

Long Time Scale Simulations of Al(100) Crystal Growth

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Abstract

We have carried out simulations of Al(100) crystal growth using a combination of classical dynamics simulations and a new long time scale simulation method based on harmonic transition state theory. Atoms are deposited using classical dynamics over a time interval of a few picoseconds, but once the system has thermalized, the long time interval in between deposition events, a millisecond, is simulated using an extension of the kinetic Monte Carlo method. Here, relevant transitions in the system are found on the fly and the need for a predetermined event table and lattice approximation are eliminated. For a given state of the system, the dimer method is used to search for the saddle points on the potential energy rim surrounding the local energy minimum. The Al(100) surface is found to grow remarkably smooth, even at temperature as low as 30 K. As multilayer structures start to form, low barrier events involving concerted displacement of a number of atoms tend to smoothen the surface.

1 INTRODUCTION

Crystal growth is one of many problems where the time scale of direct classical dynamics simulations is many orders of magnitude too short. While simulations span only a nanoseconds for a typical system size and a weeks worth of CPU time on a modern computer, laboratory experiments often involve growth of a single monolayer in a millisecond or longer. The problem is that activated events are rare events on the time scale of atomic vibrations. A common approach to address this problem is to use the kinetic Monte Carlo method (see below), but here a complete table of possible processes in the system needs to be created before hand, and the atoms need to be assigned to lattice sites. These are severe limitations since even the simplest systems can have complex dynamical processes which are hard to anticipate and local configurations where atoms do not fit on the crystal lattice may show up.

Fortunately, crystal growth from vapor typically lends itself to a nice 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, 2, 3, 4, 5, 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.

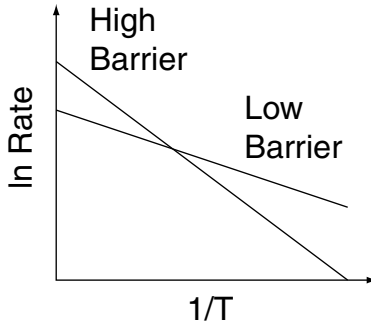


Figure 1: The temperature dependence of the rate of two different transitions is shown. The transition with the lower energy barrier corresponds to the line with shallower slope. A typical situation is shown in which the higher barrier transition has a higher prefactor (intercept with vertical axis). At low temperature, on the right side of the graph, the rate of the low barrier transition will be higher than that of the high barrier transition, and the dynamics will be dominated by events with low activation energy. At high temperature, the dynamics will be dominated by the higher entropy transition which has higher activation energy. This illustrates why a system cannot simply be heated to find events that occur on a longer time scale at low temperature.

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).

One possible method of increasing the rate of rare events is to simply heat the system. If the atoms have more thermal energy, they will be more likely to undergo transitions. Unfortunately this technique can lead to qualitatively different dynamics than at the lower temperature of interest. The situation is illustrated in Fig. 1. The temperature dependence of the rate of two different transitions is shown, one with a low activation energy and the other with a high activation energy. At low temperature, the low barrier transition will have a higher rate and dominate the dynamics. At high temperature, entropy becomes more important and the transition with a larger prefactor dominates, namely the high barrier transition.

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 Sorensen 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. 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

In the long time scale calculations presented here, between 25 and 50 dimer searches were launched from each new potential minimum visited. Dimer searches were started from configurations close to potential minima. The easiest way to choose a starting position is to make a random displacement away from the minimum. If *all* the atoms in the system are included in the random displacement, the dimer search can be biased towards finding higher energy transitions which involve many atoms. We find that it is better to displace only atoms within a local region. For each dimer search in the Al(100) growth calculations, an under coordinated surface atom was chosen at random to be the center of the initial, local displacement. The displacements had a Gaussian distribution with a mean of 0.2 Å in each degree of freedom. The region consisted of the central atom and its first and second neighbors. We have found that a continuous distribution is better than a fixed displacement size because it increases the variety of saddle points found. In principle, a scheme like this can eventually find all saddle points around a minimum simply because the starting points of the dimer search can be at any point in space. In practice, there is no guarantee that a complete list of saddle points can be found in a reasonable amount of time.

