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Self-diffusion on low-index metallic surfaces: Ag and Au (100) and (111)

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Using molecular-dynamics simulations and the embedded-atom method, we study the homodiffusion of single adatoms on flat Ag and Au (100) and (111) surfaces. Our results for the (111) surfaces indicate that when the thermal energies of the atoms become larger than the energy barriers, diffusion can no longer be represented by a simple random walk since correlations between successive jumps become important. We present a simple model that takes into account these correlated jumps and reproduces the molecular dynamics data very well. We also demonstrate that knowledge of the energy barriers is not sufficient to determine the preferred mechanism for diffusion on the (100) surface, since the prefactors for the various mechanisms can vary significantly from the value that is usually assumed. The ability of a simple transition-state theory to describe diffusion is also tested. We find, in the cases considered here, that the static barrier is equivalent to the dynamical activation energy and that the prefactor is also well described as long as the relaxation of the substrate remains small. [S0163-1829(96)09727-5]

I. INTRODUCTION

With the size of devices getting smaller, it is becoming more and more important to understand the physics of surfaces, and in particular their dynamics. One essential aspect of surface dynamics is the diffusion of adsorbates, which leads to mass transport, step flow, nucleation, and ultimately growth, and thus determines the surface morphology.[1,2] By definition, the diffusion coefficient is given by the Einstein relation

$$D=\lim_{t\to\infty}\frac{\langle R(t)^2\rangle}{2dt}, \tag{1.1}$$

where $\langle R(t)^2\rangle$ is the ensemble-averaged mean-square displacement of the diffusing particles — adatoms or clusters — and d is the dimensionality of the space in which diffusion is taking place ($d=2$ for a flat surface). While it is actually possible to measure this mean-square displacement experimentally using, for instance, field-ion microscopy (FIM), even in the case of single adatoms,[3,4] no direct information on the dynamics of diffusion can thus be obtained. Experimental knowledge of surfaces can, however, be augmented to a considerable extent by carrying out detailed molecular-dynamics (MD) simulations. In MD, the trajectories of an ensemble of atoms constituting the model are generated by integrating the classical equations of motion. This makes it possible to study, relevant to our purpose, such processes as surface diffusion.

Diffusion is usually assumed to have an Arrhenius temperature dependence,[5]

$$D=D_0\exp\left(\frac{-E_A}{k_BT}\right), \tag{1.2}$$

where E_A is the energy barrier between two equilibrium sites, i.e., local minima on the potential-energy surface for diffusion, and D_0 is a prefactor containing entropic contributions from the substrate, which depends on details of the structure. Recent progress in the theory of surface diffusion has established rigorously the validity of the Arrhenius law in the limit $E_A \gg k_BT$ (see, for instance, Ref. 6). Equation (1.2) can in fact be derived from Eq. (1.1) if we assume the diffusion trajectory to be a random walk (RW), i.e., a succession of uncorrelated diffusion events, whose frequency obeys the Arrhenius law, $\Gamma=\Gamma_0\exp(-E_A/k_BT)$. As we will see below, it is often preferable to discuss mass transport in terms of frequencies of diffusion events rather than diffusion coefficients.

Experimentally, it is extremely difficult to determine D_0 because of the narrow temperature range where data can be collected. In view of the relatively weak dependence of D on this prefactor (compared to the exponential term), it is common practice to ''assign'' it the value 10 Å^2/ps (obtained by averaging over the available FIM measurements—Refs. 4 and 7) and to determine the activation energy on the basis of a single or very few measurements in temperature. However, as we will see, the above canonical value is often inappropriate and can actually lead to large errors on the predicted diffusion properties of a surface.

It is our aim here to provide some understanding of the dynamics of diffusion on metallic surfaces. To this effect, we investigate in detail, using MD, the problem of the homodiffusion of a single adatom on the (111) and (100) surfaces of Ag and Au. As a model for the interactions between the atoms, we use the semi-empirical embedded-atom method (EAM).[8] We chose Ag and Au because EAM is more accurate for noble metals than for transition metals. Although less precise than first-principles approaches, such a simple potential-energy model is necessary in order to afford the large systems and long simulation times needed to simulate diffusion.

