

Dimer method long time scale simulations of surface growth

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ABSTRACT

We have carried out long time scale simulations where the dimer method [G. Henkelman and H. Jónsson, *J. Chem. Phys.* **111**, 7010 (1999)] is used to find the mechanism and estimate the rate of transitions within harmonic transition state theory and time is evolved by using the kinetic Monte Carlo (KMC) method. Unlike traditional applications of KMC, the atoms are not assigned to lattice sites and a list of all possible transitions does not need to be specified beforehand. Rather, the relevant transitions are found on the fly during the simulation. In growth simulations of Al on Al(100) we find that many important processes found with the dimer method are too complicated to be included in a KMC event table. The method lends itself naturally to a distributed parallel implementation. Dimer searches were calculated with screensavers on eighty PC's in order to simulation systems of several thousand atoms over timescales of milliseconds.

Keywords: dimer method, KMC, aluminum growth

1 INTRODUCTION

One of the greatest challenges in computational studies of atomic systems is the simulation of long time scale evolution. While it is relatively straightforward to iteratively solve Newton's equations, the time scale that can be simulated that way, even when the simplest interaction potentials are used, is only on the order of nanoseconds for a typical system size and a weeks worth of CPU time on a modern computer. In chemistry and materials processing, most interesting transitions are thermally activated and take place on the time scale of microseconds or even seconds. The disparity of time scales is huge and it is clearly necessary to develop different methods for simulating time evolution.

Fortunately, there is often a separation of time scales. Vibrational motion of atoms occurs on the short time scale of femtoseconds. For a typical chemical reaction or diffusion event, there are on the order of 10^{10} vibrations before there is a sufficiently large fluctuation of thermal energy in the right degree of freedom for a transition to take place. Instead of following each vibration and waiting for these rare events, one can use transition state

theory (TST) [1]–[6] to calculate the average amount of time necessary for the system to make a transition. In order to calculate a rate, a bottleneck through which the system must pass in order to make the transition must be identified. This is the so-called transition state. For solid state systems, it is often possible to assume that the system is harmonic near the energy minimum representing the initial state and near a saddle point on the energy surface in the transition state. In this case, there is a simple form of TST referred to as harmonic transition state theory (hTST), in which the rate of a transition, k , can be directly related to properties of the initial state energy minimum and the saddle point [7], [8],

$$k^{\text{hTST}} = \frac{\prod_i^{3N} \nu_i^{\text{init}}}{\prod_i^{3N-1} \nu_i^{\ddagger}} e^{-(E^{\ddagger} - E^{\text{init}})/k_B T}. \quad (1)$$

Here, E^{\ddagger} is the energy of the saddle point, E^{init} is the local potential energy minimum corresponding to the initial state, and the ν_i are the corresponding normal mode frequencies. The symbol \ddagger refers to the saddle point. All the quantities can be evaluated from the potential energy surface, at zero temperature, but thermal and entropic effects are included through the harmonic partition functions. The most challenging part in this calculation is the search for the relevant saddle point(s).

Several methods have been proposed for accelerating the dynamics of rare events. Voter has developed several important methods. One is hyperdynamics [9], [10] which involves the creation of a repulsive bias potential which fills in regions around potential energy minima but does not affect the potential energy rims separating the energy basins, including the saddle points. In another method, proposed by Sørensen and Voter, so-called temperature accelerated dynamics (TAD) [11], the temperature of the system is increased, but the dynamics are carried out in such a way that only the transitions that would have occurred at a lower temperature are extracted. Finally, Voter has developed a method called parallel replica dynamics in which many trajectories are run in parallel while waiting for transitions to occur [12]. This method accelerates the simulation time required to see a transition by using many processors.

In this work we combine the dimer method [13] for finding saddle points and rate calculations within hTST

with a kinetic Monte Carlo (KMC) method for simulating the evolution of systems over long time scales [14], [15]. This method is easy to implement and, compared to existing methods, may require less computational time for small systems.

