

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

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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.

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Precise knowledge of diffusion processes is essential to understanding 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. Yet, very little is known of the fundamentals of diffusion. Diffusion constants, for one, are notably difficult to measure and accurate data are 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 behavior 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 law⁴—for a family of related processes, the prefactor increases exponentially with the activation barrier.⁵

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. Semiempirical models, such as the embedded-atom method (EAM),⁶ 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 disagree;⁷ 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 of simulating diffusion explicitly using molecu-

lar 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 time scales; 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 of computing directly the activation barrier and the prefactor using the transition-state theory (TST) and various approximations.^{8–11} 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 the 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 ~ 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 depend linearly on temperature, confirming the validity of the Arrhenius law over a wide range of temperatures. Our results establish unambiguously the equivalence of the two methods, thus providing a useful framework for the calculation of diffusion constants.

In the TST, the rate of reaction from one equilibrium site to another, via a saddle point, is given by¹³

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

where κ is the transmission coefficient (or “recrossing rate”) and k_{TST} is the TST rate constant. ΔW is the activation free energy; the prefactor ν , the frequency at which the reaction is attempted, is given by

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

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”:

$$W(x) = \int_{x_m}^x \langle f(\lambda) \rangle_{\lambda=x'} dx', \quad (3)$$

where $\langle f(\lambda) \rangle$ is the mean force that must be applied in order to constrain the particle at position λ along the reaction path; evidently $\langle f \rangle$ 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

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

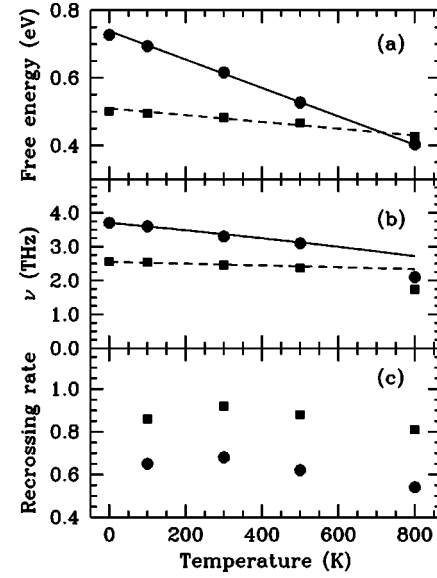


FIG. 1. (a) Activation free energy vs temperature for jumps (squares, dashed line) and exchanges (circles, full line); the lines are linear fits to the finite-temperature points. (b) Attempt-to-diffuse frequencies vs temperature; the lines are the predictions of the simple model discussed in the text.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

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 κ is given by

$$\kappa = \langle \Theta[x(+t) - x_b] - \Theta[x(-t) - x_b] \rangle_{t \gg \tau_{\text{vib}}}, \quad (4)$$

where τ_{vib} is a time characteristic of atomic vibrations and Θ is the Heaviside step function. κ 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.¹⁷

We plot in Fig. 1(a) the activation free energies ΔW 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, ΔW is very well represented by a linear function of temperature, i.e., $\Delta W = \Delta E - T\Delta S$, where ΔE and ΔS are both, *effectively*, temperature independent. The values of ΔE and ΔS are listed in Table I along

TABLE I. Comparison between TI and MD results for the jump (J) and exchange (X) diffusion activation barriers ΔE (in eV) and rate prefactors Γ_0 (in THz); also given are the entropy ΔS (in k_B) and the static energy barrier, $\Delta E(0)$. Estimated errors are given in parenthesis.

| | ΔS | ΔE | ΔE | $\Delta E(0)$ | $\ln \Gamma_0$ | $\ln \Gamma_0$ |
|---|------------|------------|------------|---------------|----------------|----------------|
| | (TI) | (TI) | (MD) | | (TI) | (MD) |
| J | 1.1(0.2) | 0.51(0.02) | 0.49(0.01) | 0.50 | 2.9(0.2) | 3.0(0.2) |
| X | 4.9(0.6) | 0.74(0.02) | 0.70(0.04) | 0.73 | 6.5(0.6) | 6.1(0.7) |

with the corresponding values for ΔE 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 favorable 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 process with a larger barrier becomes dominant at sufficiently high temperature. Thus, even at low temperature, where anharmonic effects are small, multiphononic contributions to the entropy cannot be ignored.