We examine, first, the behavior in temperature of the diffusion coefficient. The closed-packed (111) surface is particularly amenable to such a study because it has low barriers for diffusion (as determined from EAM)[9] and is extremely stable, even at elevated temperatures. The more open (100) surface, on the other hand, is a bit more complicated, in that jump is not the only possible mechanism; diffusion of an adatom can also proceed via the exchange with an atom from the substrate.[10–14] It has been observed on Ir(100) that the prefactor for self-exchange is ‘‘anomalous,’’ being much larger than the ‘‘normal’’ value (626 Å^2/ps versus $\sim$10). This clearly indicates that prefactors can vary rather widely from one surface to another, as well as from one mechanism to another, and that knowledge of the barrier heights is therefore not sufficient to determine which process occurs most frequently on a given surface. This in fact depends on the detailed energetics of the surfaces; we examine and discuss the problem for the (100) surface of Ag and Au.

We find the prefactor D_0 to be much larger for exchange than for jump on Ag, while the opposite is true on Au; likewise, we find D_0 to be much larger for exchange on Ag(100) than on Au(100). In fact, we observe a correlation between the prefactor and the height of the barrier. This is in line with our recent findings that the prefactor and the activation barrier are related to one another by the Meyer-Neldel (or compensation) law;[15] in the case at hand here, this asserts that D_0, which is a measure of the rate at which diffusion events are attempted, increases when E_A increases so as to ‘‘compensate’’ for the increased difficulty in overcoming the energy barrier.

Diffusion is often described in terms of a random walk, which offers the advantage of simplicity. We find this description to be valid at low temperatures. However, when the thermal energy of the atoms is of the order of, or higher than, about half the activation energy, diffusion can no longer be represented by a random walk because of the existence of correlations between successive diffusion events, leading to a non-Arrhenius behavior for the diffusion coefficient. We introduce a correlated-jump model that explains remarkably well the non-Arrhenius deviations.

Finally, in spite of the simplicity of the semiempirical EAM, calculating in detail the temperature dependence of the diffusion coefficient [using MD and the Einstein relation (1.1)] so as to extract the Arrhenius parameters remains a tedious exercise. It is therefore desirable to establish a possible relationship between the diffusion coefficient and quantities that can be computed on the basis of static properties alone, i.e., from the structural properties of the system at zero temperature. Such a link is provided by the simple classical transition-state theory (TST).[16] It is our aim in what follows to demonstrate the ability of the TST to predict the diffusion coefficient from static crystal properties in the harmonic limit.

Our paper is organized as follows: First, we describe, in Sec. II, the computational procedure used in our MD simulations. We present our results in Sec. III. We start with the (111) surfaces in Sec. III A, and discuss in Sec. III B our correlated-jump model for the temperature dependence of the diffusion coefficient. Diffusion on the (100) surfaces is discussed in Sec. III C, where we also examine compensation (Meyer-Neldel) effects. The applicability of TST, finally, is discussed in Sec. III D. A summary and concluding remarks are given in Sec. IV.

II. COMPUTATIONAL DETAILS

As mentioned already, the atoms were chosen to interact via the EAM potential proposed by Foiles, Baskes, and Daw[8] with the optimized parametrization of Adams, Foiles, and Wolfer.[17] Although this model has been fitted to bulk properties, it has been applied successfully to the study of various surface phenomena.[18,19]

In our MD calculations, the surfaces were approximated by slabs containing a fixed number of layers — eight in the present case (excluding the adatom) — of which the bottom two were held fixed in order to mimic the bulk. The lattice parameter of these rigid layers was determined from a series of runs on the bulk materials, as detailed below. Each of the layers contained 64 atoms, and periodic boundary conditions were applied in the lateral directions, i.e., perpendicular to the surface, so that the system is effectively infinite in the x-y plane. It has been verified that a system of this size is sufficient to yield converged values for the diffusion coefficient.[20,21] In order to keep the problem as simple as possible, all surfaces were assumed to be flat in their initial state (i.e., steps are not considered) and not reconstructed, although it is well known that Au surfaces reconstruct.[22,23] [We have addressed the problem of diffusion on the reconstructed Au(111) surface elsewhere — see Ref. 24.]

All simulations were carried out in the (N,V,T) ensemble, except for a series of bulk calculations in the (N,P,T) ensemble (using a 256-atom system) in order to determine the lattice constant at each simulated temperature, used for properly setting the bulklike layers of the substrate. In order to determine the surface diffusion coefficient [using Eq. (1.1)], the evolution of an adatom was followed at several temperatures (see Sec. III) for a time long enough to yield reliable and reproducible statistics. In practice, the runs consisted of a period of equilibration of 80 ps, followed by a period of ‘‘production’’ of 2–10 ns (depending on the number of events observed, i.e., temperature), during which statistics were accumulated. A time step of 4 fs was used to perform the numerical integration of the equations of motion.

