Multiple-Time Scale Accelerated Molecular Dynamics: Addressing the Small-Barrier Problem

Radu A. Miron
Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802, USA

Kristen A. Fichthorn
Departments of Chemical Engineering and Physics, Pennsylvania State University, University Park, Pennsylvania 16802, USA

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We present a method for accelerated molecular-dynamics simulation in systems with rare-event dynamics that span a wide range of time scales. Using a variant of hyperdynamics, we detect, on the fly, groups of recurrent states connected by small energy barriers and we modify the potential-energy surface locally to consolidate them into large, coarse states. In this way, fast motion between recurrent states is treated within an equilibrium formalism and dynamics can be simulated over the longer time scale of the slow events. We apply the method to simulate cluster diffusion and the initial growth of Co on Cu(001),where time scales spanning more than 6 orders of magnitude are present, and show that the method correctly follows the slow events, so that much larger times can be simulated than with accelerated molecular dynamics alone.

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A significant challenge in materials simulation is to achieve long-time simulations with accurate atomic detail. Accelerated molecular-dynamics (MD) methods [1–5] have shown great promise in systems whose dynamical evolution is governed by rare events. By treating rare events within the framework of transition-state theory, these methods can probe time scales that are many orders of magnitude longer than those in conventional MD simulations while retaining the accuracy of conventional MD. However, the applicability of these and other related methods has an inherent limitation: The achievable time scale is limited by the fastest rate processes. In many systems, the rates of the various available processes can span many orders of magnitude, due to the exponential dependence of rates on temperature and energy barriers. The effectiveness of rare-event simulations is limited for systems such as these.

Particularly problematic is the case where fast processes are grouped together in pools of shallow energy minima that are separated from the rest of the phase space by high energy barriers. The system may perform millions of repeated transitions between these states before escaping away and, as a result, the overall progress of the simulation is curtailed significantly. This "small-barrier" problem has been recognized in studies of metal thin-film epitaxy [6–8]. However, small barriers are ubiquitous and this problem could extend to a variety of rare-event systems, including protein folding, chemical reaction dynamics and catalysis at surfaces, polymer and glass dynamics, as well as transport on and within solids.

In this Letter, we propose a method for addressing the small-barrier problem with accelerated MD. Our method is based on the bond-boost method (BBM) [5], which is a variant of hyperdynamics [1]. We propose an extension of the BBM to detect, on the fly, groups of recurrent states connected by small energy barriers and modify the potential-energy surface (PES) locally to consolidate them into large, coarse states. This procedure enables successful application of accelerated MD to systems exhibiting multiple-time scale processes and allows for substantially larger time boosts than can be achieved by accelerated MD alone.

Hyperdynamics methods are based on modification of the PES around local energy minima but not at transition states [1]. When a bias potential $\Delta V(x)$ is added, the boosted dynamics over a time Δt_b is equivalent to the original dynamics over a longer time Δt:

$$\Delta t = \Delta t_b \langle e^{\beta \Delta V} \rangle_b, \tag{1}$$

where $\beta = 1/k_B T$ and $\langle \rangle_b$ represents a canonical average on the boosted PES. The time boost $\Delta t/\Delta_b$ increases with stronger boost $\Delta V(x)$ and decreasing temperature.

Various recipes for constructing $\Delta V(x)$ have been proposed [1–4], the latest being our BBM [5], which achieves high efficiency with negligible overhead through a simple construction of the boost potential. In the BBM $\Delta V(x)$ is a function of the nearest-neighbor bond lengths $\{r_i\}$. It has a maximum value of $\Delta V^{\max}$ at the local minimum configuration, and goes to zero when the relative stretch or compression $\epsilon_i = (r_i - r_i^0)/r_i^0$ of any bond surpasses a threshold q, where r_i^0 is a local equilibrium bond length. The functional form is

$$\Delta(x) \equiv \Delta V^{\max} A(\epsilon^{\max}) \sum_{i=1}^{N_b} \delta V(\epsilon), \tag{2}$$

where $\epsilon^{\max} = \max_i\{|\epsilon_i|\}$, N_b is the number of bonds included in the boost, $\delta V(\epsilon_i)$is the boost applied to each bond, and $A(\epsilon^{\max})$ is an envelope that has values between $[0 \ldots 1]$ and becomes zero when $\epsilon^{\max} > q$. Each time the system reaches a new state, conjugate-gradient minimization is employed to find the new configuration $\{r_i^0\}$.

