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Local bias potential in hyper molecular dynamics method

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Abstract

The hyper molecular dynamics method (Hyper-MD) with a local bias potential can be used in massive simulations on infrequent events with a very small computation overhead. In this paper, we demonstrate the validity of the local bias potential in simulation of various systems, and study how the results depend on the locality of the bias potential. For an adatom diffusion on surface or interstitial diffusion in bulk, we find that a local bias potential only related to the neighbors of the interesting atoms is good enough. Our studies also show that the Hyper-MD with a local bias potential can be used to study the surface diffusion with exchange mechanism.

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1. Introduction

A continuing challenge in atomic simulation of infrequent events, such as surface diffusion and film growth, is the time scale limitation of the molecular dynamics method. How can one conduct the long-time simulation on structural evolution, while accurately retaining the detailed information in the atomic scale? Hyper-MD (hyper molecular dynamics method) proposed by Voter opens a window to accelerate conventional MD simulations for systems in which dynamical evolution occurs via a series of rare events [1]. Hyper-MD relies on altering the potential-energy surface to reduce the computational effort spent on the localized motion near the potential-energy minima. However, the computation overhead to determine the potential surface is very heavy, generally it scales $O(N^2)$ or $O(N^3)$ in the original Voter's methods, which prohibits the application of the Hyper-MD to the large system with more than a few tens of atoms.

To reduce the computational overhead and make Hyper-MD feasible for large systems, Gong and Wilkins have proposed a local bias potential [2]. Since the local bias potential is only related to the infrequent event locally happened in the space, the computation overhead to determine the bias potential does not on the size of the whole system.

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The application to an adatom and a dimer diffusion on the surface has shown that [2], this local bias potential can correctly predict the diffusion barrier and temperature dependent diffusion constants. By using the local bias potential, one can also get a significant boost factor, which can be as large as 10^2–10^5. However, one important point which should be clarified is how the simulation results depends on the locality of the bias potential. For example, in the adatom diffusion on the surface, how many neighboring atoms should be included to determine the local bias potential. It is also interesting to know if the local bias potential can be used to other more complicated diffusion mechanism, such as exchange mechanism.

In this paper, we try to demonstrate the validity of the local bias potential. We also show that the local bias potential can be used to simulate the surface diffusion with exchange mechanism. The rest of the paper is organized as follows, in Section 2 we briefly review the Hyper-MD method and local bias potentials. In Section 3, we present the main results and some discussions. Finally, we summary our results in Section 4.

2. Hyper-MD and local bias potentials

The Hyper-MD, proposed by Voter [1], is based on the transition state theory (TST), in which the state-to-state rate constant is approximated as the flux through the dividing surface separating the states. Since we are only interested in the jumping rate from one state to another, instead of the details of the atomic processes near a local minimum, one can replace the potential energy $V_0(\mathbf{r})$ of the real system with

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \Delta V(\mathbf{r}), \tag{1}$$

where the so-called bias potential $\Delta V(\mathbf{r})$ is always larger than zero except for near the dividing surface at which $\Delta V(\mathbf{r}) = 0$. The non-negative $\Delta V(\mathbf{r})$ added on the basin assures to lower the activation energy to escape the basin, thus the jumping rate can be much larger than that on the potential surface $V_0(\mathbf{r})$ and the molecular dynamics simulation is accelerated. The relationship between time step Δt_{MD} and the boosted time step Δt_{b} is

$$\Delta t_{\mathrm{b}} = \Delta t_{\mathrm{MD}}\, \mathrm{e}^{\Delta V(\mathbf{r}(t_i))/KT}, \tag{2}$$

where K is the Boltzman constant and T is the temperature. The boost factor due to the non-negative bias potential,

$$\mathrm{BF} = \frac{\sum_i^{N_{\mathrm{tot}}} \Delta t_{\mathrm{b}}(\mathbf{r}(t_i))}{N_{\mathrm{tot}} \Delta t_{\mathrm{MD}}} = \frac{1}{N_{\mathrm{tot}}} \sum_i^{N_{\mathrm{tot}}} \mathrm{e}^{\Delta V(\mathbf{r}(t_i))/KT}, \tag{3}$$

can be as large as 10^2–10^5, dependent on the simulation temperature. Thus the time scale of the molecular dynamics method is scaled by a few orders of magnitude.

