Accelerated Molecular Dynamics Methods

A very brief introduction

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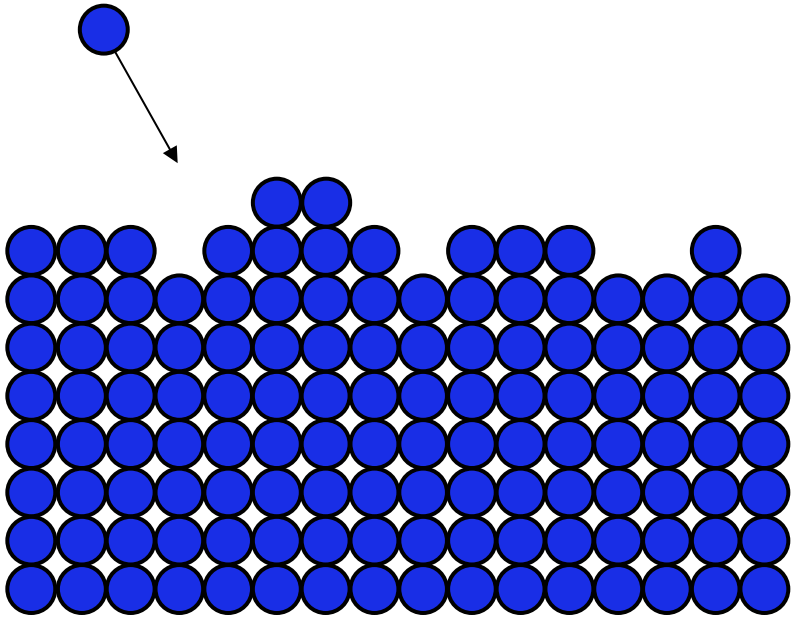
Motivation

Many important processes in chemistry, physics and materials science take place on time scales that cannot be reached by molecular dynamics, which is limited to nanoseconds (or a few microseconds for very small systems).

Often, these processes can be characterized by infrequent activated events. If we try to use our intuition to guess what events will occur, we typically make serious errors, since mechanisms are inevitably more complicated than what we would have thought. Moreover, since we cannot guess where the system is going next, we may have no idea at all what it may look like after many such activated events. We term this a "complex infrequent event system."

Examples:
- surface diffusion during film growth
- bulk precipitate formation
- dislocation motion
- crack propagation at low strain rates
- protein folding
- …

Example: Film or Crystal Growth



Deposition event takes ~2 ps

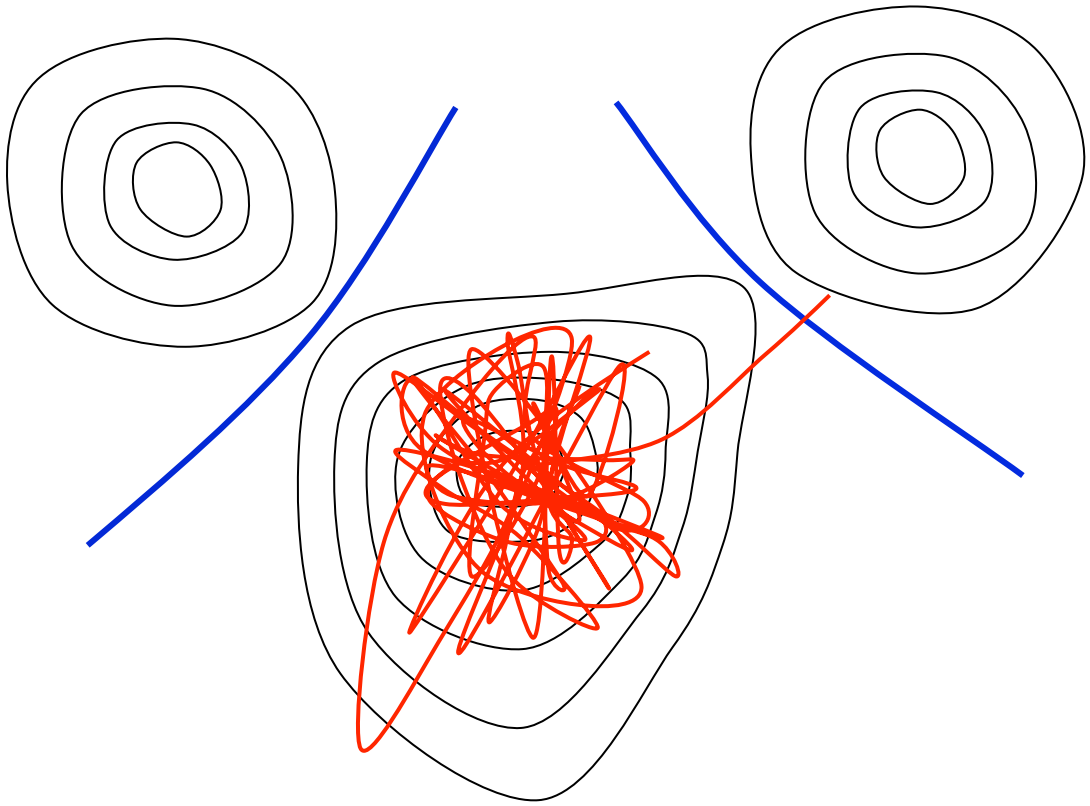
– use molecular dynamics (can reach ns)