In some cases, as discussed in the Introduction, there exists more than one mechanism via which diffusion of an adatom to a neighboring site can take place. The ‘‘macroscopic’’ diffusion coefficient is a weighted sum of exponentials, and fitting to a single Arrhenius law is therefore meaningless. It is, however, possible to separate the various contributions to the total diffusion constant by considering, rather than the diffusion coefficient, the frequency of occurrence of the various types of events, that is the number of events of a particular type observed during a given time divided by the observation time. For example, in the case where diffusion can be assimilated to a random walk, the diffusion coefficient is related to the frequency of events, Γ, as $D=l^2\Gamma/2d$, where l is the distance traveled during one diffusion event. Moreover, if we assume an Arrhenius temperature dependence for the frequency [Eq. (1.2)], then we have $\Gamma=\Gamma_0\exp(-E_A/k_BT)$ and the prefactor is $D_0\equiv D_{0\Gamma}=l^2\Gamma_0/2d$.

In the discussion that follows, we consider both descriptions (i.e., in terms of diffusion coefficients D and in terms of frequency of events Γ) in the case of the (111) surfaces, since here diffusion can only proceed by jumps; for the (100)

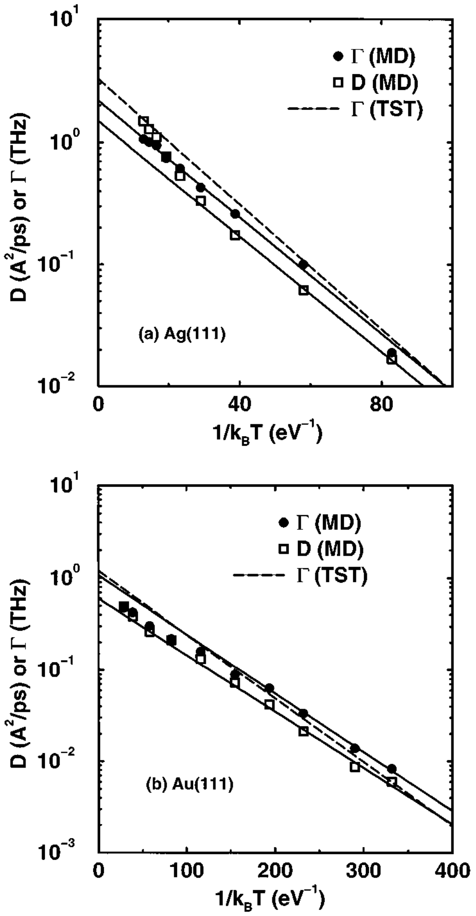

FIG. 1. Arrhenius plots of the diffusion coefficient and hop frequency for (a) Ag/Ag(111) and (b) Au/Au(111). The solid lines are Arrhenius fits to the low-temperature data. The dashed line is the prediction of TST for Γ.

surfaces, we examine only the frequencies Γ for both mechanisms.

III. RESULTS

It is of interest to study diffusion on the (111) surface of fcc metals because, as we have just discussed, it proceeds in a particularly simple manner, and also because barriers are low on this surface. This allows excellent quality diffusion data to be accumulated for a detailed test of the RW model. In addition, this surface is extremely stable in temperature, and it is therefore possible to study the phenomenon over a relatively wide range of temperatures. We present, first, in Sec. III A, our MD results for this surface, and introduce, next, in Sec. III B, a model that goes beyond the RW model and explains well the MD data, and in particular the deviations from the Arrhenius behavior.

A. (111) surfaces

We present in Fig. 1 Arrhenius plots of the diffusion coefficient and "hop frequency" for our two (111) surfaces over the temperature range 140–900 K for Ag, and 35–400 K for Au. Here, by "hop," we mean the jump of an adatom over a *single* diffusion barrier, i.e., from one site to an adjacent one. At low temperature (depending on friction and on the value of E_A), the jumps are almost exclusively to nearest neighbors, and thermalization into the sites takes place. At moderate temperature, there can be jumps to more distant equilibrium sites through successive hops; thermalization is still possible, as discussed below. At high temperature, finally, the motion becomes Brownian, and the adatom no longer has time to "sit" into a site, as we will see. A more precise, quantitative, definition of jumps (as opposed to hops) is given in Sec. III B.