The key to the success of Voter's Hyper-MD is how to determine $\Delta V(\mathbf{r})$. Since there is no any preknowledge of the potential surface, one needs to check if the system is on the dividing surface, and $\Delta V(\mathbf{r})$ must be determined at each molecular dynamics step. To reach this goal, Voter proposed a few methods to calculate the bias potential, but all of them are dependent on the global properties of the system, such as the eigenvalue and the eigenvector of the Hessian. The computation overhead in calculating the eigenvalue, which scales $\mathrm{O}(N^3)$–$\mathrm{O}(N^2)$, becomes very significantly when the system is large with a few tens of atoms. When this extra overhead becomes too large, the advantage of the Hyper-MD will disappear.

The local bias potential [2], which does not depend on the whole system, can save much computation time. The basic idea of the local bias potential is to use a much smaller Hessian matrix, which includes the most important information related to the infrequent event, to replace the Hessian matrix of the whole system. For example, the local bias potential can choose as,

$$\Delta V(\mathbf{r}(t_i)) = \frac{h}{2} \frac{\epsilon_1^2}{\epsilon_1^2 + \frac{g_{1p}^2}{d^2}} \theta(\epsilon_1), \tag{4}$$

where h and d are tunable parameters; θ is the standard step function. ϵ_1 and g_{1p} are the first eigenvalue and the corresponding eigenvector of the Hessian related to the following local potential V_l,

$$V_l(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_n) = \sum_j V(r_{ij}), \quad i = 1, \ldots, n \ll N, \tag{5}$$

where r_{ij} is the distance between atom i and atom j, $\mathbf{R}_i$ is the coordinates of the ith atom; N is the total number of moving atoms and V is the interatomic potential, which should be continuous up to the third derivatives. n is the number of atoms closely related to the infrequent event, the summation is over all the neighbors of all the n atoms. Step function $\theta(\epsilon_1)$ guarantees ΔV is zero near the dividing surface. Since the cost of constructing the bias potential $\Delta V(\mathbf{r})$ is essentially confined to diagonalize a Hessian matrix with $3n$ dimension, the computation overhead becomes much smaller than that to diagonalize a matrix with $3N$ dimension.

In order to have the smallest computation overhead, one wishes to choose n as small as possible, i.e., as local as possible for the local potential. To show how local the local bias potential can be, we study a model system with an adatom or a vacancy diffusion on fcc surfaces, in which the atomic interaction is described by Lennard–Jones potential. The potential has the form:

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

where α and β denote the adatom A and the surface atom B, respectively. In our calculations, we assume $\sigma_{BB} = \sigma_{AB} = 1.0$, and $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB} = 1.0$.

In order to know if the Hyper-MD can be used to study more complicated diffusion process, such as exchange mechanism, we also study the adatom diffusion on aluminum surface, where it is well known that exchange mechanism takes place. We use a numerical *glue* potential derived from ab initio calculation to describe the atomic interaction, in which, the potential energy is the sum of a pairwise term and a *glue* term

$$V = \frac{1}{2}\sum_{ij}\Phi(r_{ij}) + \sum_{i}U\left(\sum_{j}\rho(r_{ij})\right), \tag{7}$$

where r_{ij} is the distance between the ith and jth atom, $\Phi(r_{ij})$ is a pair potential, and U is a many-body glue term. The parameters were given by Ercolessi and Adams [3].

Calculations on fcc-(1 1 1) surface are performed using a slab with five layers of atoms, each layer containing 100 atoms. Two layers at the bottom of the slab are fixed at the perfect fcc positions to mimic the underlying infinite solid. While in the simulation of adatom diffusion on fcc-(1 1 0) surface, our model consists of six atomic layers, with 600 atoms in total. Periodic boundary condition is only imposed on the lateral directions. It is worth to point out, without the approximation of the local bias potential in the Hyper-MD, to study such a large system is almost impossible. The system was first heated up to the desired temperature using Langevin MD [4], which is integrated by a modified Beeman procedure [5]. At each temperature, the equilibration takes 10^4 time steps, the coordinates of the interesting atoms are stored over subsequent 5×10^5–2×10^6 time steps. Diffusion constant is obtained from the asymptotic behavior of the mean square displacement of the adatom.