Subsequently, the system is equilibrated in the new minimum and the boost potential is turned on. When the threshold q is exceeded, there is a short waiting time, after which minimization recommences to detect a new state, and the cycle repeats.

The effectiveness of the BBM (and all rare-event methods) is greatly curtailed when pools of shallow states are present, as we illustrate in Fig. 1. In the BBM, the time boost is controlled by the magnitude of the boost potential $\Delta V^{\max}$ [cf., Eq. (2)], which can, in principle, be tuned. However, there is an upper limit on the achievable boost, as a strong boost that exceeds the transition-state barrier does not preserve the correct dynamics of the low-barrier processes. As illustrated in Fig. 1(a), the shallow states K, L, M, and N become local peaks in this case and the minima are not effectively sampled, as the system is pushed toward the transition states. With a small boost, appropriate for shallow minima [cf., Fig. 1(b)], the system will rapidly and repeatedly cycle among K, L, M, and N and escape to state D only over a much longer time scale. Since MD simulations are limited in the total number of time steps they can cover, the bulk of the simulation time may be spent on these repeated transitions and evolution of the system is limited. Our proposed solution to this problem is to combine the large boost shown in Fig. 1(a) with "bridge potentials" ΔV^{bridge}, which span the transition states among states K, L, M, and N, as shown in Fig. 1(c). In doing this, we consolidate the shallow states K, L, M, and N into a single, coarse state. This procedure rests on the observation that equilibrium among the shallow states is reached long before any slow event $N \rightarrow D$ occurs. Since, on the time scale of the slow escape, the "fast" dynamics becomes irrelevant, we drop the requirement that $\Delta V(x) = 0$ at the fast transition states. Thus, for the escape rate $k_{N\rightarrow D}$ the entire set $K \cup L \cup M \cup N$ acts as the equilibrium "initial state" for the transition-state theory rate process.

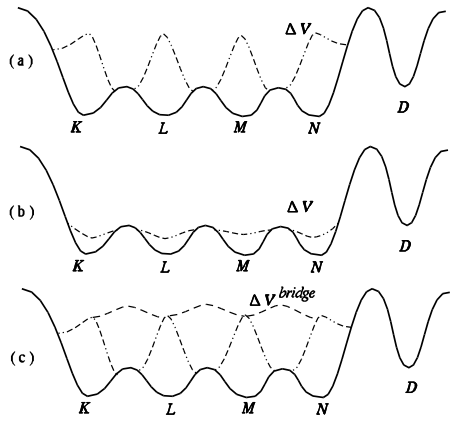

FIG. 1. One-dimensional illustration of the small-barrier problem: (a) a large boost, (b) a small boost, (c) with bridging potential ΔV^{bridge}.

The first issue in implementing the scheme shown in Fig. 1(c) is definition and detection of fast, recurrent processes. A preliminary analysis can determine the range of energy barriers corresponding to the "slow" and fast time scales. Based on this, we define a threshold barrier ΔE^{th} and assign all processes having lower barriers to the class of fast processes. The validity of treating the fast states as equilibrated depends on the number of fast states in the recurrent group, the number of slow exits, and on the energy gap between fast and slow barriers. For example, one can use the properties of Markov-chain dynamics [9] to show that the limiting (i.e., equilibrium) distribution in a chain of fast states, each of which has a slow exit with rate k_{slow}, is reached in a time of $\sim 0.2n^2/k_{\text{fast}}$, where k_{fast} is the slowest fast rate and n is the number of fast states in the basin. Thus, the slow processes out of this basin should satisfy

$$k_{\text{fast}}/k_{\text{slow}} \gtrsim 0.2n^2. \tag{3}$$

For example, $n = 4$ corresponds to a fast-slow energy barrier gap of about 0.04 eV at room temperature. If the gap is smaller, the exit pathway from the basin could be correlated with the entry and this correlation may be lost when fast states are consolidated.