The above temperature ranges were defined as follows: the lower limit was determined on the basis of the statistical quality of the data, i.e., quantity and reproducibility, over an acceptable simulation time ($\sim$4 ns, in most cases). The upper limit, on the other hand, was determined by the stability of the surface with respect to, for instance, disordering via the formation of adatom-vacancy pairs or adsorption of the adatom into the top layer of the substrate. For Ag(111), we observe signs of premelting at temperatures above 900 K (see Ref. 25; Ag melts at 1170 K in the EAM model used here). For Au(111), on the other hand, it was found that the adatom incorporates into the surface at temperatures above 400 K, a phenomenon related to the reconstruction of the surface, and which our model neglects. [The Au(111) surface undergoes a $21\times\sqrt{3}$ reconstruction;[22] the problem of diffusion on this surface was examined elsewhere — Ref. 24.]

In fact, the finite size of our simulation cell is such that reconstruction of the Au(111) surface is prohibited, therefore enabling us to study adatom diffusion on the bulklike configuration at higher temperatures than would otherwise be possible. Since reconstruction results in an increased atomic density at the surface, i.e., our finite-size supercell is less densely packed (more corrugated) than the ground-state (reconstructed) structure, we expect the energy barriers to be larger on our "artificial" surface at high temperatures than on the real bulklike surface at very low temperature. This means that we should observe, in the high-temperature regime, smaller values for the diffusion coefficient and the hop frequency than predicted by an Arrhenius law determined using the low-temperature data. (This is clearly the case for the hop frequency; for the diffusion coefficient, as discussed below, the expected decrease is compensated by an increase arising from correlations between the hops.)

According to the RW model, as discussed earlier, the jump frequency[26] and the diffusion coefficient should have the same temperature dependence; i.e., they should both obey an Arrhenius law (assuming the frequency to be Arrhenius — see below), with the same activation energy but different prefactors. We have fitted independently the MD data for Γ and D to the Arrhenius expression (using only the low-temperature points: strictly speaking, the RW model is only valid in the limit $E_A \gg k_B T$, i.e., when diffusion events are so rare that there can be no correlation between them). The resulting fits are shown as full straight lines in Fig. 1, and the parameters of the fits, E_A, Γ_0, and D_0, are listed in Table I. The values we obtain generally agree with other calculations using similar models.[9,27–31] While the hop frequency and the diffusion coefficient indeed follow the same Arrhenius dependence at low temperature — the activation energies from the Γ and D fits are equal within error and the prefactors obey the RW prescription, i.e., $D_{0\Gamma} = l^2\Gamma_0/2d = D_0$ — it is clear from Fig. 1 that D and Γ

TABLE I. Arrhenius parameters obtained from MD and TST for the various cases considered. On (100) surfaces, two mechanisms are possible: jump (J) and exchange (X). For TST, values in parentheses were obtained using the adiabatic approximation (see text).

	MD-Γ			MD-D		TST-Γ	
Surface	Γ_0 (THz)	E_A (eV)	$D_{0\Gamma}=l^2\Gamma_0/2d$ (Å^2/ps)	D_0 (Å^2/ps)	E_A (eV)	Γ_0 (THz)	E_A (eV)
Ag(111)	2.2	0.055	1.5	1.5	0.055	3.3 (2.8)	0.059
Au(111)	1.1	0.015	0.7	0.6	0.014	1.2 (1.9)	0.016
Ag(100)-J	15	0.48	31			11 (6.2)	0.47
Ag(100)-X	390	0.78	1631			13	0.78
Au(100)-J	75	0.49	156			4000	0.50
Au(100)-X	14	0.26	58			20	0.28

behave differently at high temperature, indicating a failure of the RW model. We note that the diffusion barriers are of the same order as the thermal energies. This failure, therefore, could to some extent be expected, since in the limit of temperatures much larger than the energy barriers, diffusion becomes Brownian.[6,32]

