Simple statistical model for predicting thermal atom diffusion on crystal surfaces*

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A simple model based on the statistics of single atoms is developed to predict the diffusion rate of thermal atoms in (or on) bulk materials without empirical parameters. Compared with vast classical molecular-dynamics simulations for predicting the self-diffusion rate of Pt, Cu, and Ar adatoms on crystal surfaces, the model is proved to be much more accurate than the Arrhenius law and the transition state theory. Applying this model, the theoretical predictions agree well with the experimental values in the presented paper about the self-diffusion of Pt (Cu) adatoms on the surfaces.

Keywords: adatoms diffusion, Arrhenius law, transition state theory, molecular dynamics simulations

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1. Introduction

The diffusion rate of thermal atoms on solid surfaces determines the dynamics of crystalline growth, and predicting diffusion rate is highly desirable for designing thin films or quantum dots on crystal surfaces. However, this problem has been a challenge for the existing theories. In 1889, Arrhenius[1] experimentally found that the rate of chemical reaction can be well characterized by two temperature independent constants, R_0 and E_a, in a form of

$$R = R_0 \mathrm{e}^{-E_a/k_B T}. \tag{1}$$

In the 1920s,[2] this law was derived theoretically from the transition state theory (TST) and then was widely used to characterize not only chemical reaction dynamics[3–5] but also atom diffusion on the surface (or in the body) of a material[4,6–9] as well as material degradation.[10] In the harmonic approximation of TST, the diffusion frequency for an adatom to cross over a potential barrier on surfaces is given by[11]

$$\Gamma_{\mathrm{TST}}(T) = 2\nu_0 \mathrm{e}^{-E_0/k_B T}, \tag{2}$$

where E_0 is recognized as the static potential barrier along the minimum energy path (MEP), and ν_0 is the Vineyand frequency given by[12]

$$\nu_0 = \frac{\prod_{i=1}^{3N} \nu_{\mathrm{p}}^{\mathrm{e}}}{\prod_{i=1}^{3N-1} \nu_{\mathrm{p}}^{\mathrm{s}}}, \tag{3}$$

where $\nu_{\mathrm{p}}^{\mathrm{e}}$ and $\nu_{\mathrm{p}}^{\mathrm{s}}$ are the eigenfrequencies for the equilibrium and saddle point configurations. Clearly, this expression for diffusion frequency is very similar to the Arrhenius law (Eq. (1)), and quantum modification[11] above the Debye temperature is unnecessary (such as 340 K for Cu).

The molecular dynamics (MD) simulations of adatom diffusion on crystal surfaces and relevant experimental observations show that the atomic diffusion rate could be fitted according to Eq. (2),[6,13–16] but the fitted barriers are always smaller than the static potential barriers calculated theoretically, and the prefactor is very different from the double of the Vineyard frequency.[11,13,14] It should be noted that the same empirical potential was employed both in the MD simulations and in the calculation of static potential barriers and the Vineyard frequencies, so the difference is not occasional because other uncertain factors (e.g., zero-point effect or experimental errors) were removed. The deviation in the potential barrier as large as 20% has been observed in the study of adatom self-diffusion on Pt(111)[17–19] and on Cu(001) crystal surfaces.[6,20,21] For theoretically determining R_0 in Eq. (1), the famous Meyer–Neldel compensation rule was proposed in 1937 as[22]

$$R_0 = R_{00} \mathrm{e}^{E_0/\Delta}. \tag{4}$$

However, the two parameters R_{00} and $\Delta(>0)$ have to be determined by lots of MD simulations or experimental data.[11,23]

Very recently, a statistical model was developed to predict the stability of nanodevices.[24] In this paper, the statistical model is further developed to address the above problems with the diffusion frequency expressed explicitly, which is as simple as the Arrhenius law and can reproduce Eqs. (1) and (4) under certain conditions. It is worth noting that the statistical law has been conveniently tested via MD simulations with the current computers, and particularly, the atomic events can be

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observed one by one and step by step, making the statistical results much more accurate than the corresponding experimental results. Thus, vast MD simulations were performed to test our statistical model.