2 THE LONG TIME DYNAMICS METHOD

In order to carry out the simulation of a transition in the system, the rate and mechanism of all the relevant transitions from a given initial state need to be known. Within hTST this corresponds to finding all the low energy saddle points on the rim of the potential energy basin corresponding to the initial state. The dimer method is used to search for these saddle points.

2.1 The Dimer Method

The dimer method is described in more detail in a previous publication [13]. The dimer is made up of two images (replicas) of the system. These images are separated in space by a finite distance displacement.

There are two parts to each dimer move. The first part is dimer rotation. The lowest energy orientation of the dimer is along the lowest curvature mode. If the dimer is free to rotate, the forces acting on the two images will pull the dimer to the lowest curvature mode. This is done by defining a rotational force which is the difference in the force at the two images. Minimizing the energy of the dimer with respect to this rotational force aligns the dimer with the lowest curvature mode (this feature was used by Voter in his construction of bias potentials in hyperdynamics [10]). A modified Newton's method can be used to make this rotation efficient [13]. An important aspect of the dimer method is that it only requires the first derivative of the energy, not the second derivatives.

The second part of the algorithm is translation of the dimer. A first order saddle point on a potential surface is at a maximum along the lowest curvature direction and a minimum in all other directions. In order to converge to a saddle point, the dimer is moved up on the potential energy surface along the lowest curvature mode, but down in all other directions. This is done by defining an effective force on the dimer in which the true force due to the potential acting at the center of the dimer has the component along the dimer inverted. Minimizing with respect to this effective force moves the dimer to a saddle point. With empirical potentials, minimization using the conjugate gradient method works well.

2.2 Kinetic Monte Carlo

KMC is a powerful method that can be used to extend the timescale of simulations far beyond the vibrational timescale. In a typical KMC simulation, all tran-

sitions that can ever occur in the system, along with their rates, must be known before the simulation starts. Then, given any configuration of the system, a table of all possible transitions and corresponding rates needs to be constructed. The rates can be estimated using TST if the energy surface is known [16]. The problem here is to identify and tabulate all relevant transitions ahead of time. This limits the applicability of the method to simple systems where it is possible to guess which transitions are important. Systems that can undergo complicated transitions involving several atoms, such as the aluminum system described in Sec 3, or in which atoms do not sit at lattice sites are extremely difficult to model with this approach.

If a list of possible transitions for a given initial state is available, a random number can be used to choose one of the transitions and let the system evolve to a new state. The probability of choosing a transition is proportional to its rate, r_i . On average, the amount of time that would have elapsed in order for this transition to occur is

$$\Delta t = \frac{1}{\sum r_i}, \quad (2)$$

which is independent of which transition got chosen. It may also be important to include the appropriate distribution of escape times. For random uncorrelated transitions, this is a Poisson distribution. If μ is a random number from 0 to 1, the elapsed time for a particular transition is given by

$$\Delta t = \frac{-\ln \mu}{\sum r_i}. \quad (3)$$

The system is then advanced to the final state of the chosen transition and the process then repeated.

2.3 Combined Dimer and Kinetic Monte Carlo

The dimer method can be used to relax some of the limitations of the traditional implementation of the KMC scheme. If the dimer method is used to find possible transitions, there is little limitation on the complexity in terms of the number of atoms or the spatial extent of the transition. Also, the energy barriers do not need to be known before the calculation is started. Furthermore, the atoms do not need to be mapped onto a lattice and it is not necessary to anticipate all possible states of the system.

When a new minimum structure is visited, a swarm of dimer searches is sent out. For the calculations described in Sec. 3, two hundred dimer searches were used. The results of the searches are collected. The system is quenched on either side of each saddle point in order to verify that it lies on a minimum energy path from the given initial state minimum. In the same way as described in Sec. 2.2, a transition is chosen from the list,

the system is advanced to the final state of that transition, and the time interval associated with the transition is added to the accumulated time.