It is therefore of interest to study in detail the high-temperature behavior of the surfaces in order to understand how the transition from RW to Brownian motion takes place. Before proceeding with a thorough quantitative analysis, however, it is informative to examine *de visu* the surfaces. We do this in Fig. 2 where we plot the diffusion path for an Ag adatom on the Ag(111) surface at three different temperatures — 200, 700, and 900 K (on different length scales, since diffusion is much faster at high temperatures). From these plots, it is clear that diffusion proceeds differently at low and high temperatures: While at low temperature the adatom clearly has time to ''thermalize'' into a site between two successive hops (which is, in fact, a basic assumption of the RW model), this is no longer the case at high temperature, where the adatom can ''surf'' over a few sites before thermalizing. In fact, for the highest temperature in Fig. 2, 900 K, it becomes quite difficult to identify jumps, the motion looking very much Brownian-like. We note, however, that a computer-animated display of the trajectory of the adatom on the surface, fully including the dynamics of the substrate, reveals rather clearly the somewhat jumplike character of the motion. At slightly lower temperature, 700 K, the adatom is found to thermalize much more often into the sites, making it easier to use the concept of jumps. A more quantitative way to describe this is to examine the ratio η of back to forward hops; a ''back hop'' is defined as a sequence of two successive hops that takes the adatom back to its initial position (i.e., zero net displacement). The ratio η is displayed in Fig. 3 for our two (111) surfaces. For a random walk, η is exactly 1/3, independent of temperature, as in fact observed in our simulations at low temperatures; this is, of course, consistent with our observation, above, that diffusion can be described by the RW model at low temperature. At high temperatures, however, we see a significant decrease of the ratio η, demonstrating the existence of correlations between successive hops. Moreover, it can be seen from Fig. 3 that the onset of these correlations corresponds, roughly, to a temperature equivalent to the activation barrier for diffusion extracted from the low-temperature Arrhenius fits; these are indicated by arrows in Fig. 3.

The main consequence of the existence of such correlations is larger mean-square displacements — and therefore larger diffusion coefficients — than would be expected from the simple RW model; this explains why the diffusion coefficients for Ag and Au are higher than expected at high temperatures. This is clearly the case for the Ag(111) surface, Fig. 1(a). It is also the case for Au(111), Fig. 1(b), though not as evident. The problem arises, in fact, from the combi-

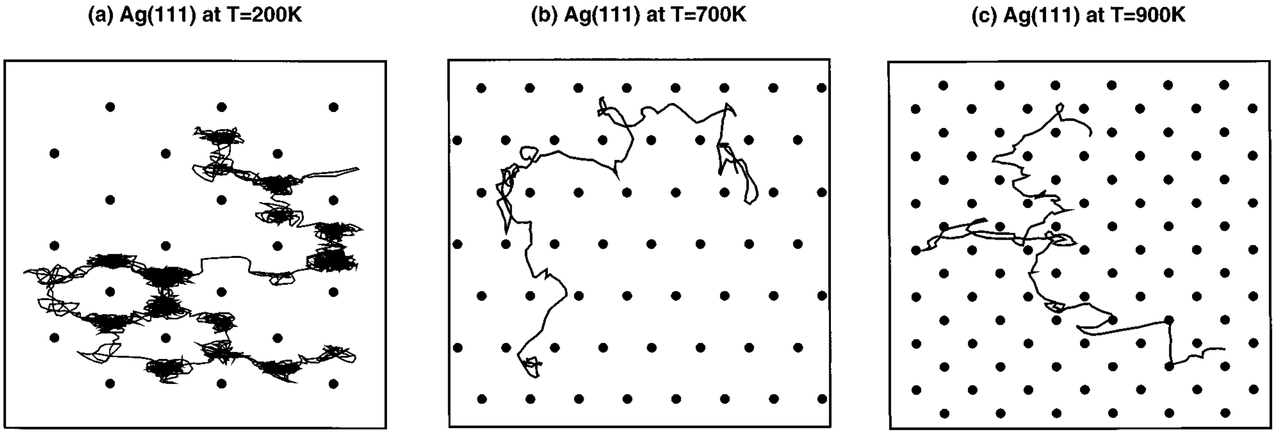

FIG. 2. Typical diffusion path of an Ag adatom on Ag(111) at (a) $T=200$ K, (b) $T=700$ K, and (c) $T=900$ K. The black dots represent the surface atoms in their ideal positions.

