Hypermolecular dynamics simulations of monovacancy diffusion

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Abstract

The validity of hypermolecular dynamics (hyper-MD) to vacancy diffusion is explored. We have obtained the diffusion constants of a monovacancy up to temperatures as low as 300 K for Al bulk and 160 K for the Al(1 0 0) surface with very large boost factors. The obtained diffusion constants and diffusion barriers are in good agreement with available experimental and theoretical data, which suggest that hypermolecular dynamics with a local bias potential is applicable to vacancy diffusion in real systems. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Point defect diffusion, such as monovacancy, divacancy and self-interstitial diffusion, often has a profound influence on the chemical, electrical and optical properties of materials. On the other hand, the diffusion of point defects plays a crucial role in the processes of mass transport, film growth and crystal growth. Therefore, over the past two decades, there have been numerous theoretical and experimental studies involving point defect diffusion [1–12]. Recently, the progress in experimental techniques such as field ion microscopy [13] has made it possible to directly observe self-diffusion on the atomic scale, but the effort has been limited to a few metals: W, Rh, Pt, Ni and Ir. Also, by means of scanning tunneling microscopy [14], one can examine individual defects on a surface under various conditions.

In the theoretical aspect, molecular dynamics (MD) is a standard tool to study the dynamical process of microstructures. However, the large interval, of the order of nanoseconds or even longer, for subsequent jumps in the process of point defect diffusion prohibits the usage of conventional MD, which usually can simulate the process with time scales up to a nanosecond. Recently, Voter provided a method to accelerate molecular dynamics, i.e., hyper-MD [15,16], which opened a window to the simulation of atomic dynamics for a microsecond or longer. However, the computational time of each hyper-MD step is much longer than that of a conventional MD step,

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and the cost for calculating the bias potential scales as the square of the number of moving atoms, which prohibits application to large systems. Very recently, Gong and Wilkins [17] proposed a local bias potential for the hyper-MD requiring no preknowledge of the saddle points of the system. Also, with this local bias potential, only little computational overload is needed. Using this local bias potential, they successfully simulated adatom and dimer diffusion on a surface with a simple model potential. The application of hyper-MD to real systems is promising.

Aluminium is an important metal material which deserves extensive experimental and theoretical research. To date, many literatures only give the vacancy formation or/and migration energies in the bulk [2,3,5,6]. For vacancies on the surface, few experimental and reliable theoretical results exist at finite temperatures, particularly at low temperatures. Stumpf and Scheffler [8] calculated the energy barriers for adatoms and vacancies on flat and stepped surfaces of Al with the ab initio method, and studied the vacancy diffusion barrier on the Al(1 1 1) surface. However, to our knowledge, the direct simulation of vacancy diffusion, specially at low temperatures, is very limited. The purpose of this paper is to provide a comprehensive study of monovacancy diffusion in Al bulk and on the Al(1 0 0) surface by using hyper-MD simulations. Although there has been successful application of hyper-MD, e.g., to adatom diffusion, using hyper-MD for vacancy diffusion is not obvious. We explore the validity of local bias potential and find that it works well for vacancy diffusion.

2. Simulation details

In this paper, we used 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,

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

where r_{ij} is the distance between the ith and jth atom, $\Phi(r_{ij})$ the pair potential, and U is a many-body glue term. The parameters were given by Ercolessi and Adams [18]. Comprehensive tests confirmed that the glue potential can give the thermal properties of Al solid and surface very close to the corresponding experimental data [18].

For adatom diffusion on the surface, all the surface atoms vibrate near their equilibrium positions, and only the adatom jumps from one position to another. So in the hyper-MD simulation, the bias potential can approximately only be applied to the adatom and its neighbors. However, a vacancy in the bulk or on the surface can diffuse only via its neighboring atoms by exchanging their positions. It is difficult to add a local bias potential like what has been done in the simulation of adatom diffusion. Since only atoms near the vacancy can jump to the vacancy, as an approximation, we only add a bias potential to the neighboring atoms of the vacancy in our present simulation. It is worth noting, that to numerically trace the moving of a vacancy is not as easy as that for adatom diffusion on the surface. At finite temperatures, we treat this problem as follows: first, we take the initial vacancy as the 'old' vacancy, then label its nearest-neighbor (NN) atoms. Second, a local bias potential is added to all NN atoms of the vacancy. If the distance between one of the NN atoms and the vacancy is smaller than a critical value of the nearest-neighbor distance, we consider that the NN atom jumps to the vacancy. Then, the vacancy moves to the new position, and we label the NN atoms again, and in this way the simulation continues.