3. Results and discussions

3.1. Size of Hessian matrix for the local potential

Since the bias potential is directly related to the first eigenvalue of the Hessian matrix, diagonalizing the Hessian matrix will contribute the most part of the computation overhead in constructing the bias potential. Obviously, one expects a small matrix which can correctly predict the dividing surface. To study how large the dimension of the Hessian matrix is necessary, we have investigated a few examples with different sizes of the Hessian matrix for the local potential.

First, we study a vacancy diffusion on the fcc-(1 0 0) surface, in which the interatomic interactions are modeled by the Lennard–Jones potential. To check how the first eigenvalue depends on the size of the Hessian matrix, i.e., the dimensionality of the local potential, we calculate the first eigenvalue with two different dimension of the Hessian matrix along the conventional molecular dynamics path. We construct the Hessian matrix with different locality of the local potential, the smallest one which includes only one atom near the vacancy and a large one which includes all the neighbors around the vacancy. As shown in Fig. 1(a) the sign

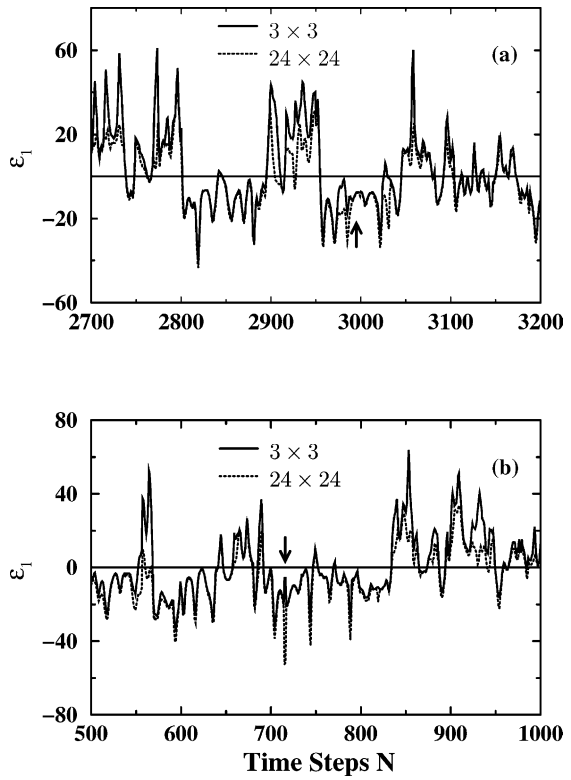

Fig. 1. The time evolution of the first eigenvalue of Hessian matrix with different dimensionality of the local potential for a vacancy diffusion on the fcc-(1 0 0) surface. (a) The first eigenvalue of Hessian matrix with the dimension 3 and 24 respectively along the trajectory of a conventional MD simulation. (b) Similar to (a), but the trajectory is obtained by hyper-MD with the smallest bias potential. The arrows indicate the position where exchange between the vacancy and the substrate atom occurs.

of the first eigenvalue from two Hessian matrixes with 3 and 24 dimension are essentially the same, which suggested that the smallest Hessian can also correctly predict the dividing surface in this system. In fact, it is very easy to understand why the smallest Hessian can give good results. For a vacancy diffusion on the fcc-(1 0 0) surface, all the surface atoms vibrate near their equilibrium positions and only the atom near the vacancy jumps from one position to another. Thus, the transition state of the vacancy is largely determined only by the status of atoms near the vacancy.

We have also checked the validity of the local bias potential on the Hyper-MD path. We performed a Hyper-MD simulation on adatom diffusion on the surface, in which the bias potential is constructed by the first eigenvalue of the Hessian matrix with dimension 3, i.e., the local bias potential including the adatom itself. On each step of this Hyper-MD path, we also calculate the first eigenvalue from a larger Hessian matrix with dimension 24. Fig. 1(b) compares the eigenvalues from two matrixes. Two different matrixes give almost the same sign and also the value of eigenvalue. Obviously, the jumping from one state to another, indicated by arrow near 400 steps, is predicted both by the small and large Hessian matrix.

The interstitial self-diffusion in the solid can also be considered as a series of infrequent events. Usually the diffusion activation energy is very large and diffusion can be very slow, thus the Hyper-MD method can be a useful tool for studying interstitial diffusion. However, the diffusion process is more complicated than the vacancy diffusion on fcc-(1 0 0) surface. Fig. 2 shows a comparison of the eigenvalues from different dimensions of the Hessian matrix. Again, the smallest Hessian matrix with dimension 3 predicts almost the same eigenvalue as what a matrix with dimension 108 does. Based on all these comparison of eigenvalues from small and large Hessian matrix, we can conclude that a very small Hessian matrix could give a good approximation to predict the dividing surface for adatom (vacancy) or interstitial diffusion.