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 along a vector $\hat{\mathbf{N}}$. For an empirical potential this can be small. Here we have used 0.005 Å. Initially $\hat{\mathbf{N}}$ has non-zero elements only in the degrees of freedom along which the system was displaced.

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.

It is not necessary to fully converge the dimer orientation at each translational step. We have found it most efficient to pick a certain tolerance for the rotational force. This sets how precisely the dimer is oriented along the lowest curvature mode before it is moved. The dimer is rotated at least once and possibly a few times until the rotational force is less than the specified tolerance. In these calculations the maximum rotational force was set at 5 meV/Å.

The dimer requires on average 400 force evaluations to converge on a saddle point. Other methods for finding saddle points using only first derivatives of the energy have been proposed [14, 15], but it is unclear how their efficiency compares with the dimer method.

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 transitions 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 section 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

$$\Delta t = \frac{1}{\sum r_i}, \tag{2}$$

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

$$\Delta t = \frac{-\ln \mu}{\sum r_i}. \tag{3}$$

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.

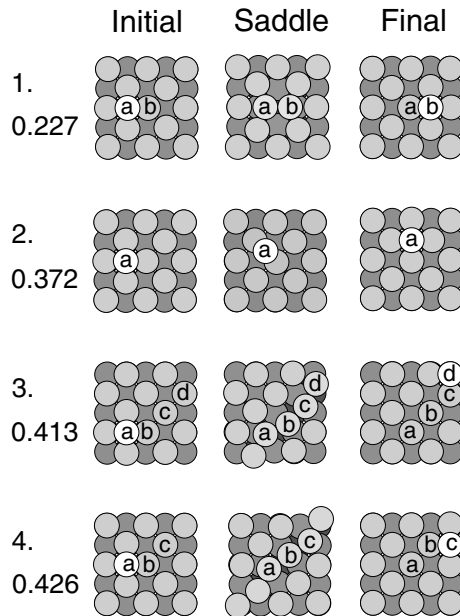


Figure 2: The four lowest energy transitions found with the dimer method for the diffusion of an Al adatom on Al(100). For each transition, the initial state, the saddle point configuration, and the final state are shown. Atoms are shaded by depth and the atoms with the greatest movement in each transition are labeled. The energy is given in eV. The lowest energy diffusion process is a two-atom concerted displacement (1). The hop (2) is of similar energy to a concerted displacement involving three (3) and four atoms (4). Because adatoms can so easily displace atoms in the surface, the Al(100) surface displays a great variety of transitions which would be hard to find by guesswork.

When a new minimum structure is visited, a swarm of dimer searches is sent out. For the growth calculations, either 25 or 50 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 section 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.

3 APPLICATION TO AL(100) DIFFUSION

Diffusion and island formation 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. The four lowest energy transitions found with the dimer method are shown in Fig. 2. A particularly interesting aspect of the Al(100) system is that a concerted displacement process has a lower energy barrier than the direct hop. This was shown by Feibelman with density functional theory calculations [18].

The dimer method was able to find a wide range of transitions from an initial state consisting of a single adatom in a four fold hollow site on Al(100). The substrate consists of 300 atoms, 50 per layer in 6 layers. The bottom two layers are held frozen and the top surface is left open to vacuum. Sixty different transitions were found with 1000 dimer searches. On average the low

energy processes: the concerted displacement involving two, three and four atoms, and the hop, were found three quarters of the time. One quarter of the time a wide collection of higher barrier transitions were found.

In the KMC scheme, it is important to find all the relevant transitions, i.e. transitions with low activation energy. Using the statistics found for the single adatom diffusion events, there is an 80% certainty of finding all four (degenerate) two-atom concerted displacements with 50 dimer searches. For an accurate simulation, this indicates that there should be many dimer searches at each step. Fortunately, they can easily be carried out in parallel on separate computers. But, even with a modest number of searches, the method can give a good, qualitative idea of how the system will behave over long time intervals.