2.4 Distributed Computing with EON

An important aspect of the long time scale method is that dimer searches are independent of each other can be calculated in parallel. We have taken advantage of this property and constructed a distributed computing system EON in which the server, eon.chem.washington.edu, keeps track of the current state of the system and responds to requests by clients. There were approximately eighty Linux and Win32 clients working on the calculation described in Sec. 3. The Win32 machines run the client application when a screen saver is activated using a system similar to the popular seti@home project.

When a new client checks in with the server, it is given application which is capable of running dimer searches on the system being simulated. The client verifies a signature of the application with the server’s RSA public key to ensure the application came from our server. The client then goes to the server for an initial configuration from which the dimer search is started. Each search takes approximately 10 minutes on an average client. If a good saddle point is found, the client calculates a prefactor for the process according to the Vineyard form in Eq. 1, minimizes from the saddle to determine the connecting minima, and returns these result to the server. When the server has accumulated enough possible processes, where enough in this case was set to be 200, it chooses one process according to the KMC algorithm and advances the system. In the simulation described in Sec. 3, four years of cumulated client CPU time was used to simulate 50,000 distinct possible processes which were used to advance the system through 1,243 KMC steps.

3 APPLICATION TO AL(100) GROWTH

Deposition of Al adatoms on an Al(100) surface was chosen as a test problem for this simulation method for a couple of reasons. First, a successful embedded atom potential of the Voter and Chen form exists for aluminum [17]. Also, this system has been extensively studied with the dimer method in reference [13]. There, it was shown that there are many transitions possible even for a single adatom on the Al(100) surface. A particularly interesting aspect of the Al(100) system is that an concerted displacement process has a lower energy barrier than the direct hop. This was shown by Feibelman with density functional theory calculations [18].

Aluminum atoms were deposited on the six layer, 128 atoms per layer Al(100) surface shown in Fig. 1A. During the simulation, nine layers were deposited at a

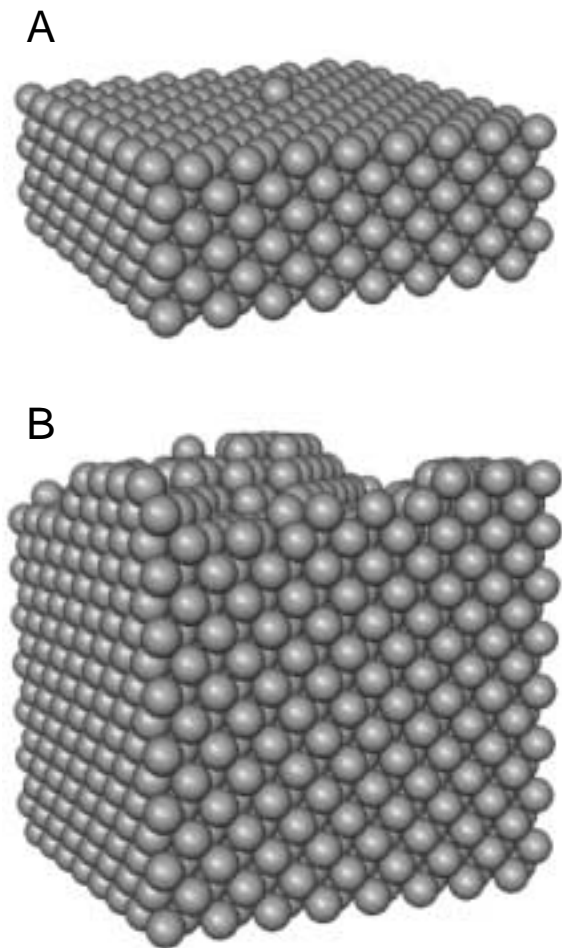


Figure 1: The initial (A) and final (B) configurations of an Al/Al(100) deposition simulation. Nine layers were deposited in 90 ms at a temperature of 30 K. Between deposition events, possible activated surface processes were found with the dimer method using the EON distributed computing system. On average 41 distinct events were found and put into a kinetic Monte Carlo event table along with a possible deposition event. In this way a multiple timescale simulation was carried out in which deposition events were simulated with classical dynamics on a femtosecond timescale and activated processes were simulated in milliseconds between deposition events.