The attempt-to-diffuse frequencies ν for the two processes are displayed in Fig. 1(b). The observed temperature dependence is insignificant relative to the exponential activation term and thus, for all practical purposes, the prefactor for diffusion via a *given* mechanism can be taken as constant. The (slow) variation of ν with temperature can be understood in terms of the following simple anharmonic model: Taking $W(x)$ to be of the form $\alpha x^2/2 - \beta x^3/3$, with $W(x_m) \equiv 0$ and $\Delta W = W(x_b) - W(x_m)$ (so that $\alpha = 6\Delta W/x_b^2$ and $\beta = 6\Delta W/x_b^3$) one easily finds from Eq. (2) (neglecting the anharmonic term in the evaluation of the integral) that, in the low-temperature limit, $\nu(T) = \nu_0 \sqrt{\Delta E - T\Delta S} / \sqrt{\Delta E}$ with $\nu_0 = \nu(0)$. We see from Fig. 1(b) that the TI data is very well fitted by this simple model (indicated by lines) up to 500 K; as expected, this approximation is no longer valid at higher temperature when the system becomes strongly anharmonic. The differences in the ν values for the two processes arise, to a large extent, from “geometrical” differences: for the above model we also have $2\pi\nu = \sqrt{6\Delta W/mx_b^2}$, where m is the mass of the diffusing entity— m_{Cu} for jump and $m_{\text{Cu}}/2$ for exchange (motion of a dimer with respect to its center of mass); taking $x_{b,X} = 1.6$ Å for an exchange (roughly $a/2$, with $a = 3.61$ Å the lattice parameter) and $x_{b,J} = 1.3$ 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, κ 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, κ 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. (1)]

$$\Gamma = 4\kappa\nu e^{-\Delta W/k_B T} \equiv \Gamma_0 e^{-\Delta E/k_B T}, \quad \Gamma_0 = 4\kappa\nu e^{\Delta S/k_B}. \quad (5)$$

The TI results for Γ 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 ΔE 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

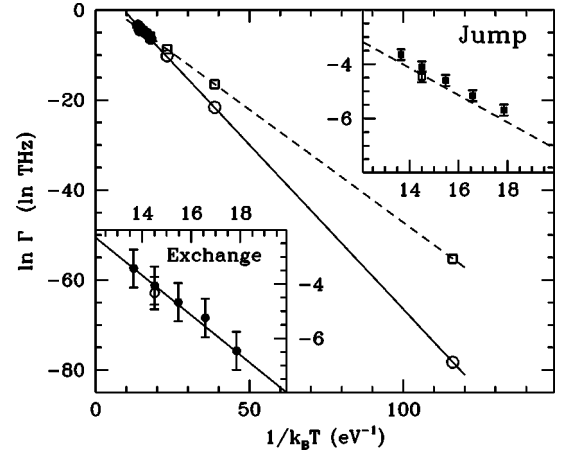


FIG. 2. Diffusion rates vs inverse temperature; the lines are fits to an Arrhenius law; estimated errors are smaller than the size of the symbols in the main graph. The open symbols are for TST/TI and the full symbols for direct MD calculations; the squares are for the jumps and the circles for exchanges. Insets: Comparison between MD and TST/TI results in the temperature range relevant to the MD data for the two mechanisms, as indicated.

barriers. The values of the prefactors Γ_0 , which we return to below, are listed in Table I.

There has been some concern that the thermostat in *NVT* simulations might lead to sizable errors in free-energy calculations (see, e.g., Ref. 18). 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 attempt-to-diffuse frequencies—well within numerical uncertainties.

In the insets of Fig. 2, 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.* 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.¹⁰ The calculations used the same potentials as in the present study; yet, for Cu jumps 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 quasiharmonic approximations, indeed, neglect the *multiphononic contributions* that profoundly affect the thermodynamic functions, especially prefactors, giving rise, as we have seen earlier, to such effects as the Meyer-Neldel law.¹⁹ When the barrier is large, it is necessary to combine many phonons in order for an event to take place. This multiphonon state is a high-energy state, and therefore involves highly-anharmonic regions of the potential surface. While this is of course true at *all* tempera-

tures, the effect is particularly striking at low temperature: because diffusion is a rare event, anharmonicities have essentially no influence on the properties of the system as a whole (which then behaves harmonically), but nevertheless *must* be taken into account for a correct description of the activated process.

It has been claimed by many authors (see for example Refs. 10, 20, and 21) that the entropy ΔS and the energy barrier ΔE 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 Γ , viz. $\Gamma = \Gamma_0 \exp(-\Delta E/k_B T)$, where Γ_0 (and thus ΔS) as well as ΔE 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 $k_B T$, merely renormalizes the prefactor [cf. Eq. (5)].

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.

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