4 DEPOSITION AND SURFACE GROWTH

Multiple time scale simulations of Al(100) crystal growth were carried by combining classical dynamics of deposition events with the long time scale simulation of the time intervals between deposition events. Interesting processes can take place during the deposition event [19, 20], but the excess energy released as the incoming atom binds to the surface dissipates quickly, in one or two picoseconds [19, 20]. This period of time can easily be simulated by direct classical dynamics. After the ‘hot-spot’ has cooled down and the system has thermalized, transition state theory can be applied for the activated diffusion processes. The long time scale calculation was done in the same way as the adatom diffusion simulation described above, but at each step a deposition process was added to the table of possible events. A smaller system was used than in the adatom diffusion simulations, the cell consisted of 32 atoms per layer. Atoms were deposited at a rate of one monolayer per millisecond ($32 \times 10^3 \text{ s}^{-1}$). A deposition process was simulated by placing an aluminum atom at a random position 10\AA above the surface and giving it an initial velocity towards the surface characteristic of the simulation temperature. Classical dynamics were run until the component of the velocity of the deposited atom perpendicular to the surface had changed sign twice. At this point the system was considered to be equilibrated and the KMC simulation took over. In this way, the short deposition time scale was simulated accurately as well as the longer time scale of thermally activated diffusion processes.

Growth at 100K was first simulated. A total of 9.5 layers were deposited in 9.8 ms. This took 500 events in the KMC simulation of which 302 were deposition events. An important question in crystal growth is how smoothly the surface grows, i.e. how well a layer gets completed before the next layers starts forming. A key issue is how an adatom that lands on top of an island manages to descend down to the more stable edge site. Typically, an adatom descends by a two-atom concerted displacement process, but the simulation also revealed interesting three- and four-atom descent processes where the adatom started out two or three sites away from the edge. The transitions involving three and four atoms have somewhat larger activation barrier, 92 meV and 126 meV, but were frequently observed in the simulation. The ease of these types of descent processes in the Al(100) system make it easy for aluminum to grow layer-by-layer, especially for this small 32 atom per layer cell.

The growth simulation was then repeated for a lower temperature, 30 K. A total of 7.3 layers were grown in 5.6 ms. The KMC simulation involved 264 events of which 232 were deposition events. Snapshots of the system during the growth simulation are shown in Fig. 3. The range of possible surface processes is then much more limited. The long range descent events observed at 100 K were not observed at 30 K. Since individual adatoms were less likely to descend, rougher surface morphology could form. But, after structures with several under-coordinated atoms had

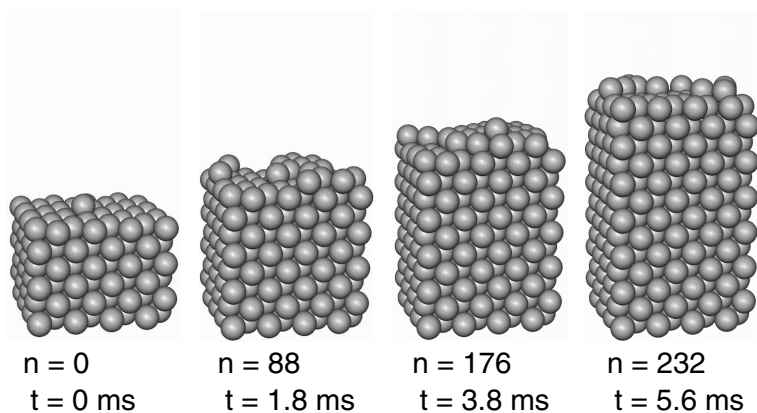


Figure 3: Seven monolayers of Al were grown at 30 K on the Al(100) substrate. The deposition rate was one monolayer per millisecond. Even at this low temperature, the layers grown are free of defects and the surface is smooth.

built up, some even not sitting at well defined lattice sites, concerted processes involving several atoms would typically occur and smoothen out the surface.

Two of these transitions are shown in Fig. 4. In the initial state of the first process, an atom has been deposited on an island consisting of four atoms resulting in a structure where five atoms are not sitting on lattice sites. Then, a transition occurs which moves all five atoms simultaneously into lattice sites, two in the top layer and the other three in a lower layer. In the other process shown in Fig. 4, a deposited atom lands on top of an island, starting a third incomplete layer. In the subsequent transition, five atoms slide down in a concerted way. The third layer atom ends up in the second layer, the two second layer atoms end up in the first layer, and two first layer atoms get pushed out into different sites. The energy barrier of these two five-atom displacement processes is only 48 meV and 45 meV. Evidently, when the surface becomes rough, low barrier cascading events where many atoms move into more stable sites become possible. Even at this low temperature, the surface morphology remains smooth, although the basic adatom diffusion process on the flat Al(100) terrace, which has an activation energy of 0.2 eV, is not active.