2. Basic models

For any thermal system composed of N atoms with their coordinates denoted by $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$, a stable state of the system corresponds to a potential valley on the potential hypersurface $V(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$. If the system crosses over a barrier to another potential valley, the state changes from one to another. In most cases, only a few atoms (named as "key" atoms below) play a key role in this process. For example, in the process of vapor deposition on a solid surface, the key atomic events are mainly the adatom diffusion via the hopping process on the surface [inset of Fig. 1(a)]. Therefore, to predict the frequency of a thermal system from one to another, we only need to consider the probability (or rate) for a key atom (the adatom) to cross over the potential barrier E_0 on an MEP that can be determined in simple ways[25,26] or by sophisticated algorithms.[15]

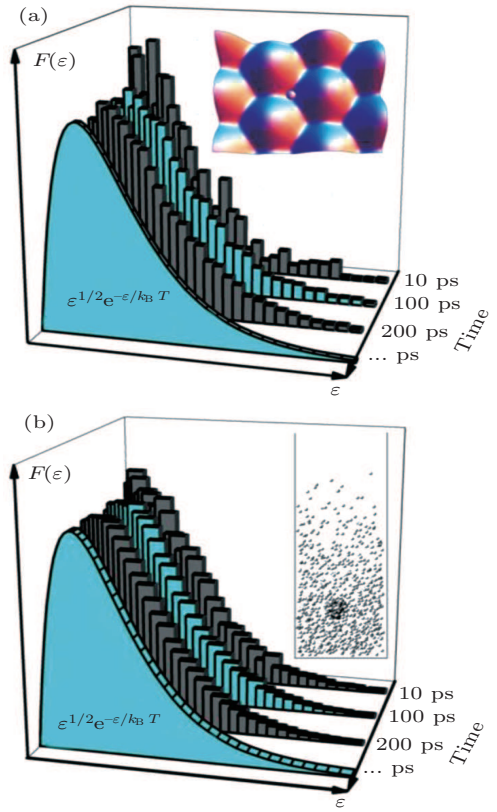


Fig. 1. (color online) The kinetic energy distribution of a Pt adatom on a Pt(111) surface at 300 K (a), and a C atom in a C_{60} molecule pushed by He gas of about 1000 atmospheres at 300 K (b). The data was drawn from the MD simulations, and the recorded energy was analyzed every 10 ps.

The kinetic energy (ε) distribution of single atoms (KEDSA), $\varepsilon^{1/2}e^{-\varepsilon/k_BT}$, can be easily derived from the classical ensemble theory for equilibrium systems. This is common for the dilute (or ideal) gas in equilibrium states since the KEDSA is just the Maxwell's velocity distribution, and holds exactly for single atoms in condensed matters, which has been proved via many MD simulations except for some very special cases.[27] As examples, figure 1 displays the kinetic energy distribution of a C atom in a C_{60} molecule and a Pt adatom on the Pt(111) surface at 300 K. The kinetic energy distribution of the Pt adatom obeys the KEDSA, and surprisingly, the single C atom still does so even if the C_{60} is being pushed by the He gas rushing from a box at about 1000 atmospheres.

According to the KEDSA, the probability of the atom crossing over the barrier ($\varepsilon > E_0$) is[24]

$$p = \frac{1}{Z}\int_{E_0}^{\infty} \varepsilon^{1/2} e^{-\varepsilon/k_B T} d\varepsilon, \tag{5}$$

where $Z = \sqrt{\pi}(k_BT)^{3/2}/2$, the partition function. Assuming that all the hopping events start when the key atom stays in the center of the potential $V(x)$ well along the MEP [Fig. 2], which should be the most probable event, the period taken by the atom of energy ε to cross over the barrier is $\delta t = \sqrt{m}\int_{x_0}^{x_1} dx/\sqrt{2(\varepsilon - V(x))}$, here, m is the atom's mass. The averaged period can be obtained via

