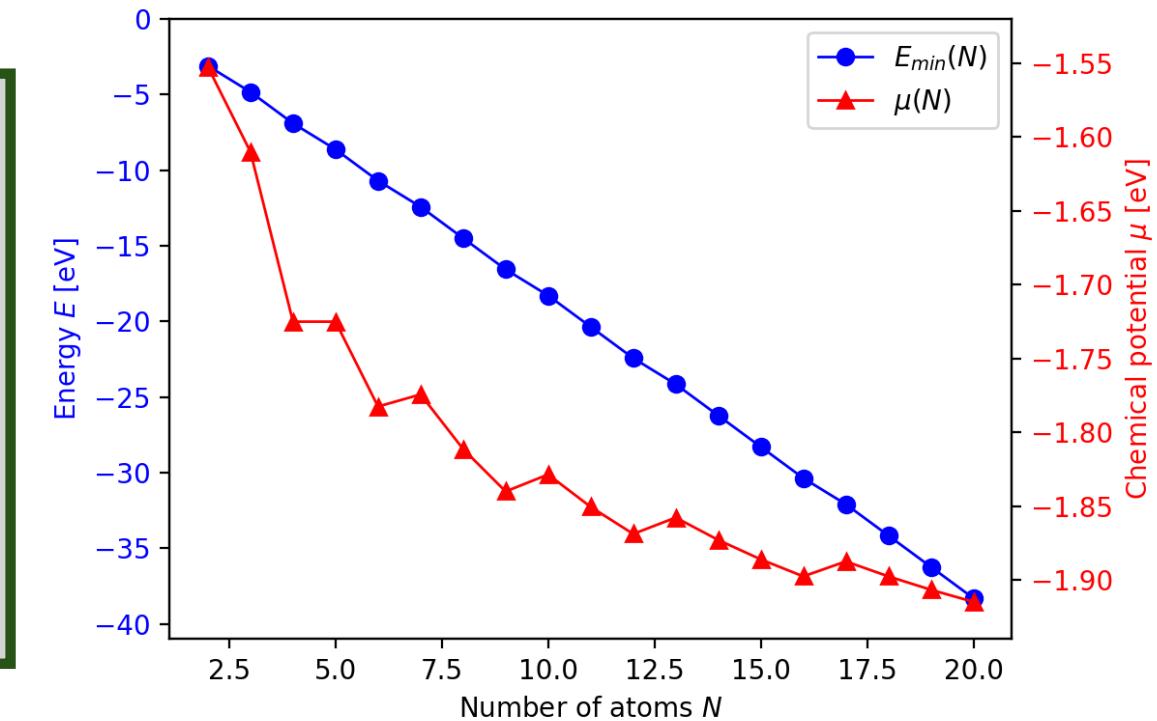
Every atom, even isolated, introduces new negative energy J_0 . Then energy is expected to decrease with increasing N of atoms. The same does not hold for chemical potential, that has an unsteady dependence on N . It reaches local minima whenever N is a perfect square but bumps immediately after, before going back to decrease.

Here, starting from a random disposition of atoms, a frame is saved whenever a new minimum configuration is found. If the algorithm is run for enough steps, the last configuration is the minimum energy configuration.



Parameters

- 1) $L_x \times L_y = 60 \times 60$
- 2) $N = 2-20$
- 3) $T = 0 \text{ K}$



2 – Equilibrium configuration

Temperature raises the probability of jumping from a low energy state to a high energy one. Microstates at $E > E_{\min}$ become accessible, and their degeneracy also must be considered. With high number of steps, it's possible to reconstruct the proportions of those configurational energies inside the ensemble.