When an event $M \rightarrow N$ occurs, we determine if the barrier $\Delta E^{\dagger}_{M\rightarrow N}$ is less than ΔE^{th}. This is done with little overhead using the step-and-slide (SAS) method [10], which is the only saddle-point finding method that converges by bracketing the transition-state energy $E^{\dagger}$. Using this method, we can evaluate whether a test value E^{test} satisfies $E^{\text{test}} < E^{\dagger}$ without knowing $E^{\dagger}$ exactly. In this case, we need only one SAS iteration with $E^{\text{test}} = E_M + \Delta E^{\text{th}}$.

If a process is tagged as fast, the initial and final states M and N are stored for pattern matching, i.e., when the system revisits state M it should "recognize" its transition to N as a fast process and activate the appropriate bridge potential. States M and N are defined locally and comprise only the pattern of bonds $\{r^0\}$ for the nearest neighbors $nn(M \rightarrow N)$ of the atom(s) that move in the transition $M \rightarrow N : M \equiv \{r^0_{nn(M\rightarrow N)}\}$. This formulation decouples local states from the global state and results in a linear increase of the storage requirement with system size.

The second element of our method is to construct a bridge potential between M and N [see Fig. 1(c)]. To this end, we define a potential $\Delta V^{\text{bridge}}_{MN}(x)$ that depends on the position x_i of the moving atom(s) i along the transition path $M \rightarrow N$. $\Delta V^{\text{bridge}}_{MN}(x)$ is constructed as in Eq. (2), with $A(\epsilon^{\max})$ replaced by an envelope $\Delta V^{\text{bridge}}_{MN}(x_i)$:

$$\Delta V^{\text{bridge}}_{MN}(x) \equiv \Delta V^{\max} \Delta V^{\text{bridge}}_{MN}(x_i) \sum_{i=1}^{N_b} \delta V(\epsilon_i). \tag{4}$$

We define a sequence of p images $\{x_i^0, \ldots, x_i^p\}$ along the

approximate minimum-energy path (MEP) for the $M \rightarrow N$ process, so that the endpoints x_i^0 and x_i^p coincide with the respective local minima. A few iterations of the SAS method can be used to establish points along the approximate MEP. More generally, the MEP can be exactly calculated using a chain-of-states method such as the nudged elastic band method [11]. The bridge envelope $A_{MN}^{\text{bridge}}(x_i)$ is comprised of local contributions $A_l(x_i)$ centered around each image x_i^l (see Fig. 2):

$$A_l(x_i) \equiv \max\left\{0, \alpha_l\left(1 - \frac{(\delta x_i^l)^2}{w^2}\right)\right\}, \tag{5}$$

where $\delta x_i^l = x_i - x_i^l$, w, and $\alpha_l \leq 1$ are parameters that control the shape of the bridge potential. If all $\alpha_l = 1$, the PES is uniformly shifted and all barrier heights are preserved. However, it is desirable to smoothen the PES inside $K \cup L \cup M \cup N$ so as to promote efficient equilibrium sampling. Based on the potential energies of the images x_i^l, the parameters α_l can be chosen so that the modified PES is approximately flat. The parameter w controls the width of the bridge potential orthogonal to the MEP. If it is too small, the bridge does not cover the MEP valley properly and creates "channels" where the system can be trapped, analogous to Fig. 1(a). If w is too large, the bridge may affect neighboring transition states. The spatial separation of transition states can be estimated from the bond-stretch threshold q used in constructing the conventional boost and it can be adjusted on the fly. In the case of an fcc crystal, w can be taken as about half the nearest-neighbor distance. The bridge envelope $A_{MN}^{\text{bridge}}(x_i)$ is defined as

$$A_{MN}^{bridge}(x_i) = \max_l\{A_l(x_i)\}, \qquad l = [0 \ldots p]. \tag{6}$$

The complete boost $\Delta V(x)$ is obtained by taking the envelope of all bond and bridge terms which are active at the particular instantaneous configuration, by merging Eqs. (2) and (4):

$$\Delta V(x) = \Delta V^{\max} \min_i(\max\{A(\epsilon_i), A_i^{bridge}\}) \sum_{i=1}^{N_b} \delta V(\epsilon_i). \tag{7}$$

