# Transition state theory of the preexponential factors for self-diffusion on Cu, Ag, and Ni surfaces

L. T. Kong and Laurent J. Lewis*

*Département de Physique et Regroupement Québécois sur les Matériaux de Pointe (RQMP), Université de Montréal, Case Postale 6128, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3J7*

The preexponential factors for self-diffusion via hopping and/or exchange on the (001), (110), and (111) surfaces of Cu, Ag, and Ni are examined within transition state theory. The calculations show that the prefactors have a weak temperature dependence above room temperature, and that within transition state theory, the Vineyard method provides a rather accurate description of them. It is also found that the present approach is able to predict prefactors within the same precision as those obtained from molecular-dynamics simulations, and better than those derived from the thermodynamical properties when the contributions from the substrate are neglected.

Detailed knowledge of surface diffusion is of utmost importance for the understanding of a number of nonequilibrium phenomena such as nucleation and growth.[1] On surfaces, for instance, the rates at which particles diffuse determine the equilibrium shape of islands and, on macroscopic time scales, the morphology of films. However, very little is known of the fundamentals of diffusion although a large amount of experimental and theoretical research has been devoted to this subject.[2]

Most theoretical determinations of the diffusion coefficients derive from the Einstein relation

$$D = \lim_{t \to \infty} \langle \Delta r^2(t) \rangle / 2dt, \tag{1}$$

where $D$ is the diffusion coefficient, $t$ is the time, $d$ is the dimension of the space in which diffusion takes place, and $\langle \Delta r^2(t) \rangle$ is the mean square displacement of the diffusing atom.

In the framework of transition state theory (TST), one assumes that the motion of the diffusing atom consists of independent, randomly oriented jumps between adjacent binding sites, which obey random-walk statistics, and therefore

$$\langle \Delta r^2(t) \rangle = n_p \nu t l^2, \tag{2}$$

where $n_p$ is the number of equivalent diffusion paths, $l$ is the distance between binding sites (jump length), and $\nu$ is the attempt-to-diffuse frequency, given by

$$\nu = \frac{k_B T}{h} \exp\left(-\frac{\Delta F_{\text{vib}}}{k_B T}\right) \exp\left(-\frac{E_d}{k_B T}\right) = \nu_0 \exp\left(-\frac{E_d}{k_B T}\right), \tag{3}$$

where

$$\nu_0 = \frac{k_B T}{h} \exp\left(-\frac{\Delta F_{\text{vib}}}{k_B T}\right) \tag{4}$$

is the prefactor for the attempt-to-diffuse frequency; here $k_B$ is Boltzmann's constant, $T$ is the temperature, $h$ is Planck's constant, $\Delta F_{\text{vib}}$ is the vibrational free energy difference between the transition (saddle-point) state and the equilibrium (binding or stable) state, and $E_d$ is the energy barrier—usually taken as the static lattice energy difference between

the transition state and the equilibrium state, although it is in principle temperature dependent. The diffusion coefficient can then be written in the Arrhenius form

$$D = \frac{n_p \nu l^2}{2d} = \frac{n_p \nu_0 l^2}{2d} \exp\left(-\frac{E_d}{k_B T}\right) = D_0 \exp\left(-\frac{E_d}{k_B T}\right), \tag{5}$$

where

$$D_0 = \frac{n_p \nu_0 l^2}{2d} \tag{6}$$

is the prefactor (or preexponential factor) for diffusion.

Both the energy barrier $E_d$ and the prefactor $D_0$ can in principle be determined experimentally by fitting the observed diffusion coefficients to an Arrhenius temperature dependence. Such experiments are, however, notably difficult since several (indirect) measurements—tedious, time consuming, and prone to errors—are needed in a reasonable range of temperatures in order to obtain reliable data. The prefactor is often simply taken to be the "usual value" of $10^{-3}$ cm$^2$/s. Likewise, most theoretical calculations have taken the prefactor for granted, focusing on the energy barriers—now more or less routine work. Nevertheless, there have been several attempts to calculate the prefactors explicitly, in particular by using molecular-dynamics (MD) simulations. An alternative approach based on TST was proposed by Vineyard[3] as follows:

$$\nu_0 = \frac{\prod_{i=1}^{3N} \nu_i}{\prod_{j=1}^{3N-1} \nu'_j}, \tag{7}$$

where $\nu_i$ and $\nu'_j$ are the $\Gamma$-point frequencies at the equilibrium state and the transition state, respectively.

