Surface diffusion coefficients by thermodynamic integration: Cu on Cu(100)

Ghyslain Boisvert,1 Normand Mousseau,2 and Laurent J. Lewis3

1) Département de Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Université de Montréal, Case Postale 6128, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3J7
2) Department of Physics and Astronomy, Condensed Matter and Surface Science Program, Ohio University, Athens, Ohio, 45701, USA
(March 24, 2022)

The rate of diffusion of a Cu adatom on the Cu(100) surface is calculated using thermodynamic integration within the transition state theory. The results are found to be in excellent agreement with the essentially exact values from molecular-dynamics simulations. The activation energy and related entropy are shown to be effectively independent of temperature, thus establishing the validity of the Arrhenius law over a wide range of temperatures. Our study demonstrates the equivalence of diffusion rates calculated using thermodynamic integration within the transition state theory and direct molecular-dynamics simulations.

PACS numbers: 68.35.Fx,66.30.Dn,82.65.Dp,68.65.+g

Precise knowledge of diffusion processes is essential to understanding non-equilibrium 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 timescales, the morphology of films. Yet, very little is known of the fundamentals of diffusion. Diffusion constants, for one, are notably difficult to measure and accurate data is available only for the simplest mechanisms on a small number of simple surfaces.2 Because diffusion is an activated (Arrhenius) process (at low enough temperatures3), small errors in the energy barriers translate into large uncertainties in the diffusion coefficients, and thus surface structure. In addition, in order to determine the pre-exponential factor, several measurements are needed in a range of temperatures over which the Arrhenius behaviour is expected to hold, which is not always feasible: in practice, the value of the prefactor is often prescribed. This is a dangerous state of affairs since diffusion obeys the Meyer-Neldel compensation law — for a family of related processes, the prefactor increases exponentially with the activation barrier.4

On the theory side, the situation is just as difficult. It is necessary, in order to describe diffusion accurately, to have a proper model for the interatomic potentials. Semi-empirical models, such as the embedded-atom method (EAM)5, while simple and sometimes remarkably accurate, lack the transferability and predictive power of first-principles methods. The latter, however, are subject to size and other limitations, and uncertainties are difficult to estimate. For instance, even for such a simple case as diffusion by jumps of Cu adatoms on the Cu(100) surface, experiment and ab initio calculations disagree6; the origin of the discrepancy remains unclear.

Because of various limitations, the technique used for computing diffusion rates also is important. The simplest option consists in simulating diffusion explicitly using molecular dynamics (MD). One advantage of this method is that a priori knowledge of the diffusion mechanism is not required. Such calculations are however too demanding for ab initio methods. Also, the simulations have to be carried out at relatively high temperatures where diffusion is “active” on MD timescales; at high temperature, however, diffusion often proceeds by the combination of several mechanisms, making it difficult to extract individual contributions. Finally, because of possible anharmonic contributions, the calculated Arrhenius law may not extrapolate to low temperatures.

Another option consists in computing directly the activation barrier and the prefactor using the transition-state theory (TST) and various approximations7,8,9. Here, however, the reaction path must be known; while this might be a limitation for bulk diffusion, it is usually not a serious problem for surfaces where diffusion is relatively well characterized. In the context of TST, and given a model for the interatomic potentials, free-energy calculations, in particular thermodynamic integration (TI), offer the most accurate route to the study of diffusion processes. In this approach, the diffusion path is followed step by step, and the free energy calculated using finite-temperature MD. The procedure works best at low temperature; at high temperature, indeed, diffusion events are more frequent and the atoms must be constrained to their equilibrium positions (see below). In this case, it might be more advantageous to use the explicit MD approach.

Because the two methods are so different, and cover different temperature ranges, and because diffusion is an
important, difficult, and yet unresolved problem in most cases, it is of utmost interest to ascertain that they lead to equivalent results. This question has been addressed previously using Monte Carlo simulations with restricted dynamics on Lennard-Jones metals [11,12], but the results were not conclusive: the energy barriers were found to differ by as much as 35% and the prefactors by a factor of $\sim 1.8$. Here we reexamine the problem in the case of Cu diffusion on Cu(100), for which detailed MD simulations with EAM potentials have recently been reported [7]; EAM provides a rather accurate description of the energetics of Cu. The TI is performed in full using MD, solving directly the TST equations. We find the explicit MD and the TST/TI calculations to be in very close agreement for both the prefactor and the energy barrier. The free-energy barrier, in addition, is found to be very important, difficult, and yet unresolved problem in most cases, it is of utmost interest to ascertain that they lead to equivalent results. This question has been addressed previously using Monte Carlo simulations with restricted dynamics on Lennard-Jones metals [11,12], but the results were not conclusive: the energy barriers were found to differ by as much as 35% and the prefactors by a factor of $\sim 1.8$. Here we reexamine the problem in the case of Cu diffusion on Cu(100), for which detailed MD simulations with EAM potentials have recently been reported [7]; EAM provides a rather accurate description of the energetics of Cu. The TI is performed in full using MD, solving directly the TST equations. We find the explicit MD and the TST/TI calculations to be in very close agreement for both the prefactor and the energy barrier.