$$\begin{aligned}\overline{\delta t} &= \frac{\int_{E_0}^{\infty}(\delta t)\varepsilon^{1/2}e^{-\varepsilon/k_BT}d\varepsilon}{\int_{E_0}^{\infty}\varepsilon^{1/2}e^{-\varepsilon/k_BT}d\varepsilon} \\ &= \frac{1}{4\Gamma_0'},\end{aligned} \tag{6}$$

where Γ_0' refers to an effective oscillation frequency. Accordingly, the rate of the hopping event is given by

$$\Gamma = \frac{4\Gamma_0'}{Z}\int_{E_0}^{\infty}\varepsilon^{1/2}e^{-\varepsilon/k_BT}d\varepsilon. \tag{7}$$

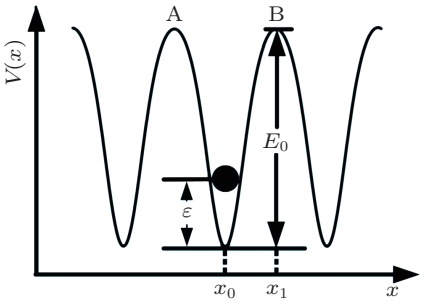


Fig. 2. Schematic of a static potential energy $V(x)$ for an atom along a minimum energy path.

This result can also be obtained from an oscillation point of view. In most cases, the kinetic energy ($\sim k_BT$) of the key atoms is significantly smaller than the static potential barrier E_0, and the atom vibrates many times within the potential well before it crosses over the barrier. To obtain the probability of the hopping over the barrier, we need to count the sample number of "sampling" events that the atom goes through the well bottom where it usually gets the largest kinetic energy (K_E) that can be used to judge if the atom can cross over the barrier (necessary condition $K_E > E_0$). On average, the sample

number should be the double of the oscillation frequency Γ_0, but one half is for barrier A (or B) [Fig. 2]. Thus, according to the KEDSA, the transfer rate over one barrier should be:

$$\Gamma = \frac{\Gamma_0}{Z}\int_{E_0}^{\infty} \varepsilon^{1/2} \mathrm{e}^{-\varepsilon/k_\mathrm{B}T}\mathrm{d}\varepsilon. \tag{8}$$

For the given energy ε, the oscillation frequency is $\nu(\varepsilon) = 1/(4\delta t)$, thus the averaged frequency is

$$\Gamma_0 = \frac{\int_0^{E_0} \nu\varepsilon^{1/2}\mathrm{e}^{-\varepsilon/k_\mathrm{B}T}\mathrm{d}\varepsilon}{\int_0^{E_0} \varepsilon^{1/2}\mathrm{e}^{-\varepsilon/k_\mathrm{B}T}\mathrm{d}\varepsilon}. \tag{9}$$

Notably, the two different ways produce the same transfer rate [Eqs. (7) and (8)] except for the difference of the prefactor. Although the expressions of Γ_0 and Γ_0' are obviously different, they are both insensitive to the temperature and have nearly the same value [Fig. 3(a)]. For example, the frequencies from Eqs. (6) and (9) for a Pt adatom on the Pt(111) surface at about 300 K are, respectively, 0.9 THz and 1.2 THz, which are close to the one (1.1 THz) drawn from the MD simulations [Fig. 3(b)].

