

T-12

Theoretical Chemistry &amp; Molecular Physics

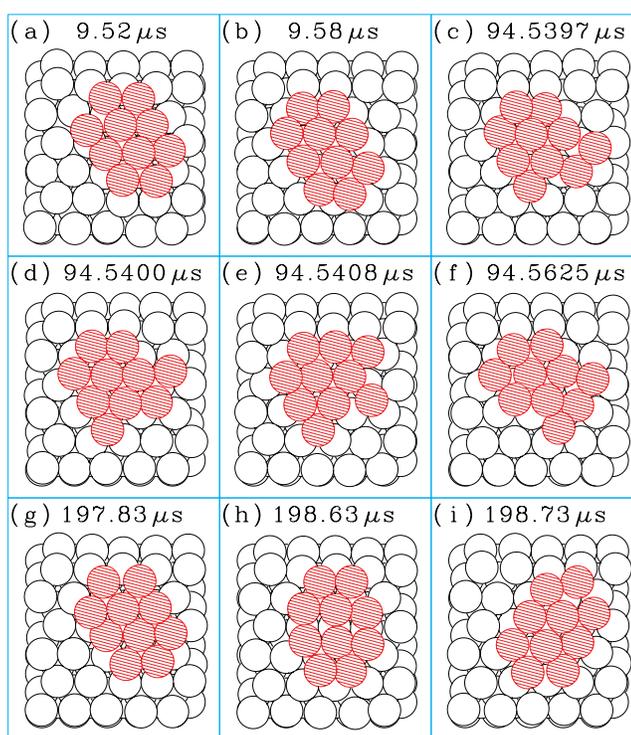
## Accelerated Molecular Dynamics of Infrequent Events

Arthur F. Voter

The molecular dynamics (MD) method is a powerful tool for detailed studies of defects in materials. For a given interatomic potential, atom positions are evolved with no other assumptions than classical mechanics, so the dynamical behavior in a simulation is “truth” for the system under study. Direct and meaningful comparisons to experiment can be made, with discrepancies attributable solely to the inaccuracy of the potential. A major drawback of molecular dynamics, however, is that it is limited to time scales of nano-seconds or less. Even massively parallel computers, which have extended the size scale to millions of atoms, have had little impact on the accessible time scale.

For many systems, the long-time dynamics can be characterized as “infrequent event” behavior; there are occasional transitions from one potential basin to another, separated by long periods of uninteresting vibrational motion. For these systems, the time scale limitations of molecular dynamics can be overcome using transition state theory (TST), in which the rate constant for escape from one state (basin) to another is approximated as the flux through the dividing surface separating the two states. The appeal of transition state theory is that dynamics are unnecessary; the TST rate is an equilibrium property of

the system and can be evaluated directly once the dividing surface is defined. Although transition state theory is not exact (due to correlations among the surface-crossing events), it is usually an excellent approximation for solid-state defect dynamics.



**Figure 1:** Evolution of a 10-atom Ag cluster on the Ag(111) surface using the hyper-MD simulation method. Three different diffusion mechanisms can be observed.

As powerful as transition state theory is, however, there is a catch: to use it requires knowledge of the dividing surfaces. If the states to which a system might evolve are not known in advance, transition state theory cannot be applied (or may be applied incompletely, missing important pathways). Many such situations occur in materials science. Examples include the healing events after ion implantation, the dynamics of a dislocation core, or the advance of a crack front.

In a T-12 Laboratory-Directed Research and Development program, an alternative approach to these types of problems is being developed [1].

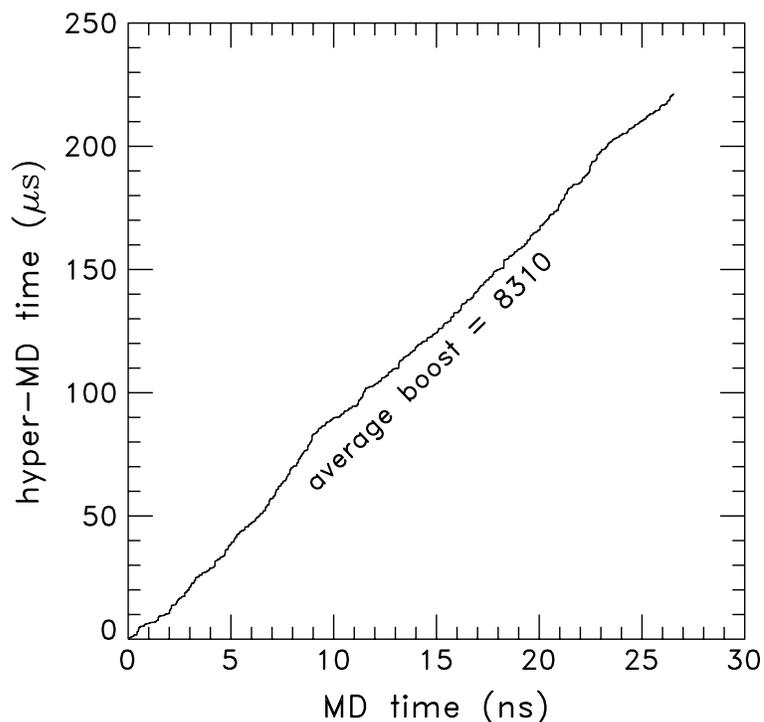
Beginning from the transition state theory approximation, a method has been derived that extends the time scale of molecular dynamics simulations without advanced knowledge of either the location of the dividing surfaces or the states through which the system may evolve. A bias potential is designed to raise the energy

of the system in regions other than at the TST dividing surfaces. Running a simulation on the biased potential gives accelerated evolution from state to state, while the elapsed time becomes a statistical property of the system. The instantaneous gain (or “boost”) in the rate at which time advances (relative to direct MD) depends exponentially on the bias potential. In the long-time limit, the dynamics on the biased potential are exact, provided that transition state theory holds and the bias potential meets certain requirements. In essence, this new method (“hyperdynamics” or “hyper-MD”) captures the advantages of both molecular dynamics and transition state theory into a single simulation approach.

The key to the method is designing a computationally tractable bias potential that is zero at the dividing surfaces (without explicit knowledge of them) and does not introduce correlated dynamical events. We have shown that such a bias potential can be constructed from local properties of the potential via the Hessian and gradient. Moreover, it can be computed using only first derivatives of the original potential, just as for regular molecular dynamics.

As an example, Figure 1 shows the results of a hyper-MD simulation following the motion of a 10-atom Ag cluster on the Ag(111) surface at  $T = 300$  K for 221 microseconds. On this time scale, the cluster does not move far, but three distinct diffusion mechanisms can be observed: concerted hopping between hcp and fcc registry (Figures 1a - 1b), periphery diffusion (Figures 1c - 1f), and a dislocation mechanism (Figures 1g - 1i). None of these mechanisms were designed into the simulation method. Figure 2 shows the evolution of the boosted time over the course of this simulation. The average boost factor is 8310 and the net computational boost is about 300.

Although much remains to be learned about the optimal application of this new method, it already appears promising as an alternative approach for processes that are too slow for molecular dynamics and too complicated for transition state theory.



**Figure 2: Cumulative boosted time during the hyper-MD simulation. The instantaneous boost ratio is the exponential of the bias potential strength at the current trajectory position.**

- [1] A. F. Voter, *J. Chem. Phys.* **106**, 4665 (1997).  
A. F. Voter, *Phys. Rev. Lett.*, in press.