Another approach follows from Eqs. (4) and (6), where the vibrational free energies can be evaluated within the harmonic approximation:
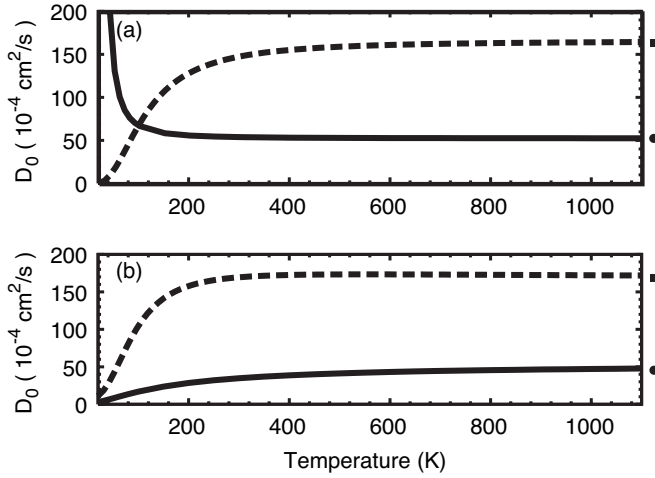
FIG. 1. Variation of the prefactors with temperature for Cu adatom diffusion on Cu(001) via hopping (solid line) and exchange (dashed line), (a) with and (b) without the contribution from the zero-point motion. Dots and squares indicate the Vineyard prefactors for hopping and exchange, respectively; these are independent of temperature.

$$F_{\text{vib}} = k_B T \sum_{\mathbf{q}} \sum_{i=1}^{3N} \ln\left[ 2 \sinh\left( \frac{1}{2} \frac{h\nu_{i\mathbf{q}}}{k_B T} \right) \right], \qquad (8)$$

where $\nu_{i\mathbf{q}}$ is the $i$th eigenfrequency at $\mathbf{q}$. Alternatively, it can also be expressed in terms of the vibrational density of states (DOS) $N(\nu)$:

$$F_{\text{vib}} = k_B T \int_0^\infty N(\nu) \ln\left[ 2 \sinh\left( \frac{1}{2} \frac{h\nu}{k_B T} \right) \right] d\nu. \qquad (9)$$

This method was used by Kürpick, Rahman, and co-workers to calculate the surface diffusion coefficients of adatoms and/or vacancies on various surfaces of Cu, Ag, and Ni.[4–9] They actually used a variant of the approach whereby the total DOS $N(\nu)$ in Eq. (9) is replaced by the *local* DOS (LDOS) $n_l(\nu) = \sum_\alpha n_{l\alpha}(\nu)$ for the diffusing atom, whose component in direction $\alpha$ is given by

$$n_{l\alpha}(\nu) = \sum_{i,\mathbf{q}} \frac{\gamma}{\pi} |u_{l\alpha}(\nu_{i\mathbf{q}})|^2 e^{-\gamma^2(\nu - \nu_{i\mathbf{q}})^2}, \qquad (10)$$

where $u_{l\alpha}$ is the displacement of atom $l$ in direction $\alpha$ corresponding to mode $\nu_{i\mathbf{q}}$ and $\gamma$ is a parameter determining the width of the Gaussian representation of a $\delta$ function. A real-space Green's function method can also be used to evaluate the LDOS.[10,11]

In the LDOS approach above, the contribution from the substrate—which is in general different at the equilibrium and transition states—to the free energy difference is neglected. Consequently, this approach is expected not to be accurate in some situations, for instance diffusion via exchange. Here, we present a study of surface self-diffusion by hopping and/or exchange on the (001), (110), and (111) surfaces of Cu, Ag, and Ni, based on embedded-atom-method (EAM) potentials,[12,13] where the vibrational free energies are evaluated according to Eq. (8) using the *full* phonon spectrum at both the equilibrium and transition states. It turns out that even in the case of diffusion via hopping, the contribution from the substrate to the free energy difference is not negligible, and consequently the present approach provides a more accurate description of the prefactors within TST.

