

Temperature accelerated dynamics

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Molecular dynamics simulations

Basics

- ▶ Assume we have a way of evaluating the forces on a collection of atoms, given their positions.
- ▶ An MD simulation describes their behaviour like this:
 1. Calculate forces on atoms
 2. Advance time by dt , move atoms accordingly, update velocities
 3. Goto 1.

Motivation for temperature accelerated dynamics

Trouble with infrequent events

- ▶ MD simulations can be performed on nanosecond time-scales
- ▶ Many atomic processes take place on larger time-scales. We shall later consider crystal growth by vapour deposition at rates around 0.1 monolayer/s
- ▶ We want a way to “speed up” simulations while retaining the correct distribution of transitions in the system
- ▶ M.R. Sørensen, A.F. Voter, J. Chem. Phys. **111**, 9599 (2000). *Temperature-accelerated dynamics for simulation of infrequent events.*

Statistical physics

Temperature in MD

- ▶ The temperature T can be defined through the entropy in terms of Boltzmann-distributed occupation probabilities for each possible state of the system.
- ▶ During a simulation, we generally want to keep temperature fixed. This allows extra energy to “dissipate” to atoms outside system, even if add atoms with high energies
- ▶ **Langevin** dynamics (we shall not bother with the precise equations) exhibit this behaviour. This prescribes the way in which velocities should be updated on each step.

Rate theory

Arrhenius' law

- ▶ Recall that the frequency of transition between (meta)stable states (normally) depends exponentially on the energy barrier E_a associated with the transition:

$$\text{activity} = \frac{\text{transitions}}{\text{time}} = \nu \exp\left(-\frac{E_a}{k_B T}\right) = \nu \exp(-\beta E_a)$$

- ▶ (We usually talk about “harmonic transition state theory”)

Trouble with time scales, revisited

Effect of temperature

- ▶ If infrequent transitions correspond to high activation energies, we can make them happen just by increasing temperature
- ▶ This causes ratios between different transition frequencies to change, leading to wrong results
- ▶ Cunning scheme for performing mock simulation at low temperature T_{low} :
 1. Somehow find all relevant state transitions using MD at high temperature T_{high}
 2. Somehow calculate the energy barrier for each transition found
 3. Extrapolate each average transition time t_{high} to what it **would** have been, t_{low} , at T_{low} , assuming harmonic TST.
 4. Pretend clock has advanced by lowest found value of t_{low} , put the system into the corresponding state, goto 1.

Basin-constrained MD

Finding relevant transitions

- ▶ Define transition: whenever system goes into a state such that a structure relaxation yields a different set of converged atomic coordinates (thus, separate relaxations are performed once in a while)
- ▶ Perform ordinary molecular dynamics simulation at high temperature
- ▶ When detecting a state transition, find the activation energy and final state using e.g. NEB method
- ▶ Invert all velocities, **preventing** state change.
- ▶ Use Langevin thermostat to continuously randomize trajectory, preventing exact backtrack
- ▶ As simulation goes on, we will find more transitions

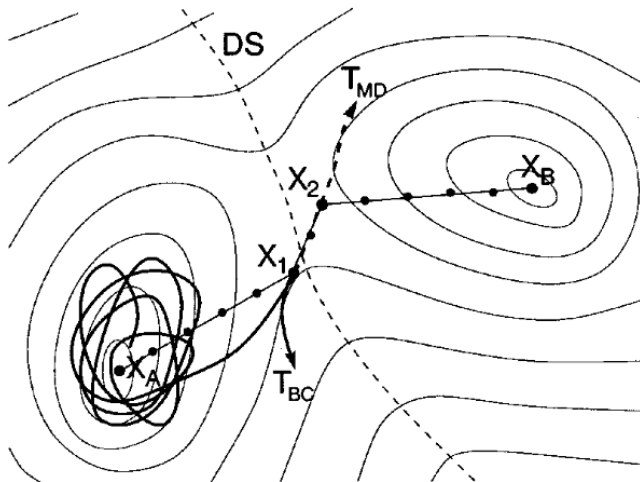
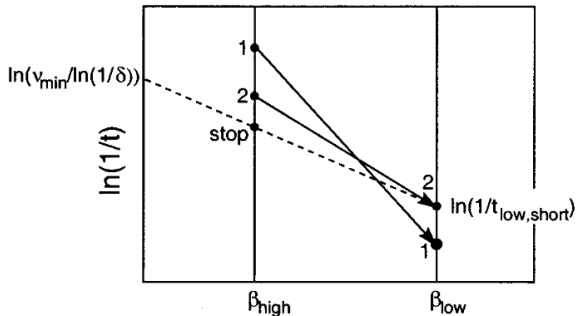


Figure: Transition found between states X_1 and X_2 ; NEB method is used to find lowest-energy path, and thus activation energy and frequency. Note that we didn't need to know transitions in advance.