To use a proper bias potential is the key to the success of the hyper-MD. Although a large bias potential will have a large boost factor, we still choose a conservative bias potential which is zero at the saddle points. Our local bias potential at the ith MD step is non-zero only when ϵ_1 is larger than zero, which reads

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

where h and d are tunable parameters; θ is the standard step function; ϵ_1 the first eigenvalue of

the Hessian matrix $\mathbf{H}\{H_{ij} \equiv \partial^2 V/\partial x_i \partial x_j\}$; and g_{1p} is the projection of the potential gradient onto the first eigenvector of $\mathbf{H}$. 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.

To simulate a vacancy diffusion in Al bulk, we choose a cubic box of 500 atoms with periodic boundary conditions in all three directions, while in the simulation of vacancy diffusion on the Al(1 0 0) surface, our model consists of 10 atomic layers, each layer containing 50 atoms. Two layers at the bottom of the slab are fixed at perfect fcc positions to mimic the underlying infinite solid. The periodic boundary condition is only imposed in the lateral directions. The system is first 'warmed up' to the desired temperature using Langevin MD [19], and the Langevin equation of motion is integrated by a modified Beeman procedure [20] with a time step $\Delta t_{MD} = 10.6$ fs. At each temperature, the equilibration takes 0.1 ns, and all physical properties are statistically averaged over the following 5×10^5 to 2×10^6 time steps.

By definition, the diffusion constant (D) is given by the Einstein relation as follows:

$$D = \lim_{t \to \infty} \frac{\langle R^2(t) \rangle}{2N_d t}, \tag{3}$$

where N_d is the dimensionality of the space in which the process is taking place ($N_d = 3$ for the bulk simulation, $N_d = 2$ for the surface simulation). $\langle R^2(t) \rangle$ is the mean square displacement of the particle undergoing diffusion. So, the diffusion constant can be obtained from the asymptotic behavior of the mean square displacement of the vacancy. Usually, the diffusion constant is a function of temperature with Arrhenius form, which reads:

$$D = D_0 \exp \left[\frac{-E_m}{K_B T} \right], \tag{4}$$

where D_0 is a 'prefactor', K_B the Boltzmann constant, T the temperature and E_m is the diffusion barrier.

3. Results and discussions

The hyper-MD simulation makes it possible to calculate the diffusion constant at room temperature. Fig. 1 shows the diffusion constants at the temperature range of 300–700 K for the Al bulk, which is obtained by calculating the mean square displacement. For comparison, we calculated the diffusion constant at high temperature ($T = 690$ K) by conventional MD simulation. All the points, from hyper-MD and conventional MD, follow a straight line, indicating that the hyper-MD with the local bias potential works properly. From the Arrhenius fitting, the diffusion barrier and the prefactor are determined to be 0.49 eV and 5.83×10^{-4} cm^2 s^{-1}, respectively. So the activation energy E_A, being the sum of the formation and diffusion energy, is 1.18 eV. It is in good agreement with the zero temperature value 1.30 eV [18] and
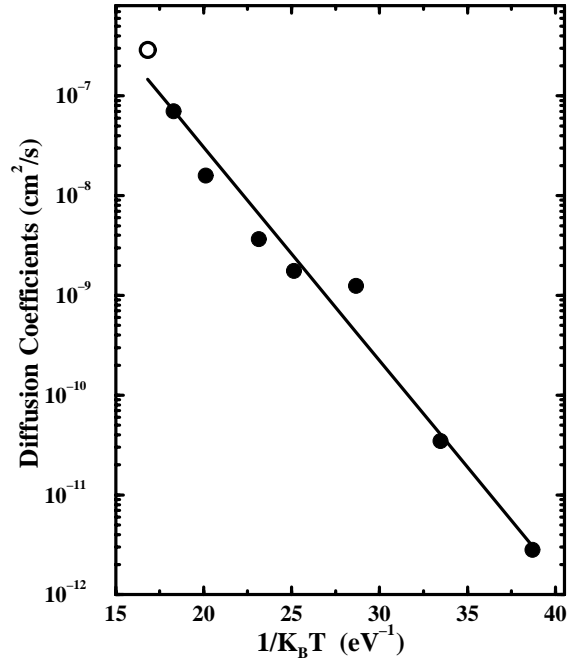

Fig. 1. The diffusion constants for the monovacancy in the bulk. The full circles and the open circle are the present hyper-MD values and the conventional MD value, respectively; the line is from the least-square fit, from which we can obtain the diffusion barrier 0.49 eV and the prefactor 5.83×10^{-4} cm^2 s^{-1}, respectively.

experimental data 1.28 eV [1]. The excellent agreement confirms the high accuracy of hyper-MD with a local bias potential.

What are shown in Fig. 2 are the diffusion constants of a monovacancy on the aluminium (1 0 0) surface between 160 and 600 K. Again, the data at $T = 580$ K are obtained from the conventional MD simulation. The Arrhenius fitting yields the diffusion barrier $E_m = 0.268$ eV, smaller than the value 0.3 eV at zero temperature, and the prefactor $D_0 = 4.18 \times 10^{-3}$ cm^2 s^{-1}. The vacancy diffusion on the surface has a lower diffusion barrier than that in the bulk, which is consistent with the higher coordination number associated with the vacancy in the bulk (12), while on the surface the coordination number of the vacancy is only 8.

