

Hyper molecular dynamics with a local bias potential

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We propose a local bias potential for the hyper molecular dynamics requiring no preknowledge of the saddle points of system. This has little computational overload and is applicable to real systems. Speedups of one to five orders of magnitude are found in the diffusion of a small cluster on a surface. [S0163-1829(99)08901-8]

Molecular dynamics simulations (MD), which have been widely used in chemistry and physics, can probe the natural time evolution of classical many-body systems up to a time scale of $\sim 10^{-9}$ sec. This time scale is adequate for studying the structural and dynamical properties, provided the relevant fluctuations decay on a much shorter time scale. For many dynamical phenomena, one can characterize the dynamics as a sequence of infrequent transitions with a long time scale. If the potential surface is known in advance, transition state theory (TST) can access the long time scale processes for the infrequent events and actual dynamics need not be performed. To simulate such infrequent phenomena without any advance knowledge of the potential surface is prohibitively expensive and is thus beyond the actual reach of the conventional MD.

Recently, based on the TST theory, Voter has provided a method to accelerate the molecular dynamics (hyper-MD), which opened a window to simulate atomic dynamics for a microsecond or longer. In Voter's scheme,^{1,2} a bias potential raises the potential energy except for the saddle points of the potential energy surface. The dynamics on the biased potential surface leads to accelerated evolution from one potential minimum to another. The key to implementation of the hyperdynamics is designing a computationally tractable bias potential $\Delta V(r)$ that does not require advance knowledge of the potential surface. Although it is difficult to define a bias potential which will not introduce any TST-violating correlation, in practice we just need a good approximation. In Voter's implementation of the bias potential, each hyper-MD step required ~ 30 times the computational work of a MD step for the simulations with only fifty-five moving atoms. The computational cost for the bias potential scaled as the square of the number of moving atoms, which prohibits the application to large systems.

A simple scheme we propose uses a local potential, so the construction of the local bias potential requires only diagonalizing a small matrix. The computational cost of each time step is only a few percent longer than that of a MD step. A significant speedup of 10^2 – 10^5 fold makes it possible to calculate diffusion constant at very low temperature. In a wide temperature range for an adatom and a dimer diffusion on a surface, our hyper-MD results are in good agreement with that of MD simulation.

To see how the bias potential works, we consider, for instance, a small cluster diffusing on a surface. Most atoms

will always oscillate at the potential minimum, except for the atoms in the cluster and occasionally its neighbors which may jump to other potential minimum. So only those n atoms in the cluster and its neighbors need to have a bias potential. A potential V_l locally related to those n atoms is,

$$V_l(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n) = \sum_j V(r_{ij}), \quad i = 1, \dots, n \ll N, \quad (1)$$

where r_{ij} is the distance between atom i and atom j ; R_i is the coordinates of the i th atom; N is the total number of moving atoms and V is the interatomic potential, which should be continuous up to the third derivatives. The summation is over all the neighbors. As discussed by Sevick, Bell, and Theodorou,³ the first order saddle points of the potential V_l can be characterized as the set of points at which (i) the lowest eigenvalues ϵ_1 of the Hessian matrix \mathbf{H} $\{H_{ij} \equiv \partial^2 V_l / \partial x_i \partial x_j\}$ is negative, and (ii) the derivative of the potential along the direction of the first eigenvector of Hessian matrix \mathbf{H} is zero. To have a more conservative bias potential which is zero at the saddle points, our local bias potential at the i th MD step is nonzero only when ϵ_1 is larger than zero:

$$\Delta V(r(t_i)) = \frac{h}{2} \frac{\epsilon_1^2}{\epsilon_1^2 + c^2 g_{1p}^2} \theta(\epsilon_1), \quad (2)$$

where h and c are tunable parameters; θ is the standard step function; g_{1p} is the projection of potential gradient onto the first eigenvector of Hessian matrix \mathbf{H} . Since $\Delta V(r(t_i))$ is only dependent on ϵ_1 and g_{1p} , the cost of constructing the bias potential $\Delta V(r)$ is essentially confined to diagonalizing the small Hessian matrix \mathbf{H} with only $3n$ dimension, where n could be an order of one. More importantly, the cost of calculating the bias potential is independent of the total number of atoms in the simulation cell.