Being sure that there are no more transitions

A range of high-temperature rates yields a different range of low-temperature permutation rates.

$$\ln(1/t) \rightsquigarrow \ln k = \ln \nu - \beta E_a$$



Temperature accelerated dynamics

Putting it together

1. Set up high-temperature basin-constrained MD simulation.
2. Continue until probability of further relevant transitions is sufficiently low.
3. Determine energy barriers E_a for each found transition using e.g. NEB. This gives us transition times t_{high} at high temperature
4. Use E_a to extrapolate from t_{high} to low-temperature transition times t_{low} assuming harmonic transition state theory
5. Change to the lowest-energy state. Fictional clock advances by t_{low} , as appropriate for the accepted transition. Goto 1.

Crystal growth by vapour deposition

Motivation

- ▶ Consider continuous deposition of silver vapour onto a silver surface. We would like to know the low-level mechanisms that determine crystal growth
- ▶ Experimentally measuring behaviour of individual atoms is not easy
- ▶ Some existing techniques (Monte Carlo) rely on knowing transitions ahead of time, which can be difficult to guess
- ▶ Temperature accelerated dynamics can be used without any prior knowledge of the system
- ▶ F. Montalenti, M.R. Sørensen, A.F. Voter, Phys. Rev. Lett. **87** 126101, *Closing the Gap between Experiment and Theory: Crystal Growth by Temperature Accelerated Dynamics*

Molecular dynamics and crystal growth

What happens

- ▶ We can insert an atom into the system whenever we like
- ▶ Atom moves towards the surface
- ▶ Trajectory deflected by delicate interactions, “steering effects”
- ▶ Atom ends up somewhere.

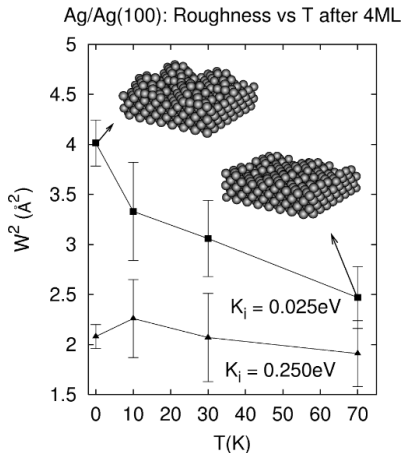
What should happen, but does not

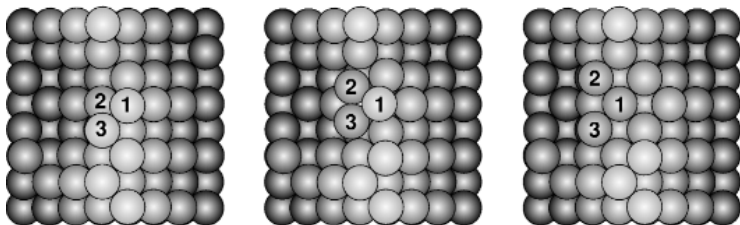
- ▶ Infrequent transitions: adsorbed atoms regularly sliding around on the surface, generally increasing smoothness

Note: if we just increased the kinetic energy and atomic flux, we would not see effects of steering.

Procedure

1. Deposit atom with low-T molecular dynamics, initial kinetic energy K_i
2. Use TAD to fast-forward until next time of deposition, carrying out surface transitions as appropriate.
3. Stop if 4 monolayers or more have been deposited, else goto 1.
4. Consider the roughness W^2 , which is the variance of surface height. Agrees with STM measurements





Example of surface transition

Complicated transition involving multiple atoms on the surface

Number of simulated events corresponds to what happens in
around 0.4 seconds **per deposition**

Conclusion

- ▶ In temperature accelerated dynamics, a high-temperature MD simulation is used to find transitions which are too slow to simulate with realistic temperatures
- ▶ While the transitions are found randomly, one can choose parameters to ensure any desired probability of having found lowest-energy transition
- ▶ The technique correctly reproduces experimental surface roughness after deposition of four monolayers of silver over several seconds
- ▶ Method relies on harmonic approximation, may not work well for all systems