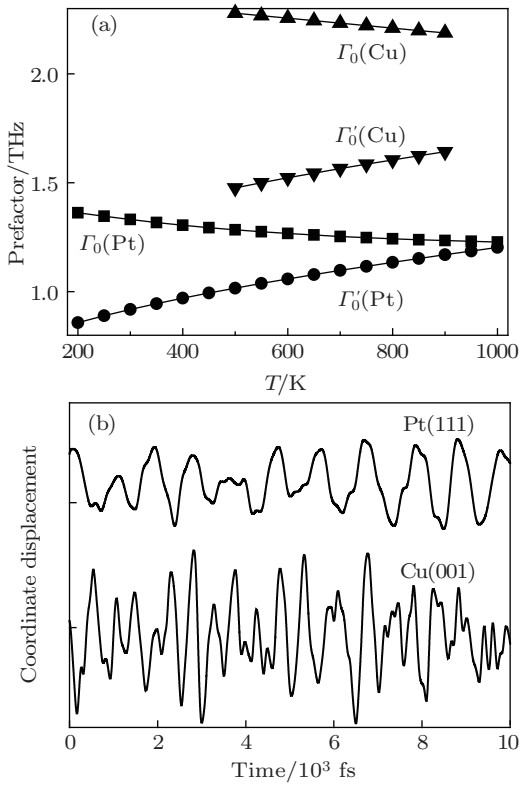


Fig. 3. Prefactor calculated via Eqs. (6) and (9) for Cu adatom on the Cu(001) surface and Pt adatom on the Pt(111) surface (a), and the corresponding oscillation drawn from the MD simulations for 300 K (b).

For comparison with the Arrhenius law and current TST, Eq. (7) or (8) can be rewritten as

$$\Gamma = \Gamma_0 F\left(\frac{E_0}{k_\mathrm{B}T}\right)\mathrm{e}^{-E_0/k_\mathrm{B}T}, \tag{10}$$

where $F(x)$ is a universal function

$$F(x) = \frac{2}{\sqrt{\pi}}\int_0^{\infty}(x+x')^{1/2}\mathrm{e}^{-x'}\mathrm{d}x'. \tag{11}$$

As shown in Fig. 4(a) and Table 1, $F(E_0/k_\mathrm{B}T)$ increases monotonically with E_0 for given temperature T and can be well fitted by

$$F(E_0) = C\mathrm{e}^{(E_0/\Delta)^\alpha}. \tag{12}$$

This is very similar to the formula with $0.5 \le \alpha \le 1.0$ presented in recent literatures to modify the Meyer–Neldel rule [Eq. (4)].[11,12,28,29]

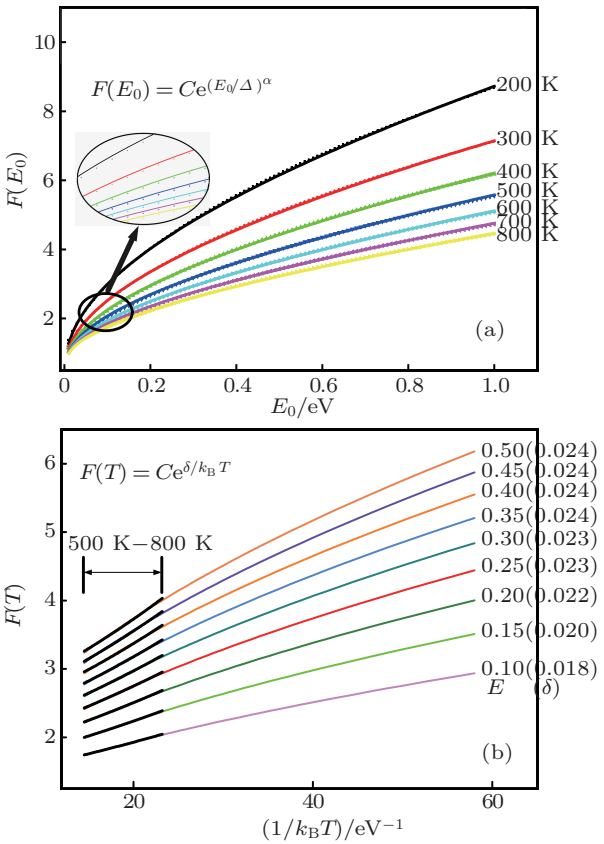


Fig. 4. (color online) The function $F(E_0/k_\mathrm{B}T)$ [Eq. (11)] change with E_0 (a) and $1/k_\mathrm{B}T$ (b) can be well fitted by $F(E_0) = C\mathrm{e}^{(E_0/\Delta)^\alpha}$ and $F(T) = C\mathrm{e}^{\delta/k_\mathrm{B}T}$, respectively. The units for E_0, Δ, δ are eV, while K for temperatures.