Time to next deposition is ~1 s

- diffusion events affect the film morphology
- mechanisms can be surprisingly complex

--> need another approach to treat these

Infrequent-Event System



The system vibrates in 3-N dimensional basin many times before finding an escape path. If we could afford to run molecular dynamics long enough (perhaps millions of vibrations), the trajectory would find an appropriate way out of the state. It is interesting that the trajectory can do this without ever knowing about any of the other possible escape paths.

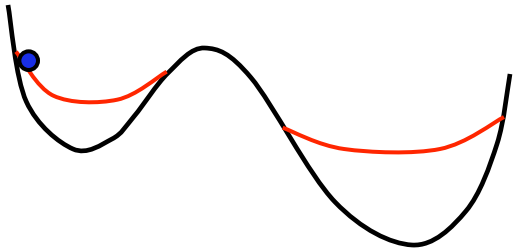
Accelerated Dynamics Philosophy

The philosophy of the accelerated dynamics approach is to let the trajectory, which is smarter than we are, find an appropriate way out of each state. We have developed a few different methods to accomplish this, based on sound statistical mechanical concepts. With these methods, we can follow a system from state to state, reaching time scales that we may never be able to reach with molecular dynamics. Even if we can only afford to run a single realization of a long-time state-to-state trajectory, we may get a glimpse of the nature of the system on that longer time scale (e.g., ms or s), gaining an understanding that is hard to achieve any other way. Virtually every system we have studied so far using accelerated dynamics methods has behaved in some way that we did not expect.

We currently have three methods in this class, summarized pictorially on the next slide.

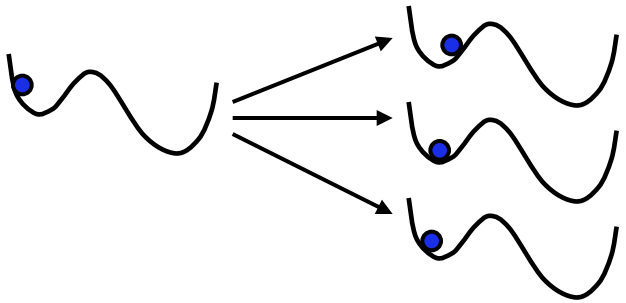
Accelerated Molecular Dynamics Methods

Hyperdynamics



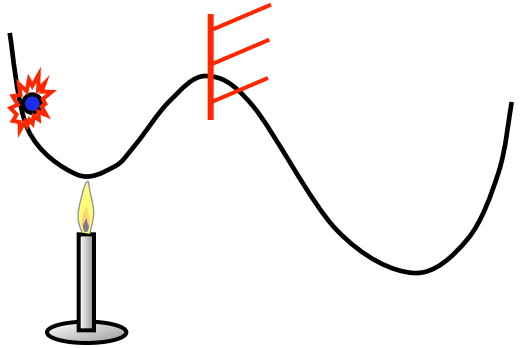
Builds on transition state theory and importance sampling to hasten the escape from each state in a true dynamical way. The boosted time is calculated as the simulation proceeds.
(AFV, J. Chem. Phys., 1997)

Parallel Replica Dynamics



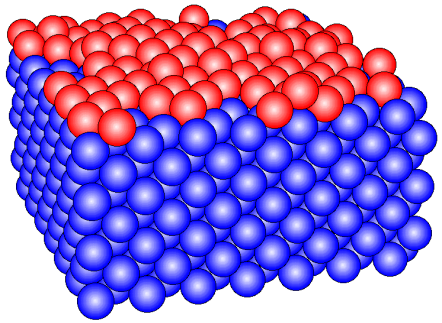
Harnesses parallel power to boost the time scale. Very simple and very general; exact for any infrequent event system obeying exponential escape statistics.
(AFV, Phys. Rev. B, 1998)