A simulation was also carried out at an intermediate temperature, 70 K. As the temperature was lowered from 100 K to 30 K, the average barrier height of observed transitions also dropped, as expected. At 100 K the system was able to cross barriers of 0.18 eV, but at 30 K the highest barrier that was overcome was less than 50 meV.

Animations of the growth and ripening simulations can be viewed on the web at <http://eon.chem.washington.edu>.

5 EFFICIENCY

It is important to know how a simulation method scales with system size. To determine this, we can consider how the number of force evaluations changes when the system is doubled in size. Force evaluations are considered rather than total computational time, because the evaluation of the force can scale differently depending upon the complexity of the interaction potential. In favorable situations, evaluation of the force scales linearly with system size.

When a system size is doubled, the number of transitions that can occur in the system is also doubled. In the crudest implementation of the simulation method, the number of dimer searches would then increase in proportion to the system size. If, however, the transitions are local, i.e.

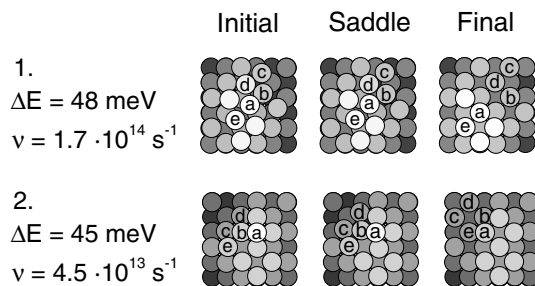


Figure 4: Two processes observed during the 30 K deposition simulation of Al atoms on Al(100) shown in Fig. 3. At this low temperature only very low energy processes can occur. The surface tends to grow rough temporarily and regions with islands stacked on top of islands form. The initial state of the first process resulted from classical dynamics simulations of the deposition of atom (a) on top of a four atom island consisting of atoms (b), (c), (d), and (e). The five atoms are not sitting at lattice sites. In a concerted, activated process all five atoms move to lattice sites, two in the top layer ((a) and (e)) and three in the lower layer ((b), (c), and (d)). In the second process, five atoms slide in a concerted way down the side of an island stack. The adatom (a) in the third layer moves down to the second layer, while two atoms in the second layer, (e) and (b), move to the first layer and two atoms in the first layer get pushed into different sites in the first layer. The barrier for these two multi-atom, sliding processes is remarkably low, less than 0.05 eV, and is active at 30 K even though adatom diffusion on the flat (100) terrace, which has a barrier of 0.22 eV, is not active.

they only involve a small subset of the atoms, then large portions of the system will be unaffected by any one transition. Transitions that can take place in these unaffected regions will not require repeated dimer searches for saddle points. Rather, only the transitions which are affected by the last transition need to be updated and new transitions need to be added only for the region where the last transition took place. With the dimer method, it is also relatively straight forward to reconverge a set of known saddle points which have changed only slightly because of a nearby transition. Therefore, if the transitions are local, the number of new dimer searches that need to be carried out after a transition has occurred will not change as a function of the system size.

Another aspect to the scaling is the time increment at each transition. When the system size is doubled, there are on average twice as many transitions possible. The time increment for each transition will then be half as long, as can be seen from Eq. 2. If the simulation is carried out in such a way as to cover a fixed time interval, then twice as many transitions need to be simulated in a system that is double in size. The number of force evaluations required to simulate a fixed length of time, therefore, scales linearly with system size.

This method for carrying out long time scale dynamics simulations is efficient enough for it to be implemented with first principles calculations of atomic interactions such as density functional theory. We have implemented the method in the VASP code [21, 22, 23, 24]. More information about the implementation can be found on the web site <http://ikazki01.chem.washington.edu/vasp/>.

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