Figure 1 shows $\Delta V(r)$ for one-dimensional dimer interaction with Lennard-Jones potential. The $\Delta V(r)$ bias potential is nonzero in a small region of potential minimum around $r = 1.15$, and has a smooth crossover at the inflection point. Too small h will just lead to an insignificant speed up, while too large h will significantly shift the potential energy at the minimum, causing a repulsive force which would block the motion from one potential minimum to another.

Our test calculations on fcc(111) surface are for adatom and dimer diffusion. We employ the Lennard-Jones potential conventionally using energy ϵ and length σ ,

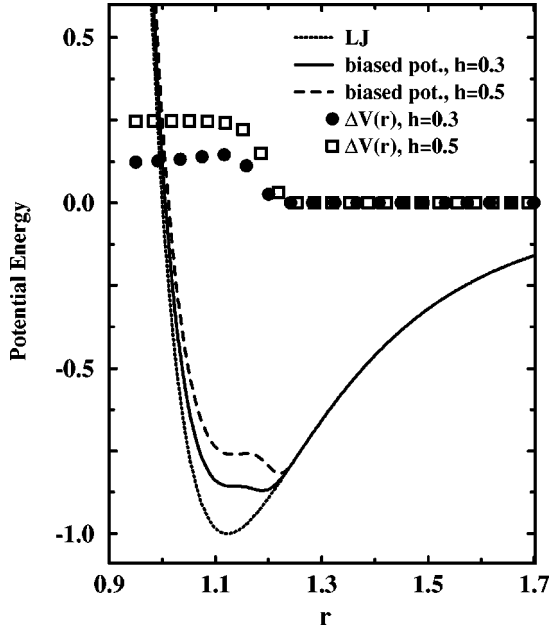


FIG. 1. Typical bias potential $\Delta V(r)$ (solid line) for Lennard-Jones potential $V(r)$ (dotted line) as a function of dimer separation r . The bias potential used in this paper is nonzero only where the second derivative of $V(r)$ is greater than zero. This conservative approach yields a small region when the biased potential $V(r) + \Delta V(r)$ (long dash-short dash) speeds up the molecular dynamics. Nonetheless we find significant speedups. [The Lennard-Jones parameters are $\epsilon = \sigma = 1$].

$$V(r_{ij}) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^6 \right], \quad (3)$$

where α and β denote the atom A in the dimer (adatom) on surface and the surface atom B, respectively. In all calculations, we assume $\sigma_{BB} = \sigma_{AB} = 1.0$, and $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB} = 1.0$. We use five layers of atoms to mimic the surface, each layer contains 100 atoms. The atoms in the top three layers are allowed to move and atoms at the bottom two layers are kept fixed. The simulation cell is periodic in x and y direction and free in z direction. The Langevin equation of motion is integrated by a modified Beeman procedure⁴ with a time step $\Delta t_{\text{MD}} = 0.01$, which is doubled at the low temperature. The Langevin damping was taken to be 1.0.

Figure 2 shows how hyper-MD dramatically extends the temperature range $1/T = 20$ for MD to $1/60$ both for the adatom and the dimer ($\sigma_{AA} = 0.7$) (Ref. 5) diffusion. The diffusion constant shown in the figure is the average of results from three bias potentials ($h = 0.25, 0.30, 0.35$). The hyper-MD results are in agreement with the MD results. The least-square-root fitted to the Arrhenius relationship yields the activation energy, 0.26 ± 0.006 for the adatom on fcc(111) surface and 0.32 ± 0.007 for the dimer on fcc(111) surface.

The computational simplicity of each hyper-MD step ensures a 10^2 to 10^5 fold speed up of the average boost factor. As shown by Voter, the integration time step in hyper-MD is exponentially scaled by the bias potential, so that the instantaneous boost factor is

