

Temperature accelerated dynamics: introduction and application to crystal growth

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ABSTRACT

Temperature accelerated dynamics (TAD) simulations allow one to reach long time scales without needing any *a priori* information on the system dynamics. As a consequence, TAD is a powerful method for simulating complex phenomena where the dynamics is highly unpredictable and the time scale is longer than the one reachable by standard molecular dynamics (ns- μ s). In this paper we focus our attention on crystal growth. We give an overview of the TAD method, and we demonstrate that at low temperatures a TAD simulation can be faster than a standard molecular dynamics simulation by several orders of magnitude, allowing one to match typical experimental time scales of seconds or longer. Moreover, we explicitly show how critical it is to match the experimental time scale, in order to predict the correct geometry of the growing surface.

Keywords: temperature accelerated dynamics, surface diffusion, crystal growth

1 Introduction: long time scales and lists of mechanisms

Computer simulations are a very useful tool in building an atomic-level understanding of complex phenomena such as bulk or surface diffusion, defect formation and propagation in solids, catalysis, and crystal growth. Atomistic simulations include molecular dynamics (MD) and Kinetic Monte Carlo (KMC) simulations. In MD simulations one solves numerically the Newton equations of motion for the system. For a given description of the interatomic forces, and neglecting quantum effects, MD gives an exact description of the system dynamics. Unfortunately, MD simulations can only reach a time scale of ns- μ s, depending on the system size. Typical experiments, on the other hand, can last for several seconds, so that there is a gap of several (6-9) orders of magnitude between experimental and MD time scales. This gap can be closed if the KMC method [1] is used: instead of solving the Newton equations, one pretends to know in advance all possible diffusion mechanisms and the corresponding rates, for each visited state. A certain transition is then accepted with a probability

proportional to its rate. It is virtually impossible to include every possible diffusion mechanism into a KMC-list, so that often only simple, single-atom mechanisms are considered. This can be a serious limitation since many-atom processes have been revealed in many systems (for example, see Refs. [2]–[5]). In crystal-growth simulations, it can be also a hard task to include the possibility of off-lattice site configurations.

Summarizing, MD simulations allow the system to evolve freely, but only on a short time scale, whereas KMC simulations allow one to reach long time scales, but they require some fundamental *a priori* information on the system dynamics. Very recently, Henkelman and Jónsson have presented a KMC-based method [6] where a predefined event table is not needed, and no lattice constraints on the positions are imposed. Although it is still not proven that all relevant mechanisms can be considered, the authors demonstrated that many-atom mechanisms are indeed included, so that this method looks like a promising new tool for improving the quality of KMC simulations.

Three new methods which permit one to accelerate MD simulations, so that experimentally relevant time scales can be reached, have been proposed by Voter [7]–[9], and by Voter and coworkers [10], [11]. None of these methods requires *a priori* information on the possible diffusion mechanisms. In the hyperdynamics method [7], [8] a boost in the dynamics is obtained by adding to the real interatomic potential a *boost potential*, which accelerates events by lowering their diffusion barriers. In the parallel replica method [9], on the other hand, acceleration is obtained by exploiting parallel implementation on several processors. Finally, in the temperature-accelerated dynamics (TAD) method [10], [11] the (slow) evolution of the system at a given low temperature is extrapolated from the (fast) dynamics at a higher temperature. In this paper we shall focus our attention on the TAD method.

2 The temperature-accelerated dynamics (TAD) method

The temperature accelerated dynamics method [10] requires harmonic transition state theory (hTST) to hold,

i.e. the rate k of an event must be described by:

$$k = \nu_0 \exp(-E/k_B T), \quad (1)$$

where ν_0 is a frequency prefactor, T the substrate temperature, k_B the Boltzmann constant and E the activation energy of the mechanism. Under this assumption, the distribution of first escape times t from a given state A reads:

$$f(t)dt = k \exp(-kt)dt, \quad (2)$$

with k satisfying Eq.(1). In general, at low temperatures events occur on long time scales, and at a certain low temperature T_{low} simulating the process by which the system exits state A may require a simulation time too long for standard MD. In order to accelerate the dynamics of the system at a temperature T_{low} , we choose a higher temperature $T_{high} > T_{low}$, and we collect a sequence of escape times from the initial state at T_{high} . For each attempted transition i , we compute the escape time $t_{i,high}$ and the activation energy E_i (using the nudged elastic band method, in a recent version presented in Ref. [12]). Each escape time $t_{i,high}$ is extrapolated to T_{low} through the simple relation

$$t_{i,low} = t_{i,high} e^{E_i(\beta_{low} - \beta_{high})}, \quad (3)$$

where $\beta_{low} = 1/(k_B T_{low})$ and $\beta_{high} = 1/(k_B T_{high})$. It is easily demonstrated [10] that the escape times extrapolated in this way at T_{low} are correctly drawn from the escape-time distribution relative to T_{low} (see Eq.(2)). We move the system out of A by choosing the mechanism with the shortest extrapolated time at T_{low} . As shown in Ref. [10], if the total time t_{high} spent in state A while building the sequence of escape times exceeds

$$t_{high,stop} \equiv \frac{\ln(1/\delta)}{\nu_{min}} \left(\frac{\nu_{min} t_{low,short}}{\ln(1/\delta)} \right)^{\beta_{high}/\beta_{low}}, \quad (4)$$

where $t_{low,short}$ is the shortest extrapolated time detected so far in the state, we can conclude, with uncertainty δ , that $t_{low,short}$ is indeed the fastest possible escape from A . In Eq.(4), ν_{min} is an assumed lower limit among all possible frequency prefactors. When $t_{high} = t_{high,stop}$, we can move the system out of A following the mechanism whose extrapolated time is $t_{low,short}$, and restart the procedure from the new state. By simulating a total time $t_{high,stop}$, we can advance the simulation clock at T_{low} by $t_{low,short}$. The boost in the dynamics in accepting the transition is given by $t_{low,short}/t_{high,stop}$.

3 Crystal growth by TAD

A crystal growth simulation can be ideally divided into two separate phases: deposition and diffusion (see Fig. 1). To model deposition, a new atom is released far away from the surface (in the simulation it is sufficient to place it just outside two cutoff radii from the closest



Figure 1: Standard MD allows one to simulate deposition, since few ps of simulation are sufficient to model the process. Diffusion between subsequent depositions, on the other hand, occur on the s time-scale. In order to reach this long time scale we use the TAD method.

surface atom), with a certain initial kinetic energy. As soon as the atom starts feeling the interaction with the surface, it is accelerated towards it and it finally impacts against the atoms occupying the topmost layers of the surface itself. If the initial kinetic energy of the atom is low (thermal, as in physical vapor deposition), the excess condensation energy produced by the adsorption of the atom on the surface is readily dissipated, so that the atom is now thermalized on the surface. Note that while the impinging atom approaches the surface, its dynamics cannot be described as a sequence of activated events. Therefore, the TAD method is not suitable for accelerating the deposition process. Luckily, deposition can be easily simulated with standard MD since it only takes few ps for the newly deposited atom to reach the surface and thermalize. A detailed description of our deposition procedure can be found in Ref. [13]. The costly part of the simulation is the evolution of the system in between successive depositions. In order to match typical experimental fluxes (< 0.1 ML/s), the system must be evolved for $\sim 1s$ before depositing a new atom. Obviously, such a time scale is way out of reach for standard MD. Since during this phase the system is in an infrequent-event regime characterized by activated events, we can use TAD to accelerate the dynamics. As shown in the next Section, at low enough temperatures, the boost in the dynamics given by the TAD method is sufficient to match experimental time scales.