Temperature Accelerated Dynamics

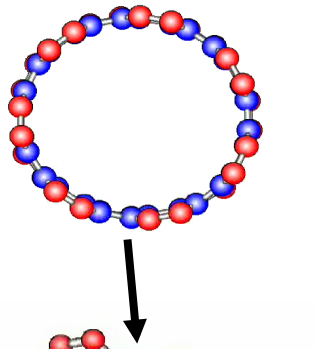


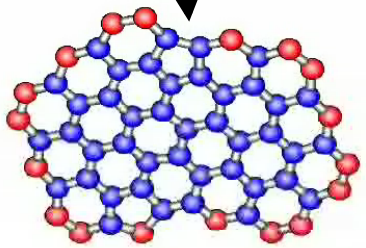
Raise T to make events happen more quickly. Filter out events that should not have happened at correct T. More approximate, but more powerful.
(M.R. Sorensen and AFV, J. Chem. Phys., 2000)

Wide range of systems can be studied

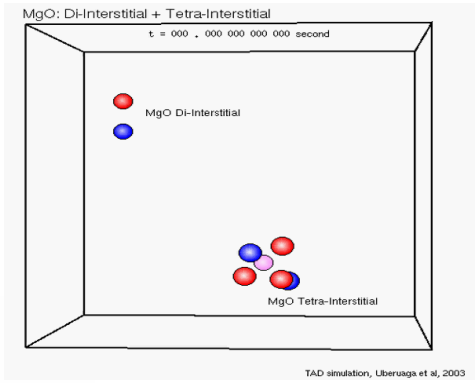


Cu/Ag(100), 1 ML/25 s
T=77K, Sprague et al, 2002

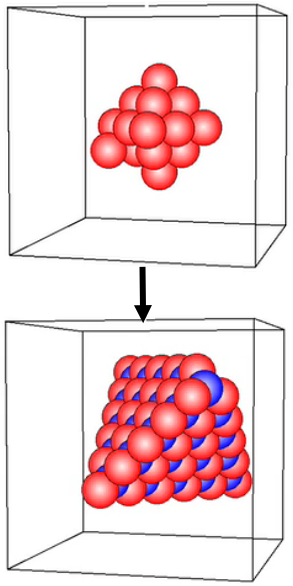




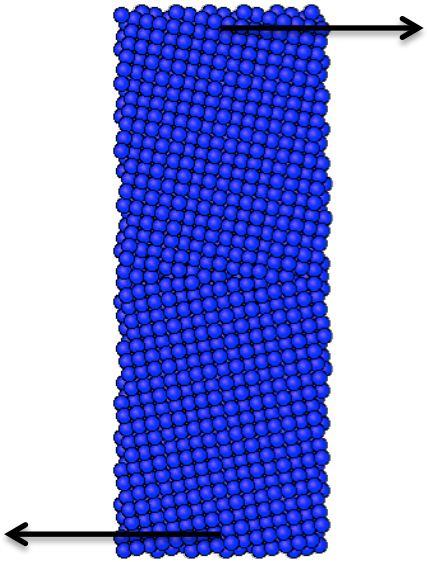
Annealing nanotube slices, μs, Uberuaga et al, 2011.



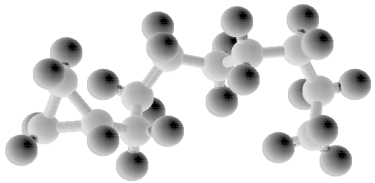
Interstitial defects in MgO, ps – s, Uberuaga et al, 2004.



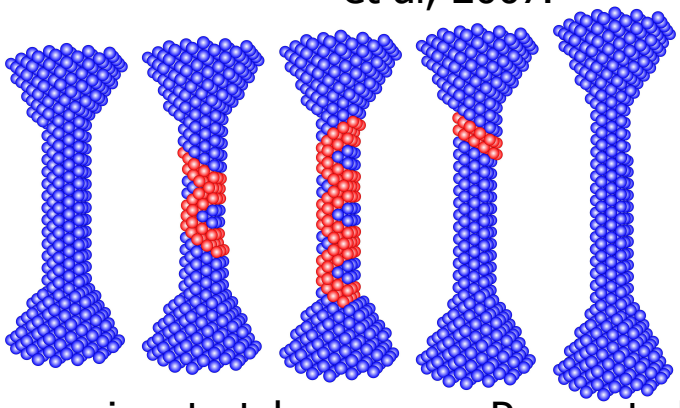
Cu void collapse to SFT, μs, Uberuaga et al, 2007.



Driven Cu GB sliding, 500 μm/s
Mishin et al, 2007.



Hexadecane pyrolysis, μs, Kum et al, 2004.



Ag nanowire stretch, μs - ms, Perez et al, TBP.

Recent brief review: Perez et al, Ann. Rep. Comp. Chem. **5**, 79 (2009).