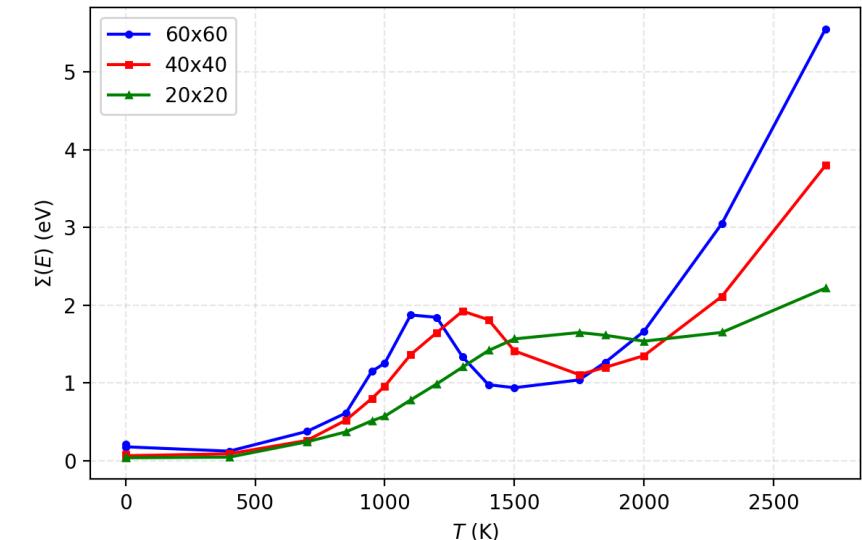
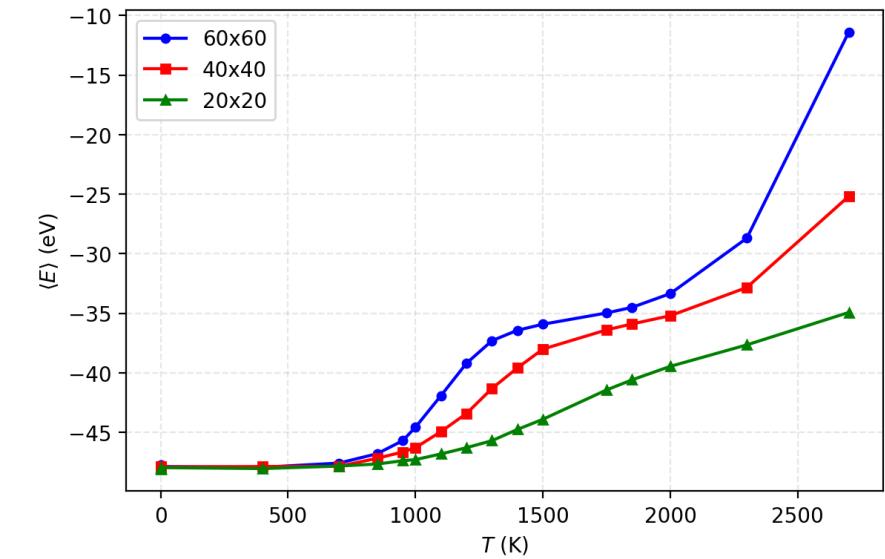
$$\langle A \rangle_{(N,V,T)} \approx \frac{1}{N} \sum_j^* A_j$$

Physically, it's like a transition of phase. At high temperature all the configurations are accessible and the average energy increases, entropy and disorder dominate. At low temperatures most of the times the system finds itself in the minimum energy configuration. In between, the system oscillates back and forth excited states.

Parameters

- 1) $L = 60, 40, 20$
- 2) $N = 25$
- 3) $T = 1 - 2700 \text{ K}$

Smaller grids diminish the number of possible configurations. Atoms find themselves close more often, thus lowering the average energy.



Documentation

All the graphs and animations featured in this presentation are the result of the simulations available in the GitHub repository [zosojack/lab-cms](#). Tutorials on the use of the **CMS module**, comprising its theoretical background, can be found in the [zosojack/tutorials](#) folder.

Thanks for your attention.

Backup

Hyp. Kinetic Monte Carlo

Problem: diffusion are interesting but rare events. MD simulations have the adatom vibrate in place most of the time.

Solution: if **neat time-scale separation** between vibrations (ps) and diffusions (ns), continuum MD trajectory can be replaced with **Markov chain of discrete jumps**.

- Uncorrelated jumps;
- Time independent transition rates;
- After mixing time, equilibrium is reached;
- Strong imposition:
Detailed balance

$$k_{jl} P^{eq}(x_l) = k_{jl} P^{eq}(x_j)$$

- Rates given by HTST harmonic transition state theory, Arrhenius law:

$$k_{HTST} = \nu e^{\frac{-E_b}{k_B T}}$$

- Our implementation: Bortz-Kalos-Lebowitz algorithm

$$\sum_{p=1}^i \sum_{q=1}^{j-1} k_{ij} < \rho < \sum_{p=1}^i \sum_{q=1}^j k_{ij}$$

- Random escape time:
- $$\tau = -\frac{\ln(\xi)}{k}$$
- Solid-on-solid model 1° neigh.:
- $$\varepsilon_k = J_0 + n_k^{(1)} J_1$$
- Uniform deposition rate:
- $$k_{\text{depo}} = \phi L_x L_y$$

Hyp. Metropolis Monte Carlo

Problem: ensemble averages are impossible to compute analytically.

Solution: importance sampling over configurations generated in accordance with their probability reveals their statistical relevance.

Probability of finding energy E_i depends on number of microstates that give that value

$$P^{\text{eq}}(E_j) = \frac{1}{Z} \Omega_j e^{-\frac{E_j}{k_B T}}$$

Then, since

$$S_j = k_B \ln \Omega_j$$

Equilibrium minimizes free energy

$$P^{\text{eq}}(E_j) = \frac{1}{Z} e^{-\frac{E_j - S_j T}{k_B T}}$$

Rates are chosen in order to fulfill detailed balance, guaranteeing to sample over stationary state.

$$k_{ji} = P_{ji}^{\text{sel}} \times P_{ji}^{\text{app}}$$

where:

$$P_{x_i \rightarrow x_j}^{\text{acc}} \equiv \begin{cases} 1 & \text{if } E_j \leq E_i \\ e^{-\frac{E_j - E_i}{k_B T}} & \text{if } E_j \geq E_i \end{cases}$$

Solid-on-solid model 1° neigh.:

$$\varepsilon_k = J_0 + n_k^{(1)} J_1$$

+ Metropolis Monte Carlo

Simulations were run in parallel with multiple seeds. Minimum energy in 2B.1 is to be read as minimum energy between the minima in each seed, while mean energy in 2B.2 as the average of the sample averages over each seed.

Number of thermalization steps is decided **graphically**, fixed where the fluctuations of energy seem to stabilize around a mean value.