4 Application: Ag/Ag(100)

In recent works, the procedure described in the previous Section has been successfully applied to different systems: Cu/Cu(100) [14], Cu/Ag(100) [15], and Ag/Ag(100) [4]. For all of these systems, we matched experimental deposition fluxes reported in the literature. Here we briefly summarize some of the results obtained for the Ag/Ag(100) system. More details can be found in Ref. [4]. Our goal was to reproduce the deposition flux of 0.075 ML/s used in recent experiments by Costantini *et al* [16]. Since we considered a system size of 32 atoms per layer, in order to match the experimental flux,

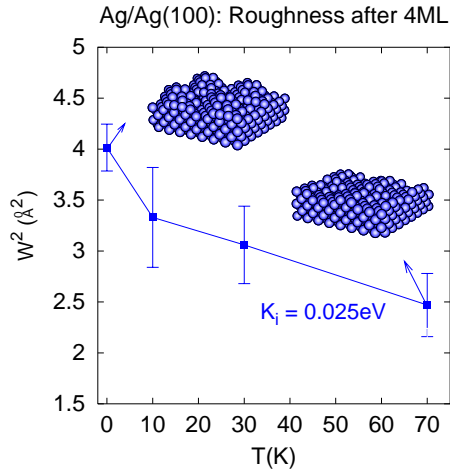


Figure 2: Roughness *vs* T after 4ML for the Ag/Ag(100) system. Data are taken from Ref. 4. Impinging atoms were deposited with an initial kinetic energy $K_i = 0.025\text{eV}$. The usual condition of normal incidence was considered. Error bars are single standard deviations from the mean, computed by running 10 independent simulations at each temperature. In the two insets, typical surfaces grown at 0 K (left) and at 70 K (right) are shown.

we needed to deposit, on average, one new atom every $\sim 0.42\text{s}$. We decided to deposit 4ML, so that the total simulation time required was roughly one minute ($\sim 54\text{s}$), and to see in which range of temperatures the TAD method allowed us to reach the desired coverage within two weeks of CPU time on our SGI R10000 workstation. It turned out that for $T \in [0, 70]\text{K}$, we could actually match experimental time scales, thus obtaining a boost in the dynamics (with respect to standard MD) of ~ 8 orders of magnitude. In this low-temperature range, one may expect that no (or few) diffusion mechanisms take place. Instead, activated mechanisms play a key role

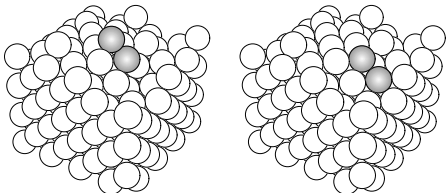


Figure 3: Typical smoothing mechanism, recorded at $T = 70\text{K}$, at a coverage of 3.5 ML. Left panel: initial position. Right panel: final position. Two atoms (gray) are involved in the mechanism.

in determining the geometry of the growing surface, as

demonstrated in Fig. 2, where the roughness of the surface is plotted as a function of the temperature. Passing from 0 K to 70 K, the roughness strongly drops, so that some smoothing events must get activated even at such low temperatures (see also Ref.[17]). An example of such a mechanism is given Fig. 3. Despite its complexity (two atoms are involved in a concerted motion), the activation energy of this mechanism is only $\sim 0.09\text{eV}$. The mechanism was detected during a 70 K simulation, and it occurred on the μs time scale. Other mechanisms [4] require even longer time scales, so that without matching the actual experimental deposition flux, we would have missed them, and we would have predicted the wrong surface geometry. It is also interesting to notice that the surface grown at $T=0\text{K}$ is very rough (see the left inset of Fig. 2). This is due to the *steering effect* [13], [18]: if 3D structures are present on the surface, the impinging atoms are likely to start feeling the interaction with the surface through the atoms composing such structures. Consequently, impinging atoms will tend to bend towards surface protrusions. If the initial kinetic energy of the atoms is low enough [13] this steering effect causes noticeable roughening.

5 Limitations, recent developments and new possibilities

In Section 4 we showed that the TAD method can give boosts of several orders of magnitude with respect to standard MD. It was possible to obtain such a great boost because of the low substrate temperature and the small system size. Depending on the system, in order to match experimental time scales at high temperatures and/or to consider large sizes, the TAD method as presented in the original paper [10] (and in Section III) may not guarantee sufficient boost. However, we are presently working on several possible ways to speed up a TAD simulation. A first improvement was proposed in Ref. [11] where it was shown that if a state is revisited more than one time, the total time $t_{high,stop}$ we need to simulate in the state before accepting a transition can be lowered more and more at each visit, until a condition of maximum effectiveness is reached. This happens when the total time τ accumulated in the state since the first visit satisfies:

$$\tau \geq \left[\frac{\ln(1/\delta)}{\nu_{min}} \right] \exp(E_{min}\beta_{high}), \quad (5)$$

where E_{min} is the lowest activation energy detected so far in the state. Note that if Eq.(5) holds, E_{min} represents, within uncertainty δ , the minimum possible barrier to escape from the state. At this point, the estimate of $t_{high,stop}$ given by Eq.(4) can be safely replaced by:

$$t_{high,stop} = t_{high} \exp[(E_i - E_{min})(\beta_{low} - \beta_{high})], \quad (6)$$

where E_i is the activation energy of the mechanism with the fastest extrapolated time, and t_{high} is the time (computed since the last time the system entered the state) when the mechanism was first detected. Summarizing, as soon as the total time accumulated in the state is sufficient to guarantee that the minimum possible activation energy E_{min} is known, $t_{high,stop}$ can be estimated via Eq.(6) instead of Eq.(4). As shown in recent applications [11], [19], an additional boost easily exceeding one order of magnitude can be obtained by using the improvement here above described. Note that no additional approximations beyond the ones required by the standard TAD method have been introduced. It would be certainly appealing to exploit such additional boost starting from the first visit to a state, instead of being forced to wait until Eq.(5) is satisfied (note that for a state seldom revisited, the total accumulated time τ may never satisfy Eq.(5)). In order to reach this goal, one needs to know E_{min} for each visited states *before* starting the TAD procedure. A possible way to obtain this information may involve running a fixed (low) number of saddle searches by using the dimer method [5] each time the system enters a new state.

Other ways to speed up a TAD simulations could involve parallel implementation. For example, the time spent in accepting a transition may be shortened by using parallel replica simulations [9] instead of MD while building the sequence of escape times. Additional processors may also be exploited in the calculation of the activation energies.

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REFERENCES

[1] A.B. Bortz, M.H. Kalos, and J.L. Lebowitz, J. Comput. Phys. **17**, 10 (1975); D.T. Gillespie, J. Comput. Phys. **22**, 403 (1976); A.F. Voter, Phys. Rev. B **34**, 6819 (1986).
 [2] P.J. Feibelman, Phys. Rev. Lett. **65**, 729 (1990).
 [3] F. Montalenti and R. Ferrando, Phys. Rev. Lett. **82**, 1498 (1999).
 [4] F. Montalenti, M.R. Sørensen, and A.F. Voter, Phys. Rev. Lett. **87**, 126101 (2001).
 [5] G. Henkelman and H. Jónsson, J. Chem. Phys. **111**, 7010 (1999).
 [6] G. Henkelman and H. Jónsson, J. Chem. Phys. **115**, 9657 (2001).

[7] A.F. Voter, J. Chem. Phys. **106**, 4665 (1997).
 [8] A.F. Voter, Phys. Rev. Lett. **78**, 3908 (1997);
 [9] A.F. Voter, Phys. Rev. B **57**, R13985 (1998).
 [10] M.R. Sørensen and A.F. Voter, J. Chem. Phys. **112**, 9599 (2000).
 [11] F. Montalenti and A.F. Voter, J. Chem. Phys. (*in press*).
 [12] G. Henkelman and H. Jónsson, J. Chem. Phys. **113**, 9978 (2000).
 [13] F. Montalenti and A.F. Voter, Phys. Rev. B **64**, 081401(R) (2001).
 [14] T.C. Germann, F. Montalenti, and A.F. Voter, *in preparation*.
 [15] J.A. Sprague *et al*, *in preparation*.
 [16] G. Costantini, F. Buatier de Mongeot, C. Boragno, and U. Valbusa, Surf. Sci. **459**, L487 (2000).
 [17] C. R. Stoldt, K.J. Caspersen, M.C. Bartelt, C.J. Jenks, J.W. Evans, and P.A. Thiel, Phys. Rev. Lett. **85**, 800 (2000).
 [18] S. van Dijken, L.C. Jorritsma, and B. Poelsema, Phys. Rev. Lett. **82**, 4038 (1999).
 [19] F. Montalenti *et al*, *in preparation*.