rate of 100 layers per second at 30 K. The final configuration is shown in Fig. 1B. Before each KMC move, a total of 200 possible processes were found using dimer searches. On average, 41 of these processes were distinct. In addition to these possible activated surface processes, the deposition process was added to the KMC event table. If the deposition event was selected, the surface was heated to 30 K during a 0.1 ps thermalization period. Then a new atom was placed 8 Å above the highest surface in a random location and given an initial velocity towards the surface with an incident ki-

netic energy of 0.1 eV. The deposition was simulated for 2 ps during which the adatom attaches to the surface. Two layers of atoms above the three frozen bottom layers were thermostated during the deposition to absorb the attachment energy of the adatom. In this way, a multiple timescale simulation was carried out in which deposition events were simulated on the femtosecond timescale and activated processes occurred on the millisecond timescale between deposition events.

During the simulation 1,165 events of 1,243 were deposition events. The 78 activated transition had an average activation energy of 0.04 eV. Fifty-one of these activated events were smoothening events in which some atoms descended at least one layer. Most of these activated events involved several atoms, and taking into account the complicated geometry of the surface, would not be included in a preconceived KMC event catalogue. Surface atoms were also rearranged during the deposition events. Of the 1,165 deposition events, 118 involved some displacement of surface atoms from one site to another. In some cases atoms were left in non-lattice sites, making the prediction of possible events nearly impossible.

Some overall statistics of the deposition simulation are shown in Fig. 2. The top panel shows the number

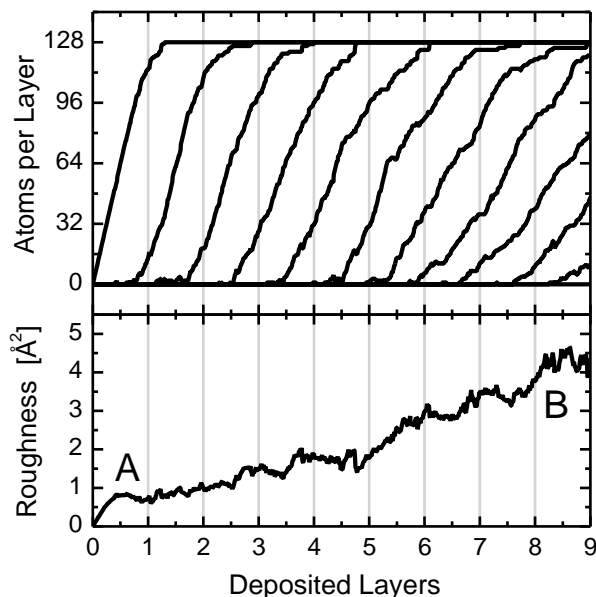


Figure 2: The number of atoms in each layer during the Al/Al(100) growth simulation is shown in the upper panel. At first the atoms are deposited almost layer-by-layer, but as the simulation progresses a mound forms and the surface roughness, shown in the lower panel, rises. At the end of the simulation there are three to four exposed layers.

of atoms in each layer as the atoms are deposited. If the layers were to grow exactly layer by layer, this plot

would consist of a set of parallel lines with a new layer being occupied only when the previous layer is filled. Instead, the surface becomes rougher during the simulation, and by the end of the simulation there are clearly three exposed layers on the surface. This can also be seen in Fig. 1B in which a mound has started to form on the left side of the surface and a valley on the right. The surface roughness, given by the height-height correlation function is shown in the lower panel of Fig. 2. Clearly the roughness has not reached an equilibrium value after depositing nine layers, and there is a need for some statistical averaging. This calculation will also be compared with pure deposition simulations in order to determine the importance of activated processes during Al/Al(100) deposition.

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