The complete algorithm is as follows. After each event, we start off with a low boost, i.e., $\Delta V^{\max} \lesssim \Delta E^{\text{th}}$, which preserves the correct fast dynamics. The low boost allows accurate dynamics of the fast events, albeit with low acceleration. As each new shallow state is encountered, it is stored and the appropriate bridge potential is constructed. Eventually, the shallow states are exhausted. If no new state is encountered during a predefined waiting time t^{wait}, the boost strength is increased to the desired high value, the bridges are activated, and the simulation switches to the time scale of the slow events. We chose t^{wait} larger than the average waiting time for a process having the threshold barrier, i.e., $t^{\text{wait}} > \nu^{-1} \exp(\beta \Delta E^{\text{th}})$, where ν is an appropriate prefactor. In each new state, the simulation code performs local pattern matching against stored states to find the applicable bridge potential terms. With efficient state recognition algorithms, the computational overhead is generally less than 10% of the normal simulation time for our test cases, and should remain low for a finite number of fast processes.

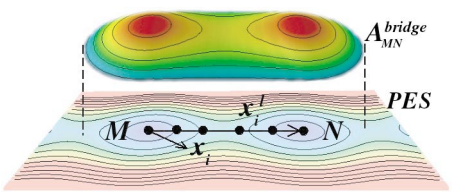

FIG. 2 (color online). Schematic shape of the bridge potential connecting two shallow minima $M - N$. A_{MN}^{bridge} is a function of the distances from the instantaneous position x_i to several images x_i^l placed along the MEP.

To illustrate our method, we simulate kinetic phenomena related to the heteroepitaxial thin-film growth of Co on a Cu(001) surface. The interaction potential is a slightly modified version of the tight-binding (second-moment approximation) potential in Ref. [12], adjusted to obtain a better fit of density functional theory calculations of energy barriers and growth modes [13]. This system is a prime example of the small-barrier problem, which also occurs on other fcc(001) surfaces [6,7] where diffusion along island edges is much faster than isolated adatom hopping. Here, edge diffusion is about 10^6 faster than adatom hopping at room temperature and trimer rotation is about 10^8 times faster than adatom hopping. Fast trimer rotation leads to a pool of 24 shallow states. Without bridge boosting, simulations (even accelerated MD) would be hopelessly limited by the short time scale of edge hops.

We first investigate adatom and small island diffusion. The energy barriers for various processes are shown in the table with Fig. 3. Hopping along island edges is much faster than events that lead to center-of-mass motion of small islands, which are mainly collective shearing mechanisms. Dimers, trimers and heptamers have a high mobility, comparable to that of the isolated adatom. The trimer hops via a concerted jump of two atoms, while the heptamer hops via concerted shearing of three atoms in the middle row. A less favorable mechanism for heptamer hopping involves an edge adatom climbing on top of the cluster and descending again. Single adatom exchange can occur in this system [14]; however, due to the high energy barrier (0.92 eV) it is not active on the time scale and temperature range covered in these simulations.

We implement bridge boosting using a threshold of $\Delta E^{\text{th}} = 0.4$ eV. For constructing the bridging potentials, the MEP is approximated as a straight line, which yields a particularly simple implementation of Eqs. (5) and (6). After each event, a low boost of $\Delta V^{\max} = 0.2$ eV is

Process	ΔE^{static} (eV)	ΔE^{MD} (eV)	
Adatom hop	0.63	0.63	
Dimer hop	0.62	0.63	
Adatom edge hop	0.30		
Trimer rotation	0.10		
Trimer hop	0.64	0.65	
Heptamer hop	0.56	0.57	

FIG. 3 (color online). Energy barriers ΔE for various diffusion processes of Co/Cu(001). Static values are obtained with the step-and-slide method [10].

maintained until no new process occurs for a time $t^{\text{wait}} = 10^{-2}\exp(\beta\Delta E^{\text{th}})$ ps. Then, the boost is increased to $\Delta V^{\max} = 0.6$ eV. By overcoming the small-barrier limitation, we achieve boosts ranging from 10^4 at 450 K to 10^8 at 250 K and slow island diffusion is correctly captured. Energy barriers from static calculations and bridged, accelerated MD simulations are shown in the table with Fig. 3 and exhibit excellent agreement.