In order to obtain the diffusion coefficients, one thus requires information on both equilibrium and transition states. For self-diffusion via hopping on the low-index surfaces of fcc metals, these states are usually well defined by surface symmetry. Specifically, for the (110) surface, the adatom can diffuse along two nonequivalent directions: along and across the [110] direction. Consequently, there is one equilibrium state (face centered) and two saddle points. For the (111) surface, there are two possible equilibrium states, corresponding to the fcc site and the hcp site, according to the stacking sequence of the atomic layers; the saddle point lies roughly at the edge center. For the exchange mechanism, however, the saddle point cannot be determined simply by symmetry. In the present study, the climbing image nudged elastic band method[14,15] was used to identify the saddle point, which is the point along the minimum-energy path that has the highest total energy.

Computational details are as follows. Model systems for Cu, Ag, and Ni were constructed as supercells in a slab geometry with an adatom on one side of the slab; in all cases, the three bottom layers on the other side of the slab were held fixed in order to mimic the presence of the bulk. All other atoms were free to move except the adatom at the transition state, whose $x$ and $y$ coordinates were fixed so as to force it to stay at the saddle point. Periodic boundary conditions were applied in the lateral ($x$ and $y$) directions while the $z$ direction was free. The interactions between atoms were described by the EAM empirical potentials developed by Adams, Foiles, and Wolfer;[13] the cutoff distance was set to $1.5a_0$ ($a_0$ is the equilibrium lattice constant of the fcc lattice). The model systems were first subjected to molecular-statics relaxation in order to minimize the energy; this was done using a conjugate-gradient scheme. After relaxation, the equilibrium lattice energies and consequently the energy barriers were determined. The full phonon spectra were then calculated, yielding the vibrational thermodynamical properties. The Brillouin zone was sampled according to the Monkhorst-Pack scheme.[16] Prior to calculating the prefactors, convergence with respect to surface cell size, slab thickness, and density of the $\mathbf{q}$-point mesh was examined. Slabs of $10 \times 10 \times 10$ for the (001) and (111) surfaces and $5 \times 7 \times 10$ for the (110) surface, with a $16 \times 16 \times 1$ Monkhorst-Pack $\mathbf{q}$-mesh for (001) and $20 \times 20 \times 1$ for (110) and (111) surfaces, were found to be adequate to achieve convergence and were therefore adopted in the subsequent calculations.

The calculated energy barriers were found to be in agreement with previous investigations.[6–9,20–23] They are of no particular interest here; rather, we focus on the prefactors ($D_0$) deduced from Eqs. (4) and (6). Figure 1(a) shows the variation of the prefactors for Cu adatom diffusion via hopping and exchange on Cu(001) as a function of temperature. One sees that the prefactor for hopping decreases rapidly in the temperature range 0–100 K, and is nearly constant after ~300 K. The prefactor for the exchange mechanism shows the opposite trend: it first increases rapidly, then remains

TABLE I. Preexponential factors for adatom self-diffusion on some low-index surfaces of Cu, Ag, and Ni, in unit of $10^{-4}$ cm$^2$/s. $e$ indicates diffusion via exchange, otherwise it is via hopping. ∥ denotes diffusion along the [110] direction, while ⊥ is across. $f$ is for the fcc site as the equilibrium state, while $h$ is for the hcp site. "Full" indicates prefactors obtained by the full phonon spectrum, "LDOS" by the local density of states approximation, and "MD" by molecular-dynamics simulations. "AFW" (Ref. [13]), "VC" (Ref. [17]), "RGL" (Ref. [18]), and "FBD" (Ref. [19]) indicate potentials employed. Values in parentheses are prefactors without the contribution from the zero-point energy.