In the TST, the rate of reaction from one equilibrium site to another, via a saddle point, is given by [13]

$$k = \kappa \cdot k_{\text{TST}}, \quad k_{\text{TST}} = \nu e^{-\Delta W/k_B T},$$  \hspace{1cm} (1)

where $\kappa$ is the transmission coefficient (or “recrossing rate”) and $k_{\text{TST}}$ is the TST rate constant. $\Delta W$ is the activation free energy; the prefactor $\nu$, the frequency at which the reaction is attempted, is given by

$$\nu = \left[\frac{k_B T}{2\pi m}\right]^{1/2} \left[\int_{\text{well}} e^{-[W(x) - W(x_m)]/k_B T} \, dx\right]^{-1}.$$  \hspace{1cm} (2)

The integral in Eq. (2) runs between two transition sites a distance $L$ apart, say from $x_b - L$ to $x_b$, via the equilibrium site at $x_m$. $W(x)$ is the “potential of mean force”:

$$W(x) = \int_{x_m}^{x} < f(\lambda) >_{\lambda=x'} \, dx',$$  \hspace{1cm} (3)

where $< f(\lambda) >$ is the mean force that must be applied in order to constrain the particle at position $\lambda$ along the reaction path; evidently $< f >$ is zero if $x = x_m$ or $x = x_b$. $W$ can be obtained numerically by calculating the mean force at several points along the diffusion path using constrained MD [14].

### Table I. Comparison between TI and MD results for the jump (J) and exchange (X) diffusion activation barriers $\Delta E$ (in eV) and rate prefactors $\Gamma_0$ (in THz); also given are the entropy $\Delta S$ (in k_B) and the static energy barrier, $\Delta E(0)$. Estimated errors are given in parenthesis.

|          | $\Delta S$ (kJ/mol) | $\Delta E$ (eV) | $\Delta E(0)$ (eV) | $\ln \Gamma_0$ | $\ln \Gamma_0$ (MD) |
|----------|---------------------|-----------------|-------------------|-----------------|---------------------|
| J        | 1.1(0.2)            | 0.51(0.02)      | 0.49(0.01)        | 0.50            | 2.9(0.2)            |
| X        | 4.9(0.6)            | 0.74(0.02)      | 0.70(0.04)        | 0.73            | 6.5(0.6)            |

FIG. 1. (a) Activation free energy vs temperature for jumps (squares, dashed line) and exchanges (circles, full line); the lines are linear fits to the finite-temperature points. (b) Attempt-to-diffuse frequencies vs temperature; the lines are the predictions of the simple model discussed in the text. (c) Transmission coefficients vs temperature.

The TI calculations were carried out using MD and EAM potentials. As in Ref. [7], the surface was modeled by a slab consisting of eight layers, each containing 64 atoms, with the bottom two fixed in their equilibrium lattice positions; periodic boundary conditions were applied in the two lateral directions. We investigate here the four temperatures 100, 300, 500, and 800 K; this will permit a comparison with our earlier MD calculations, which covered the range 650–850 K [7]. Most calculations were done in the NVT ensemble, using a Nosé thermostat to control the temperature [15]; however, we have also done some calculations in the NVE ensemble to assess the effect of the thermostat. At each point along the reaction path, the system was first equilibrated for 48 ps, then statistics accumulated for a further 120 ps. At the highest temperatures, the atoms lying close to that undergoing diffusion were attached to their equilibrium positions with harmonic springs. Several values of the spring constant were examined and the mean force obtained by extrapolating to zero [16].

The transmission coefficient $\kappa$ is given by

$$\kappa = <\Theta[x(x+t) - x_b] - \Theta[x(-t) - x_b] >_{t \geq \tau_{\text{vib}}}$$  \hspace{1cm} (4)

where $\tau_{\text{vib}}$ is a time characteristic of atomic vibrations and $\Theta$ is the Heaviside step function. $\kappa$ was obtained by averaging over 100 different initial configurations, taken at 1.2 ps intervals from a MD run with the adatom constrained at the saddle point. Each of these was run for 1.2 ps both backward and forward in time [7].