It is well known that vacancies diffuse by the exchange mechanism, i.e., one of its nearest-neighbor atoms jumps to the vacancy position, and the vacancy is considered to move to a new position. However, the vacancy on the surface has a quite different environment compared with the vacancy in the bulk. It is interesting to know if the vacancy exchanges the position via all its neighbors. In the present simulation, detailed studies for the diffusion pathway of a vacancy on the surface have been analyzed. The top view of the pathways in the diffusion of a monovacancy on the Al(1 0 0) surface at room temperature is sketched in Fig. 3. We find that, at very low temperatures, vacancy diffusion proceeds only in the top layer of the slab, while the diffusion starts to involve the second-layer atoms when the temperature increases up to about 350 K. Also, the higher the temperature is, the more the second-layer atoms are involved in the diffusion, although the atoms in the top layer play the major role in the diffusion process. We have calculated the formation energy of the vacancy, and found that the monovacancy formation energy, 0.57 eV in the top layer, is much lower than 0.947 eV in the second layer. The large dif-
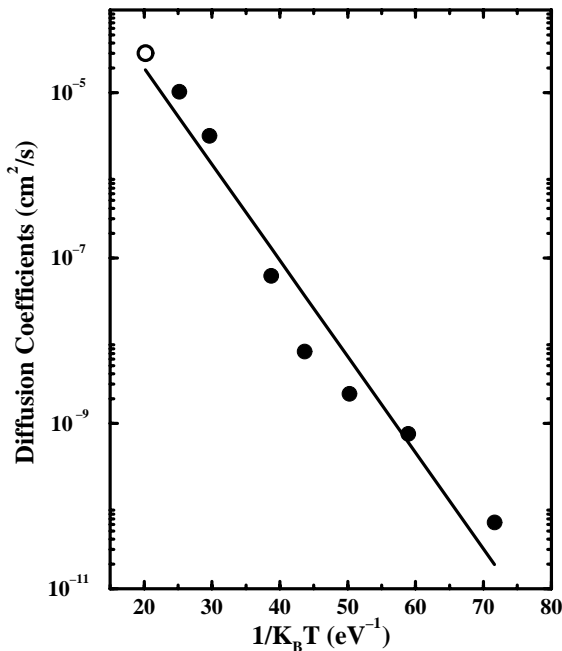

Fig. 2. The temperature-dependent diffusion constants for a vacancy on the Al(1 0 0) surface. The full circles and the open circle are our calculated data, and the line is from the least-square fit.
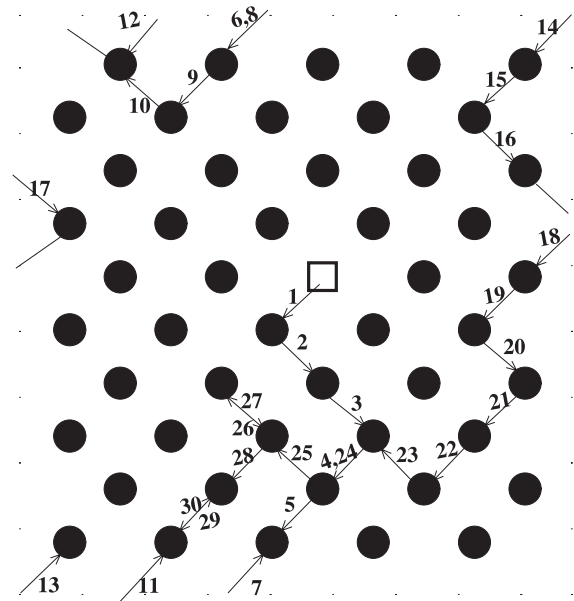

Fig. 3. The pathways (arrows) of vacancy diffusion on the surface at room temperature. The filled circles represent the surface atoms, the square denotes vacancy, and the numbers near the arrows are the step numbers of the vacancy migration. In this figure, we show 30 jumps of the vacancy.

ference of formation energy between the lop layer and the second layer suggests that the vacancy can diffuse into the second layer only at high temperatures, which is in agreement with our simulation.