| (001) | (001)$_e$ | (110)$_\parallel$ | (110)$_\perp$ | (110)$_e$ | (111)$_f$ | (111)$_h$ | Remarks |
|---|---|---|---|---|---|---|---|
| | | | | Cu | | | |
| 55 (35) | 149 (169) | 34 (26) | 88 (60) | 251 (156) | 1.65 (1.46) | 1.57 (1.39) | 300 K, Full, AFW |
| 54 (43) | 163 (173) | 34 (30) | 87 (72) | 249 (196) | 1.64 (1.54) | 1.56 (1.47) | 600 K, Full, AFW |
| 54 | 165 | 33 | 83 | 235 | 1.72 | 1.71 | Vineyard, AFW |
| 52 | 200 | 44 | 270 | | 4.6 | | Ref. 20, Vineyard, VC |
| 25 | | 11 | | | 1.2 | | Ref. 6, LDOS, RGL |
| 8.7 | | | | | | | Ref. 8, LDOS, FBD |
| 9.0 | | | | | | | Ref. 8, LDOS, VC |
| 7.29 | | 6.29 | 9.97 | | | | Ref. 9, LDOS, 300K, FBD |
| 7.43 | | 6.39 | 11 | | | | Ref. 9, LDOS, 600K, FBD |
| | | | | Ag | | | |
| 37 (27) | 82 (87) | 29 (24) | 67 (51) | 259 (173) | 2.78 (2.45) | 2.80 (2.46) | 300 K, Full, AFW |
| 37 (32) | 85 (88) | 29 (27) | 67 (58) | 256 (209) | 2.78 (2.61) | 2.80 (2.62) | 600 K, Full, AFW |
| 39 | 85 | 29 | 69 | 265 | 2.66 | 2.68 | Vineyard, AFW |
| 39 | 200 | 27 | | 250 | 4.1 | | Ref. 20, Vineyard, VC |
| 8.1 | | | | | | | Ref. 8, LDOS, FBD |
| 23 | | | | | | | Ref. 8, LDOS, VC |
| | 31 | 1361 | | | | 1.5 | Ref. 21, MD, FBD |
| | | | | Ni | | | |
| 53 (31) | 109 (133) | 40 (28) | 95 (56) | 279 (137) | 2.99 (2.46) | 2.89 (2.36) | 300 K, Full, AFW |
| 52 (39) | 125 (139) | 40 (34) | 92 (71) | 268 (188) | 2.99 (2.70) | 2.88 (2.60) | 600 K, Full, AFW |
| 55 | 129 | 46 | 99 | 289 | 2.86 | 2.88 | Vineyard, AFW |
| 54 | 400 | 40 | | 280 | 6.2 | | Ref. 20, Vineyard, VC |
| 37 | | 14 | | | 1.8 | | Ref. 6, LDOS, VC |
| 9.3 | | | | | | | Ref. 8, LDOS, FBD |
| 36 | | | | | | | Ref. 8, LDOS, VC |

unchanged. The "transition" point corresponds roughly to the passage from the quantum to the classical regime (Debye temperature). Indeed, we may rewrite Eq. (8) as

$$F_{\text{vib}} = \frac{1}{2}\sum_{\mathbf{q},i} h\nu_{i\mathbf{q}} + k_B T \sum_{\mathbf{q},i} \ln\left[1 - \exp\left(-\frac{h\nu_{i\mathbf{q}}}{k_B T}\right)\right], \quad (11)$$

and treat the contribution of the zero-point energy [first term of Eq. (11)] to $\Delta F_{\text{vib}}$ as a correction to the energy barrier. Incorporating the remaining term into Eqs. (4) and (6), we find the prefactors in both cases to first increase and then remain nearly constant with increasing temperature, as can be observed in Fig. 1(b); in effect, the present classical model predicts a weak temperature dependence for the prefactors. This can also be verified in Table I, which lists all calculated prefactors at both 300 and 600 K, for hopping on the (001), (110), and (111) surfaces and exchange on the (001) and (110) surfaces of Cu, Ag, and Ni. The prefactors are found to be in the range $10^{-1}–10^{-4}$ cm$^2$/s, in line with the value of $10^{-3}$ cm$^2$/s that is generally used. From these

data, we also observe that a higher energy barrier usually corresponds to a greater prefactor, a correlation that is known as the compensation effect or Meyer-Neldel rule.[24]

The prefactors were also calculated using the Vineyard method [Eqs. (6) and (7)], that is, using only the frequencies at the $\Gamma$ point; the results, shown in Fig. 1 and also given in Table I, are found to be quite comparable to the "exact" values; this was anticipated because the Vineyard method can be regarded as the high-temperature limit of the exact TST method if $\Gamma$-only phonons are considered (see the Appendix of Ref. 9). Thus, the Vineyard method is a good approach for calculating diffusion prefactors within TST, provided that the temperature is high enough, while not exceeding the range of validity of TST and the harmonic approximation.