Table 1. Parameters in Fig. 4(a).

T	200	300	400	500	600	700	800
Δ	1.4×10^{-7}	2.6×10^{-6}	3.1×10^{-5}	3.7×10^{-4}	0.002	0.006	0.013
α	0.103	0.116	0.131	0.153	0.173	0.191	0.207

For the given E_0, the function $F(E_0/k_\mathrm{B}T)$ decreases monotonically with T (increases with $1/T$) [Fig. 4(b)] and can be fitted in the temperature range of 500 K–800 K by

$$F(T) = C\mathrm{e}^{\delta/k_\mathrm{B}T}, \tag{13}$$

and thus equation (10) can be rewritten as

$$\begin{aligned}\Gamma &= \Gamma_0 C\mathrm{e}^{-(E_0-\delta)/k_\mathrm{B}T} \\ &= R_0\mathrm{e}^{-E/k_\mathrm{B}T}.\end{aligned} \tag{14}$$

This Arrhenius expression is just the result of TST.[5,11] Clearly, if equation (14) is fitted (R_0 and E being regarded as constants) to the experimental rate of any thermal process, then the fitted potential barrier E should be smaller than the real one E_0 by δ. This difference has been observed in the study of adatom and dimer self-diffusion by hopping or exchanging on Cu(100) and Cu(111) surfaces, and the differences amounting to 0.010 eV–0.030 eV,[11,14] are in good agreement with the δ values presented in Fig. 4(b).

It should be pointed out that when the kinetic energy of the atoms ($\sim k_{\rm B}T$) is close to or exceeds the static potential barrier E_0, the oscillation picture is no longer reasonable and therefore equation (9) does not holds exactly. In such cases, Equations (6) and (7) have to be used to calculate the prefactor, and the rate, respectively.

3. Applications

Applying the basic model, we study the adatom (Pt, Cu, and Ar) diffusion on surfaces by using classical MD simulations, which can provide detailed information. The interaction potential for Pt and Cu atoms is described by the TB-SMA,[30] and the {6–12} Lennard–Jones (L–J) function is applied for Ar atoms. A substrate consists of 7 atomic layers each with 16×16 atoms arranged in an fcc plane, on which periodic boundary conditions are imposed. The bottom atoms of the substrate are assigned velocity to imitate the effect of a thermal bath at the given temperature T, which has been detailed in our previous papers[25,26] where the procedure for the calculation of the potential energy $V(x)$ and potential barrier E_0 is also presented. In all the MD simulations, we just recorded the frequency of the hopping events.

For Pt adatom diffusion on the Pt(111) surface, the simulations ran for ten temperature points ranging from 100 K to 1000 K, providing over 5000 hopping events where the difference of the frequency is below 1% for each temperature point (about 9000 events for 1000 K)[Fig. 5(a)] . The MD result (Fig. 5(a)) of the Pt adatom diffusion can be fitted by Eq. (1) with an potential barrier of 0.147 eV and a prefactor of 3.8 THz, denoted by $E_{\rm af}$ and $R_{0\rm f}$ [Table 2], respectively. In Pt(111) surface, there are two sites for difference barriers, an fcc site with 0.173 eV and an hcp site with 0.168 eV, which have nearly the same weight, thus the average of the two barriers is used as the theoretical static potential barriers (E_0) in this paper. Based on the analysis, the E_0 (0.171 eV) is larger than the $E_{\rm af}$ by 0.024 eV, which is in good agreement with the δ shown in Fig. 3(b).

This result can also be well fitted by Eq. (8) with a prefactor $\Gamma_{0\rm f} = 2.6$ THz and an potential barrier $E_{0\rm f} = 0.171$ eV, which is close to E_0. As shown in Fig. 3(a), the Γ_0 calculated via Eq. (9) is insensitive to the temperature and decreases from 1.3 THz down to 1.2 THz when the temperature increases from 200 K up to 1000 K. It is close to 1.1 THz drawn from the MD simulations of a Pt adatom on Pt(111) surface at about 300 K [Fig. 3(b)]. As expected, the double of Γ_0 approximates the fitted prefactor $\Gamma_{0\rm f}$ because the adatom may escape from the potential well via either the left or the right saddle on the MEP.