However, it is worth to point out that, small Hessian matrix from the local potential is only an approximation to the global Hessian matrix. In principle, the dividing surface must be determined by the global Hessian matrix. Mathematically, the eigenvalue of a large matrix can be hardly approximated by a small matrix, although other matrix elements could be very small. So a natural question is why the local bias potential based on Eqs. (4) and (5) works well for adatom (vacancy) or interstitial diffusion. Physically, in such a system as tested above, the dividing surface of the interesting atom is mainly determined by the interesting atom itself. The other reason could be that the form of the bias potential which only depends on the first eigenvalue is a very conservative

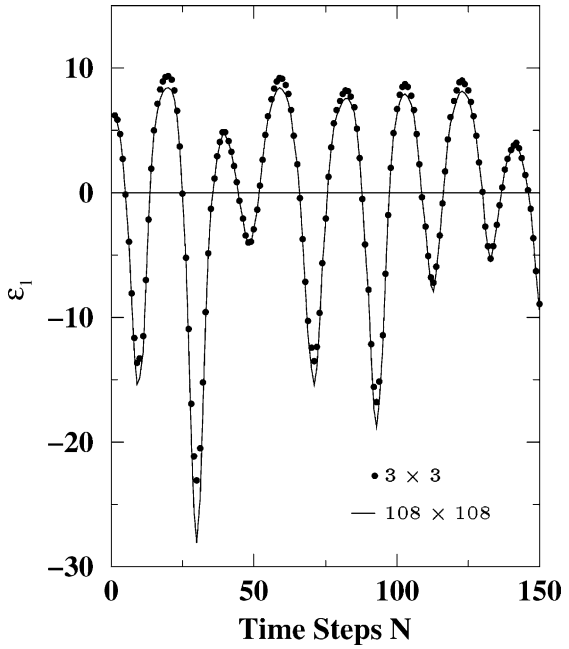

Fig. 2. The time evolution of the first eigenvalues with different dimensionality of two local potentials, for an interstitial diffusion in the bulk. The close agreement between two eigenvalues suggests that the smallest Hessian matrix related to the interstitial itself can correctly predict the dividing surface for the adatom diffusion.

determination of the dividing surface. In this way, although using the eigenvalue of a small matrix to replace the eigenvalue of a large Hessian matrix is a coarse approximation, the conservative choice of the local bias potential leads to a reasonable determination of the dividing surface.

3.2. Exchange mechanism by local bias potential

We have shown that local bias potential can be applied to the adatom diffusion on the surface with hopping mechanism [2]. As we know, adatom diffusion on some surfaces, such as fcc-(1 0 0) can have more complicated mechanism, like exchange mechanism. In order to check if Hyper-MD can be used to study surface diffusion with exchange mechanism in real system, we implement the same procedure of the local bias potential to aluminum surface to study the surface diffusion at different temperatures, for ab initio calculations show that exchange diffusion is preferred for all Al surfaces rougher than Al(1 1 1) [6]. We constructed the local bias potential from the first eigenvalue of Hessian matrix with dimension about 60. We tracked the adatom and its nearest neighbors during the simulation.

We find that Hyper-MD with the local bias potential can predict the exchange mechanism of adatom diffusion on the surface. We show three components of the coordinates for adatom and a substrate atom in Fig. 3. The sudden change of the Z coordinate as shown in Fig. 3 clearly indicates the adatom exchanges with substrate atoms. Through the exchange process, the adatom higher above the surface becomes a substrate atom, and