Comparing with data from other calculations, we find that our prefactors agree quite well with those reported by Liu *et al.*,[20] especially the set obtained using the Voter-Chen potential and the Vineyard method. Further, the present prefactors, calculated in the framework of the TST, agree with

TABLE II. Differences in vibrational free energies and prefactors for adatom hopping on the (001) and (110) surfaces (along the [110] direction) obtained using the full phonon spectrum ("Full") and the local density of states approximation ("Local") at 600 K. The values in italics are read from various figures in Refs. 6 and 7.

| Surface | | $\Delta F_{vib}$ (meV) | | $D_0$ ($10^{-4}$ cm²/ps) | | References |
|---------|---|------|-------|------|-------|------------|
| | | Full | Local | Full | Local | |
| Cu | (001) | 21.00 | 61.17 | 54 | 25 | This work |
| | | | *60* | | 25 | Ref. 6 |
| | | | 123.4 | | 7.43 | Ref. 9 |
| | | | *110* | | 9.0 | Refs. 7 and 8 |
| | | | *120* | | 8.7 | Refs. 7 and 8 |
| | (110) | 44.70 | 91.42 | 34 | 14 | This work |
| | | | *100* | | 11 | Ref. 6 |
| | | | 131.5 | | 6.39 | Ref. 9 |
| Ni | (001) | 20.94 | 51.35 | 52 | 29 | This work |
| | | | | | 37 | Ref. 6 |
| | | | *40* | | 36 | Refs. 7 and 8 |
| | | | *110* | | 9.3 | Refs. 7 and 8 |
| | (110) | 33.59 | 73.77 | 40 | 19 | This work |
| | | | | | 14 | Ref. 6 |

those deduced from molecular-dynamics simulations (no approximations) by Lewis *et al.*[21] In contrast, there are significant discrepancies—sometimes by as much as a factor of ~8—with results obtained using the LDOS approximation of Refs. 6, 8, and 9; also the agreement of LDOS prefactors with Vineyard or MD results is rather poor.

In order to clarify the origin of these differences, viz., ascertain that our calculations are correct, we recalculated some of our prefactors using the LDOS scheme; the results are listed in Table II and are found to agree very well with those of Refs. 6–9, modulo the differences arising from the use of different interatomic potentials. Thus, evidently, the effect of neglecting the contribution from the substrate to the vibrational Helmholtz free energy can be significant: the vibrational free energy is usually overestimated by a factor of about 2 and, as a consequence, the prefactors are underestimated—in the present cases also roughly by a factor of 2.

To summarize, we have studied the self-diffusion by hopping and/or exchange on the (001), (110), and (111) surfaces of Cu, Ag, and Ni within the framework of transition state theory and the embedded-atom method. The energy barriers and prefactors are in good agreement with those from previous calculations, in particular MD calculations, thereby establishing the validity of the method. Our calculations indicate that the prefactors depend weakly on temperature at sufficiently high temperature (~300 K or above). The results also suggest that, within the framework of transition state theory, the Vineyard method gives very acceptable diffusion prefactors. Finally, we find that the prefactors obtained using the LDOS approximation, which neglects the effect of the substrate, are somewhat inaccurate.

The approach described in this Brief Report, based on a detailed evaluation of the phonon spectra at both equilibrium and transition states, therefore proves useful for a direct, straightforward evaluation of diffusion coefficients. One objective of this work is to pave the way to an accurate and systematic scheme for calculating diffusion coefficients. Ultimately, one would hope to be able to work within the framework of *ab initio* approaches. We have attempted to do so but it turns out that the computational resources required to yield prefactors with the desirable accuracy is still somewhat beyond current capabilities. Nevertheless, the methodology is promising and should be further explored.

*Corresponding author: Laurent.Lewis@UMontreal.CA

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