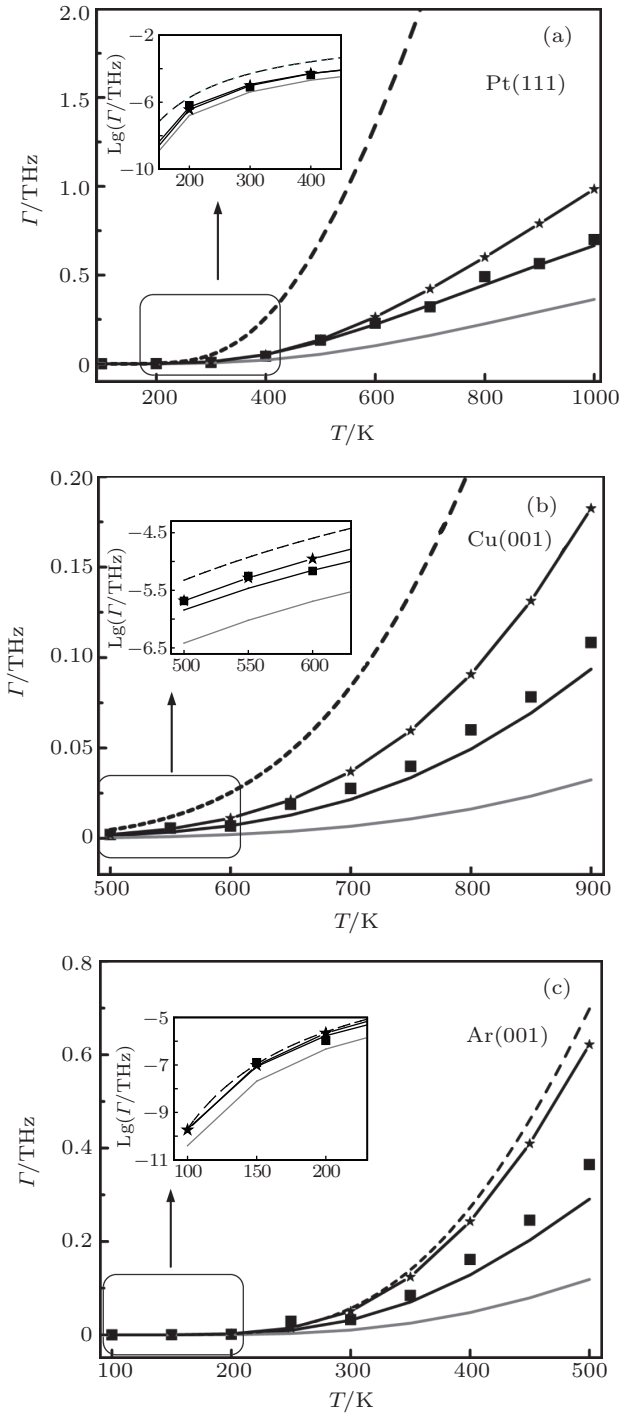


Fig. 5. Atomistic diffusion frequency rate drawn from MD simulations (solid squares) for diffusion of Pt adatom on the Pt(111) surface (a), Cu adatom on the Cu(001) surface (b), and Ar adatom on the Ar(001) surface (c), compared with the theoretical calculations via the model [Eqs. (8) and (9)] (solid lines), or via the Arrhenius law with a prefactor equal to $2\Gamma_0(T)$ (gray lines), or equal to the harmonic frequency $F_{\rm h}$ (dashed lines). The result of TST is denoted by star lines.

Applying Eq. (8) with E_0 and the double of $\Gamma_0(T)$ shown in Fig. 3(a), we obtained a Γ–T curve, which is in accord with

the result of MD simulations [Fig. 5(a)]. As a comparison, the prediction from Eq. (1) with $E_a = 0.171$ eV and $R_0 = 2\Gamma_0(T)$, or R_0 replaced with the harmonic frequency ($F_h = 18$ THz, calculated from the static potential energy $V(x)$ at the equilibrium point), and from TST are also presented, showing that our theory is much more accurate than the others.