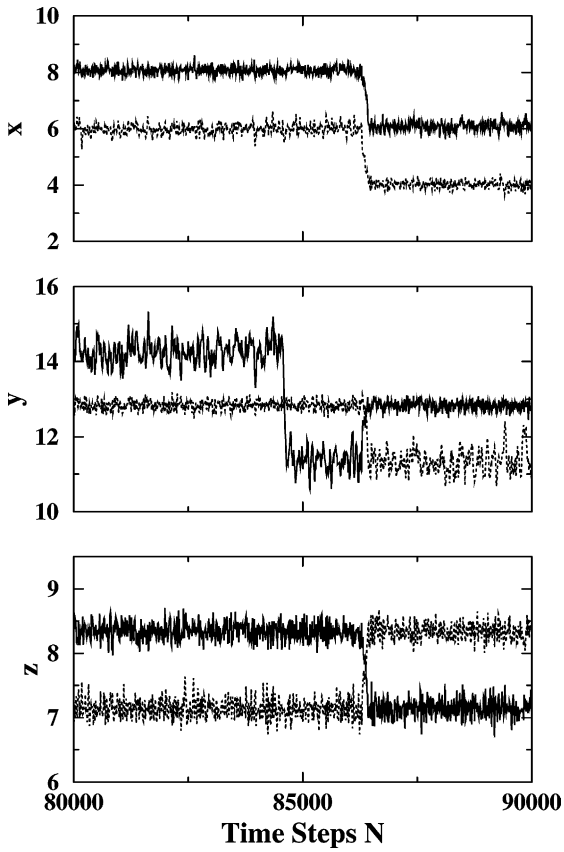

Fig. 3. The coordinates of the adatom and a selected substrate atom for the adatom diffusion on the Al(1 1 0) surface on the Hyper-MD trajectory. The sudden change of Z coordinates indicate an exchange of the adatom with a substrate atom.

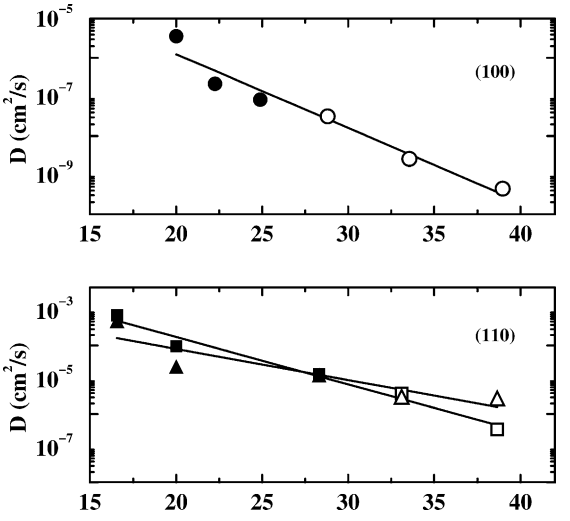

Fig. 4. Temperature dependence of the diffusion constants for an adatom on Al(1 0 0) surface (up panel) and Al(1 1 0) surface (low panel). The full and the open circles are our calculated data by conventional MD and Hyper-MD, respectively, and the line is the least-square fit to the Arrhenius relationship, squares in lower panel for diffusion along (0 0 1) direction and strangles for diffusion along $(1\,\bar{1}\,0)$ direction. The Hyper-MD method can simulate the dynamical process at much lower temperature than the conventional MD method does.

the another substrate atom jumps out of the surface and then becomes the new adatom.

The diffusion constants calculated for adatom diffusion on different aluminum surfaces are shown in Fig. 4. At high temperature, we simulate the adatom diffusion by conventional MD method and calculate the diffusion constant from the mean square displacement, while at low temperature, we perform simulations by Hyper-MD method. The diffusion constants both from conventional MD and Hyper-MD simulations, which follows the same straight line (Fig. 4), confirms the correctness of the Hyper-MD simulation on adatom diffusion via exchange mechanism. By fitting the obtained data to the Arrhenius relationship, we find the diffusion barriers to be 0.436 eV for Al(1 0 0), 0.318 eV (along (0 0 1) direction) and 0.21 eV (along $(1\,\bar{1}\,0)$ for Al(1 1 0), which are in agreement with the experimental and calculated data from DFT-LDA [7].

4. Summary

It has shown that Hyper-MD with local bias potential can predict the correct diffusion constant for adatom or interstitial diffusion. In this paper, we have discussed how large the Hessian matrix for the local bias potential is necessary. By comparing the sign of the eigenvalue of different Hessian matrixes with different size, we have demonstrated that for the diffusion processes like vacancy diffusion on the surface or interstitial diffusion in the bulk, the local bias potential with a very small size can work well. Although, the sign of the first eigenvalue with different size of the Hessian could be sometimes different, the conservative choice of bias potential can help us to get a reasonable results. So we can conclude that the Hyper-MD with the local bias potential could be safely used in the simulation of the surface or bulk diffusion with a small overhead of computation.

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