The wealth of diffusion processes exhibited by Co/Cu(001) is difficult to capture with traditional simulation methods such as lattice-based kinetic Monte Carlo (KMC), where the relevant rate processes must be input to the simulation and real-space effects of mismatch-induced strain cannot be handled easily. Accelerated MD inherently contains all rate processes, enabling efficient "prejudice-free" simulation in real space on experimental time scales. By consolidating edge diffusion and trimer rotation processes (shown in the table with Fig. 3), we can tune the boost to the slow time scale of adatom and cluster diffusion, and we can simulate growth of Co/Cu(001) on time scales of seconds at temperatures up to 300 K. With such capabilities, we can probe the influence of cluster diffusion on submonolayer thin-film morphology during growth, a topic that heretofore has been treated with approximate rate equations [15,16] and KMC [6,16,17].

As an example, we compared MD and KMC simulations of Co/Cu(001) growth at $T = 250$ K, $F = 0.1$ ML/s, up to 0.54 ML. A five-layer substrate with 1296 atoms/layer was used for capturing correct island densities. Because of island diffusion, in particular, dimer mobility, the average saturation island density n_x is reduced to 70% of the value found in KMC simulations at the same conditions with diffusion barriers that match ours within 5% [18]. The reduction in n_x results from island coalescence due to island mobility, which occurs in our simulations but not in the KMC simulations [18]. Detailed results will be reported elsewhere.

In conclusion, we present a general method for allowing accelerated MD simulations to cover rare-event, multitime scale processes. Assuming a separation of fast and slow time scales, the method treats fast processes as equilibrated on the slow time scale, and consolidates pools of "shallow" states detected on the fly into coarser states. The slow dynamics is preserved, and the simulation time scale can be tuned to the slow events of interest. We applied this method to simulate the initial growth of Co on Cu(001), where the influence of cluster diffusion on film morphology could be observed in condensed phases.

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[1] A. F. Voter, J. Chem. Phys. **106**, 11 (1997).
[2] M. M. Steiner, P. A. Genilloud, and J. W. Wilkins, Phys. Rev. B **57**, 10236 (1998).
[3] S. Pal and K. A. Fichthorn, Chem. Eng. J. (Lausanne) **74**, 77 (1999).
[4] J.-C. Wang, S. Pal, and K. A. Fichthorn, Phys. Rev. B **63**, 085403 (2001).
[5] R. A. Miron and K. A. Fichthorn, J. Chem. Phys. **119**, 6210 (2003).
[6] O. Biham, I. Furman, M. Karimi, G. Vidali, R. Kennett, and H. Zeng, Surf. Sci. **400**, 29 (1998).
[7] M. R. Sørensen and A. F. Voter, J. Chem. Phys. **112**, 9599 (2000).
[8] F. Montalenti and A. F. Voter, J. Chem. Phys. **116**, 4819 (2002).
[9] E. Cinlar, *Introduction to Stochastic Processes*, (Prentice-Hall, Englewood Cliffs, NJ, 1975).
[10] R. A. Miron and K. A. Fichthorn, J. Chem. Phys. **115**, 8742 (2001).
[11] G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. **113** , 9901 (2000).
[12] N. A. Levanov, V. S. Stepanyuk, W. Hergert, D. I. Bazhanov, P. H. Dederichs, A. A. Katsnelson, and C. Massobrio, Phys. Rev. B **61**, 2230 (2000).
[13] R. Pentcheva and M. Scheffler, Phys. Rev. B **61**, 2211 (2000).
[14] F. Nouvertné, U. May, M. Bamming, A. Ranape, U. Korte, G. Güntherodt, R. Pentcheva, and M. Scheffler, Phys. Rev. B **60**, 14382 (1999).
[15] J. Villain, A. Pimpinelli, L. Tang, and D. Wolf, J. Phys. I (France) **2**, 2107 (1992).
[16] M. C. Bartelt, S. Güinther, E. Kopatzki, R. J. Bema, and J. W. Evans, Phys. Rev. B **53**, 4099 (1996).
[17] S. Liu, L. Bönig, and H. Metiu, Phys. Rev. B **52**, 2907 (1995).
[18] R. Pentcheva , K. A. Fichthorn, M. Scheffler, T. Bernhard, R. Pfandzelter, and H. Winter, Phys. Rev. Lett. **90**, 076101 (2003).