Table 2. The potential barriers calculated along the MEP (E_0), or produced by fitting Eq. (8) (E_{0f}), Eq. (1) (E_{af}) to the MD results, and the corresponding fitted prefactor Γ_{0f} (THz), R_{0f} (THz).

Elements	E_0/eV	E_{0f}/eV	E_{af}/eV	Γ_{0f}/THz	R_{0f}/THz
Pt(111)	0.173	0.171	0.147	2.6	3.8
	0.168				
Cu(001)	0.434	0.430	0.401	9.7	19.2
Ar(001)	0.162	0.159	0.144	6.0	10.3

In order to compare with the experimental measurements, the *ab initio* (VASP) calculation of $V(x)$ for Pt adatom diffusion on the Pt(111) surface was performed in a slab composed of four Pt(111) layers with each of 8×8 atoms. Periodic boundary conditions were imposed both parallel and perpendicular to the surface and the ultrasoft pseudopotentials used for the electron-ion interactions with a cutoff energy of 233.73 eV.[31] Then the theoretical static potential barrier E_0 is 0.28 eV. Based on the above analysis, the fitted barrier E (Eq. (14)) is about 0.26 eV, which is in good agreement with 0.25 eV or 0.26 eV in Refs. [18]–[20].

For Cu adatom hopping on the Cu(001) surface, the temperature range covered by the MD simulations is 500 K–900 K, which is a little narrower than the range for the diffusion of Pt adatom. This selection considers the fact that the melting point of Cu crystal is only 1300 K, and the static potential barrier (0.431 eV) does not allow the adatoms to diffuse within the timescale of MD simulations below 500 K. Even if the temperature is higher than 700 K, the diffusion rate is yet much slower than the Pt adatom, and our simulations provided about 1000 hopping events for each temperature point above 700 K. The MD result of the Cu adatom diffusion [Fig. 5(b)] can also be well fitted by the Arrhenius law, producing $R_{0f} = 19.2$ THz and $E_{af} = 0402$ eV [Table 2], which is smaller than the theoretical static one (0.431 eV) by 0.029 eV that is close to the δ (0.024 eV) shown in Fig. 3(b).

If fitted with Eq. (8), it produces a exact potential barrier $E_{0f} = 0.43$ eV and a prefactor $\Gamma_{0f} = 9.7$ THz. It is natural that Γ_{0f} is about four times of Γ_0 [Fig. 3(a)] calculated with Eq. (9) because the atom may escape from four possible saddles on the (001) surface. The fitted potential barrier E (Eq. (14)) is about 0.40 eV. This result is in good agreement with the experimental observation of Breeman and Boerma, who obtained $E_{af} = 0.39$ eV and $R_{0f} = 10$ THz.[21] Another experiment gives nearly the same potential barrier (0.4 eV) but a smaller prefactor (0.8 THz).[20]

Considering that the L–J potential for an Ar atom's interaction is different from the one for Pt and Cu atoms, we performed similar MD simulations of the adatom self-diffusion on Ar(111) and Ar(001) surfaces, and got the same conclusions as for the Pt and Cu adatoms. Figure 5(c) demonstrates the results for Ar(001) surface diffusion, where the interaction for Ar atoms was deliberately intensified by ten times so as to provide results comparable to the Cu adatom.

4. Conclusions

Based on the fact that the kinetic energy distribution of single atoms in condensed matters always obeys $\varepsilon^{1/2}e^{-\varepsilon/k_BT}$, a simple model was developed to predict atomic diffusion rate with the static potential along the MEP, and has been proven by MD simulations to be more accurate than the Arrhenius law and TST. Since the prediction of our model needs only the static potential, which can be easily obtained via common *ab initio* calculations, this model could be widely used to understand the thermal atom motion, to precisely predict and design molecular processes in many areas of science.

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