The computational simplicity of each hyper-MD step ensures a 10^2- to 10^5-fold speedup of the average boost factor. As shown by Gong and Wilkins [17], we compute the time through scaling each MD time step by the average boost factor (BF), i.e., $t = BF \sum \Delta t_{MD}$. Over the direct molecular dynamics simulation time in N_{tot} steps, one can define BF for the boosted time:

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

Fig. 4 shows the temperature dependence of average boost factors for a vacancy diffusion in bulk and on the surface (the insert). In both cases,
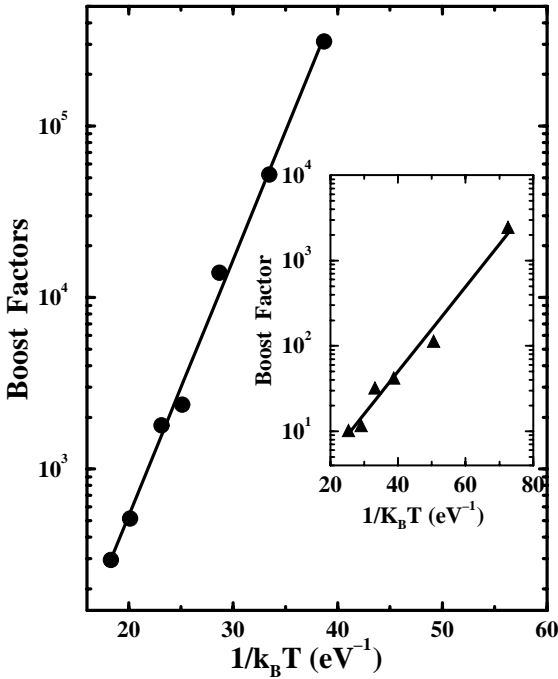

Fig. 4. The temperature dependence of average boost factors for a vacancy on the surface and in the bulk (the local bias parameters are $h = 1.6 \times 10^{-3}$, $d = 0.25$). The filled symbols are our calculated results, and the lines correspond to the least-square fit. Insert: vacancy diffusion on the surface ($h = 3 \times 10^{-4}$, $d = 0.5$). For all cases, we find significant speedups.

the boost factors exponentially increase as the temperature decreases. From low to high temperature, the boost factors range from 10^2 to 10^5. The very large boost factor makes it possible to study the dynamical process at low temperatures.

In summary, we have calculated the diffusion constants for a monovacancy in aluminium bulk and on the Al(1 0 0) surface using hyper-MD simulations. The present studies show that the approximation of the local bias potential is applicable to vacancy diffusion. The results show that the diffusion barriers are about 10% lower than those obtained at the zero temperature. By comparing the pathways of single-vacancy migration on the surface at different temperatures, we find that, at low temperatures, vacancy migration involves its nearest-neighbor atoms only in the top layer, while the migration of the vacancy starts to involve the nearest-neighbor atoms of the second layer at a relatively high temperature. Moreover, with a local bias potential, the present studies successfully demonstrate the validity of hyper-MD in treating with a rare event such as point defect diffusion at relatively low temperatures.

Acknowledgements

References

[1] A. Seeger, D. Wolf, H. Mehrer, Phys. Stat. Solidi B 48 (1971) 481.
[2] M.J. Fluss, L.C. Smedskjaer, M.K. Chason, D.G. Legnini, R.W. Siegel, Phys. Rev. B 17 (1978) 3444.
[3] T.W. Gullion, M.S. Conradi, Phys. Rev. B 36 (1987) 3880.
[4] N.V. Doan, Philos. Mag. A 58 (1988) 179.
[5] A. De Vita, M.J. Gillan, J. Phys. Condens. Matter 3 (1991) 6225.
[6] P.J.H. Denteneer, J.M. Soler, J. Phys. Condens. Matter 3 (1991) 8777.
[7] A. Seeger, Defect Diffus. Forum 95–98 (1993) 147.
[8] R. Stumpf, M. Scheffler, Phys. Rev. B 53 (1996) 4958.
[9] G. Boisvert, L.J. Lewis, Phys. Rev. B 56 (1997) 7643.
[10] U. Kürpick, T.S. Rahman, Phys. Rev. B 59 (1999) 11014.

[11] J.R. Hahn, H. Kang, Phys. Rev. B 60 (1999) 6007.
[12] A. Ural, P.B. Griffin, J.D. Plummer, Phys. Rev. Lett. 83 (1999) 3454.
[13] G.L. Kellogg, Surf. Sci. Rep. 21 (1994) 1.
[14] G. Binning, H. Rohrer, Ch. Gerber, E. Weibel, Phys. Rev. Lett. 49 (1982) 57.
[15] A.F. Voter, J. Chem. Phys. 106 (1997) 4665.
[16] A.F. Voter, Phys. Rev. Lett. 78 (1997) 3908.
[17] X.G. Gong, J.W. Wilkins, Phys. Rev. B 59 (1999) 54.
[18] F. Ercolessi, J.B. Adams, Europhys. Lett. 26 (1994) 583.
[19] H. Haberland, Z. Insepov, M. Moseler, Z. Phys. D 26 (1993) 229.
[20] J.C. Tully, G.H. Gilmer, M. Shugard, J. Chem. Phys. 71 (1979) 1630.