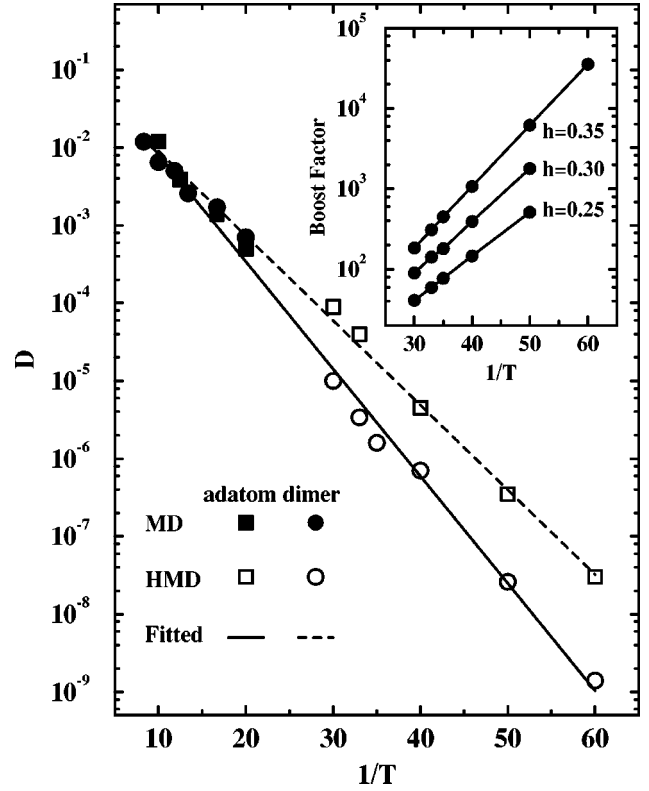


FIG. 2. Hyper molecular dynamics and molecular dynamics computation of the temperature-dependent diffusion constant D for adatom and ad-dimer on fcc (111) surface. Least-square fitted line yields activation energies 0.26 and 0.32 for adatom and dimer, respectively. Inset: over temperature range shown, boost factor $\sim \exp(h/(2T))$. Unfortunately increasing bias-potential parameter h increases the noise. The hyper molecular dynamics D 's were averages of the three h 's with the error typically a factor of 2.

$$\frac{\Delta t_b(r(t_i))}{\Delta t_{\text{MD}}} = e^{\beta \Delta V(r(t_i))}. \quad (4)$$

At a long time scale, one can define an average boost factor BF for the boosted time over the direct molecular dynamics simulation time in N_{tot} steps:

$$BF = \frac{\sum_i^{N_{\text{tot}}} \Delta t_b(r(t_i))}{N_{\text{tot}} \Delta t_{\text{MD}}} = \frac{1}{N_{\text{tot}}} \sum_i^{N_{\text{tot}}} e^{\beta \Delta V(r(t_i))}. \quad (5)$$

Equation (5) shows that BF depends only on the bias potential, so the success of hyper-MD will essentially depend on the choice of the bias potential. The inset of Fig. 2 shows the temperature dependence of average boost factor for a dimer ($\sigma_{AA} = 0.7$) with parameter $h = 0.25, 0.30, 0.35$. From low to high temperature, the boost factors range from 10^2 to 10^5 . For the adatom, we get boost factors very similar to that of dimer (not shown in the figure). We find that the slope for $\log(BF)$ versus $1/T$ is very close to $h/2$ for all cases, i.e., $BF \sim \exp(h/2T)$. Those large boost factors do not require using any preknowledge of the potential energy surface for both the adatom and dimer.

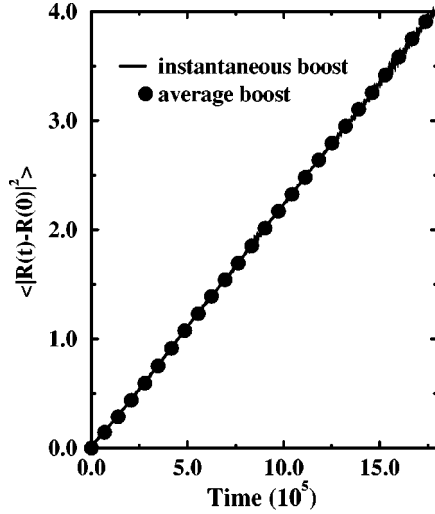


FIG. 3. Near identity of the mean-square displacement versus time computed by “average boost factor” approach (filled circles), with that by instantaneous boost factor approach (line). The average-boost-factor approach typically reduces computational effort of the diffusion constant D by a factor of thousand.