We plot in Fig. 1(a) the activation free energies $\Delta W$ as a function of temperature for both mechanisms possible.
on this surface, viz., jump and exchange; the static (0 K) values are also indicated. In both cases, $\Delta W$ is very well represented by a linear function of temperature, i.e., $\Delta W = \Delta E - T \Delta S$, where $\Delta E$ and $\Delta S$ are both, effectively, temperature-independent. The values of $\Delta E$ and $\Delta S$ are listed in Table I along with the corresponding values for $\Delta E$ from the direct MD simulations. For both diffusion processes, the TI and MD barriers are in excellent agreement with the static barriers.

We note from Fig. 1(a) that, in spite of the fact that it has a larger activation barrier, exchange diffusion is more favourable than jump diffusion above 800 K or so. This is a manifestation of the Meyer-Neldel rule [4,5]: the prefactor for exchanges is much larger (20 times — cf. Table I) than that for jumps, thus compensating for the smaller activation term. Compensation is so efficient that the observed temperature dependence is almost negligible, again, on an Arrhenius plot. The differences in the $\nu$-values for the two processes arise, to a large extent, from “geometrical” differences. For the above model we also have $2\pi \nu = \sqrt{6 \Delta W / m a^2}$, where $m$ is the mass of the diffusing entity — $m_{\text{Cu}}$ for jump and $m_{\text{Cu}}/2$ for exchange (motion of a dimer with respect to its center of mass); taking $x_{b,X} = 1.6 \text{ Å}$ for an exchange (roughly $a/2$, with $a = 3.61 \text{ Å}$ the lattice parameter) and $x_{b,X} = 1.3 \text{ Å}$ for a jump $[a/(2\sqrt{2})]$, we find, indeed, $\Delta W_j / x_{b,J}^2 \approx \Delta W_X / x_{b,X}^2$.

The transmission coefficient is the probability that a diffusion event actually takes place once the saddle point is reached. For both mechanisms, $\kappa$ depends relatively little on temperature, as can be seen in Fig. 1(c). For jumps, the transmission coefficient is about 0.9, and thus has little effect on the diffusion prefactor. For exchanges, $\kappa$ is close to 0.6, and the effect is slightly more important.

The diffusion rate is the product of transition rate, transmission coefficient and number of equivalent reaction paths. (The diffusion constant is obtained from the diffusion rate by multiplying by a geometrical factor.) For both jumps and exchanges, there are four equivalent paths and we thus have [cf. Eq. (4)]:

$$\Gamma = 4 K v e^{-\Delta W / k_B T} \equiv \Gamma_0 e^{-\Delta E / k_B T}, \quad \Gamma_0 = 4 K v e^{\Delta S / k_B}$$  \hspace{0.5cm} (5)$$

The TI results for $\Gamma$ are presented in Fig. 2. The data are extremely well fitted by an Arrhenius law at all temperatures, even as large as 800 K. The resulting values of $\Delta E$ are nearly identical to those determined earlier by fitting to the free energies. The slight temperature dependence of the attempt-to-diffuse frequencies and the transmission coefficients has, as anticipated, no visible effect on the Arrhenius barriers. The values of the prefactors $\Gamma_0$, which we return to below, are listed in Table II.

There has been some concerns that the thermostat in NVT simulations might lead to sizable errors in free-energy calculations (see, e.g., Ref. [15]). In order to test this, we have carried out some TI calculations for both jump and exchange at 500 K, using both NVT and NVE algorithms. Differences were found to be insignificant — at most 0.007 eV on free energies and 0.01 THz on diffusion rates — well within numerical uncertainties.

In the inset of Fig. 1(b), finally, we compare closely the TI results with the MD simulations. The former covers the range 0–800 K, while the latter is for 650–850 K. The TI and MD calculations are found to be in complete agreement for both diffusion mechanisms over the whole temperature range relevant to the MD data.
temperature range. This establishes without ambiguity that the two different computational schemes complement one another exactly. In addition, our calculations demonstrate that the range of validity of the Arrhenius law can extend over a much wider range of temperatures than is normally assumed.

Free-energy calculations of the barriers for jump diffusion on Cu and Ag (100) surfaces based on the harmonic approximation to TST have been reported recently [11]. The calculations were carried out using the same model potentials (EAM) as in the present study; yet, for Cu jump on Cu(100), a prefactor 10 times smaller than that found here was obtained. Numerical error cannot be totally excluded as the cause for this discrepancy, but the consistency between our TI and MD results strongly suggests that this is not the case. Rather, it is more likely a problem with methodology: the harmonic and quasi-harmonic approximations neglect the multiphononic contributions which affect deeply the thermodynamic functions, especially prefactors, giving rise, as we have seen earlier, to such effects as the Meyer-Neldel law [1].

It has been claimed by many authors (see for example Refs. [10, 20 and 21]) that the entropy $\Delta S$ and the energy barrier $\Delta E$ depend on temperature. Our results provide no evidence for this. The separation of the different terms in Eq. (1) is somewhat arbitrary and largely a matter of definition. The simplest expression for $\Gamma$, viz. $\Gamma = \Gamma_0 \exp(-\Delta E/k_BT)$, where $\Gamma_0$ (and thus $\Delta S$) as well as $\Delta E$ are effectively independent of temperature, is able to account very precisely for both the TI and the MD data over the full range of temperatures considered. Indeed, the entropy term, after dividing by $k_BT$, merely renormalizes the prefactor [cf. Eq. (1)].

We have reported a detailed comparison of the rates for jump and exchange self-diffusion on Cu(100) as obtained from full thermodynamic integration and direct molecular-dynamics simulations. We find the two methods to be in perfect agreement over a wide range of temperatures. Our results clearly demonstrate that a simple representation of the diffusion rate in terms of a static energy barrier (which defines the activation term) and a temperature-independent entropy (which defines the prefactor), as they appear in the usual transition state theory, accounts fully for the dynamics of isolated adatoms. Furthermore, the present study clearly demonstrates the equivalence of the diffusion constants obtained within TST/TI and from direct MD simulations.

Acknowledgements — We are grateful to Benoît Roux for useful advice in the initial stages of this project. This work is supported by grants from the Natural Sciences and Engineering Research Council (NSERC) of Canada and the “Fonds pour la formation de chercheurs et l’aide à la recherche” (FCAR) of the Province of Québec. One of us (G.B.) is thankful to NSERC and FCAR for financial support.

References

[1] E. Kaxiras, Comp. Mat. Sci. 6, 158 (1996).
[2] G. L. Kellogg, Surf. Sci. Rep. 21, 1 (1994).
[3] T. Ala-Nissila and S.C. Ying, Prog. Surf. Sci. 39, 227 (1992).
[4] G. Boisvert, L.J. Lewis, and A. Yelon, Phys. Rev. Lett. 75, 469 (1995).
[5] E. Kaxiras, Surf. Sci. Rep. 21, 1 (1994).
[6] S.M. Foiles, M.I. Baskes, and M.S. Daw, Phys. Rev. B 33, 7983 (1986).
[7] G. Boisvert and L.J. Lewis, Phys. Rev. B 56, 7643 (1997).
[8] M. Bockstedte and M. Scheffler, Z. Phys. Chemie 200, 195-207 (1997).
[9] D. Maroudas and R. A. Brown, Phys. Rev. B 47, 15562 (1993).
[10] U. Kürpick, A. Kara, and T.S. Rahman, Phys. Rev. Lett. 78, 1086 (1997).
[11] A. F. Voter and J. D. Doll, J. Chem. Phys. 80, 5832 (1984).
[12] P.V. Kumar, J. S. Raut, S.J. Warakomski, and K.A. Fichthorn, J. Chem. Phys. 105, 686 (1996).
[13] S. Glasstone, K. J. Laidler, and H. Eyring, Theory of Rate Processes, McGraw-Hill, New York, 1941.
[14] G. Ciccotti and J. P. Ryckaert, Comp. Phys. Rep. 4, 345 (1986).
[15] S. Nosé, Mol. Phys. 52, 255 (1984).
[16] E. Paci and G. Ciccotti, J. Phys.: Condens. Matter 4, 2173 (1992).
[17] B. Roux and M. Karplus, J. Phys. Chem. 95, 4856 (1991).
[18] U. Kürpick, A. Kara, and T.S. Rahman, Phys. Rev. Lett. 80, 204 (1998).
[19] G. Boisvert, N. Mousseau, and L.J. Lewis, Phys. Rev. Lett. 80, 203 (1998).
[20] L.B. Hansen, P. Stoltze, K.W. Jacobsen, and J.K. Nørskov, Surf. Sci. 289, 68 (1993).
[21] D. E. Sanders et al. Surf. Sci. 264, L169 (1992).