Figure 3 demonstrates that the mean-square displacement computed with instantaneous boost factor is nearly identical to that computed with the average boost factor, the latter approach leading to a significant speed up in the calculation of the mean-square displacement. Comparing to the identical integration time step in the conventional MD simulation, the position-dependent time step $\Delta t_b(r(t_i))$ in hyper-MD complicates the calculation of the mean-square-displacement for diffusion constant,

$$\begin{aligned} \langle [|\mathbf{R}(t+t_0) - \mathbf{R}(t_0)|]^2 \rangle &= \frac{1}{nN_{t_0}} \sum_{t_0}^{N_{t_0}} \sum_{j=1}^n [|\mathbf{R}_j(t+t_0) - \mathbf{R}_j(t_0)|]^2 \\ &= 4Dt, \end{aligned} \quad (6)$$

where N_{t_0} is the number of initial configurations used in the average. We compute the time t in Eq. (6) in the following two ways: In the first method, the integration time is summed up with the instantaneous time step, i.e., $t = \sum \Delta t_b(r(t_i))$. In the second method, we scale each time step by the average boost factor, i.e., $t = BF \sum \Delta t_{\text{MD}}$. These two methods give indistinguishable results. A typical comparison for an adatom ($T=0.02, BF=1732$) is shown in Fig. 3. However, the first method, using instantaneous boost factor, requires an average over many initial configurations ($\sim 10^4$), and the computational cost is $10^1 - 10^3$ more expensive than in the second method which usually requires an average over $\sim 10^2$ of initial configurations.

Figure 4 demonstrates the validity of the local boost approach—scaled motion occurs only at the deep minimum of the total potential. The region close to the saddle points is never boosted. In the figure, we show *only* the *biased* trajectory of an adatom and a dimer moving on fcc(111) surface, at the temperature 0.01666 and 0.0333, respectively. We find that at this specific temperature, even with a bias potential, the adatom spends about 98% of the total steps moving in the biased potential minimum. The crossover near the saddle points from one potential minimum to another uses only

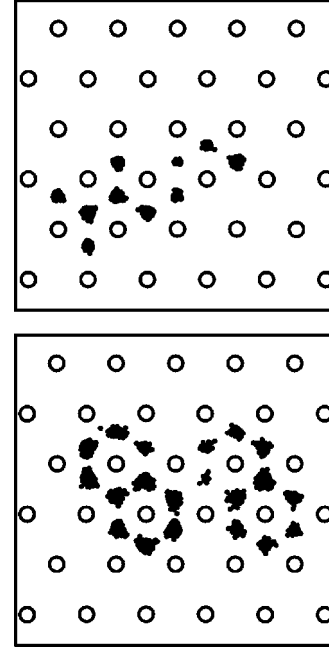


FIG. 4. The biased trajectory (filled dots) on fcc (111) surface for an adatom (upper panel, $T=0.0166, BF \approx 8000$) and for a dimer (lower panel, $T=0.0333, BF \approx 87$). The open circles represent the surface atoms. To make the figure clear, the trajectory for one atom in the dimer is shifted by two atomic distances along the horizontal direction in the plot. The conservative local bias potential defined by Eq. (2) has never boosted the region near the line connecting two nearest neighbor atoms, where the saddle points are supposed to be for the diffusion of an adatom and a dimer.

about 2% of the total number of time steps. This suggests that, without the biased potential, the crossover near the saddle points would use only 2.5 steps per million.

Recently, Steiner *et al.* have proposed an alternative local bias potential scheme requiring even less computational effort at each time step.⁶ Since it does not determine the saddle point, the preknowledge of potential surface is necessary and it must estimate a correction for the boost through the saddle points. The two approaches have not been compared for the same problem; where each will prove most useful is an open question.

In summary, we have shown that the hyper-MD scheme proposed is a powerful approach to extend the simulation time up to microsecond and even longer. For constructing the bias potential, we have devised a scheme, which does not require preknowledge of the potential surface. In contrast to Voter’s method, the present scheme costs very little computational work in constructing the bias potential, a typical run for a dimer on fcc(111) shows that the CPU time for each time step increased only by a few percent. With the current scheme, we can easily obtain a BF as large as $10^2 - 10^5$, which makes possible to study the diffusion behavior down to very low temperature. The obtained hyper MD results are in good agreement with MD simulations. This provides a practical method to simulate the real large system.

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