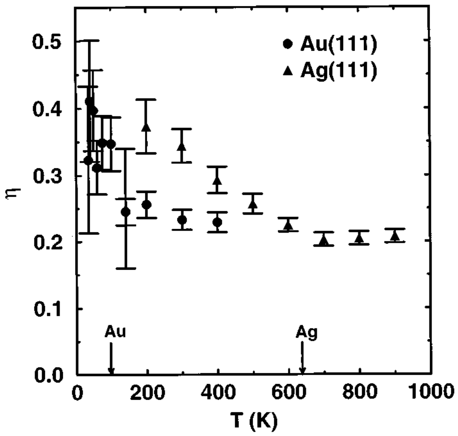

FIG. 3. Proportion η of back hops on the (111) surfaces as a function of temperature. For a random walk, $\eta=0.33$ exactly. The arrows indicate the activation energies for the two systems.

nation of two effects: correlations, which tend to cause diffusion to be larger than Arrhenius, and lower surface density, absent on Ag(111), which, as discussed earlier, causes the hop frequency to decrease.

Figure 1(a), which is not complicated by reconstruction effects, also reveals that, in contrast to the diffusion coefficient, the hop frequency is Arrhenius at all temperatures (and actually provides an excellent route towards determining the Arrhenius parameters). This is due to the fact that the hop frequency, essentially the probability of going over a barrier of energy via thermal agitation, must be proportional to a Boltzmann factor in the classical case (cf. Sec. III D), whereas D carries along structural aspects of the surface, and in particular correlations; of course, the two are essentially equivalent in the absence of correlations, as we have seen.

We have also calculated the ''static'' energy barriers within the framework of TST. They are listed in Table I and will be discussed in more detail in Sec. III D. We find them to be in excellent agreement with the values deduced from the low-temperature Arrhenius fits. This observation, together with the above discussion, suggests an explanation for the contradictory results reported earlier on the relationship between the static energy barrier and the dynamical activation energy on (111) surfaces: Using diffusion-coefficient data from their high-temperature MD simulations (i.e., k_BT of the order of or larger than the static barrier), and fitting to an Arrhenius law, Sanders and DePristo,[28] using various interatomic potential models, found activation energies substantially larger (by a factor of 1.2–7.8) than barriers obtained from static minimization calculations for Ag and Rh. This disagrees with the results reported by Liu and Adams,[33] who observed no significant difference between the two when using hop frequency (rather than diffusion coefficient) data for Ni. As we have seen above, the frequency Γ is Arrhenius at all temperatures, whereas the diffusion coefficient D is not. In fact, if we use our high-temperature diffusion data to determine the Arrhenius parameters, we obtain, for Ag, $E_A=0.10$ eV, instead of 0.055 eV at low temperatures.

Correlated jumps — sometimes called ''long'' jumps because of the larger mean-square displacement they correspond to—have already been observed in MD simulations.[28,34–36] Also, some experimental evidence of the phenomenon has been reported, e.g., for Pb/Ge(111),[37] Na/Cu(001),[38] and Pd/W(211).[39] In all these experiments, the barrier energy is much higher than the temperature. The presence of long jumps has been described using various theoretical approaches:[32,40–42] in these, a coefficient of friction between adatom and substrate is introduced, and the occurrence of long jumps in various regimes of friction, and as a function of the E_A/k_BT ratio, is assessed. Going from low to high temperature, diffusion changes from single-jump to Brownian motion. We find, comparing our MD results with such theories (see, e.g., Fig. 2 in Ref. 32), that our systems are in a regime of moderate friction.

In another spirit, Voter and Doll have proposed a generalization of the TST in which more than one final state is allowed in diffusion events and dynamical corrections are incorporated in a rigorous manner.[43] This formalism, which is also valid at high temperatures, has been shown to reproduce very well the results of MD for the (100) surface of a Lennard-Jones crystal.[44] On the (111) surface at high temperatures, the behavior of the diffusion coefficient is perfectly in line with that observed here; i.e., deviations from the Arrhenius law are seen.[45] The formalism of Voter and Doll is based on input data from the simulation of ''half-trajectories,'' i.e., between transition and equilibrium states, and therefore offers an advantage over full MD simulations at low temperatures, where long enough runs cannot be afforded. However, it does require simulations to be carried out at every temperature where the diffusion coefficient is needed. In what follows, we propose a simple, intuitive, phenomenological model — which is basically an extension of the random-walk model — that allows for the existence of arbitrary long jumps and explains quite well the MD data without introducing additional parameters compared to the simple RW model.

B. Correlated-jump model

The non-Arrhenius behavior of the diffusion coefficient observed in our MD simulations can be understood using the following simple model. First, we exploit the fact that the frequency at which an energy barrier is crossed depends on temperature in an Arrhenius way, i.e., $\Gamma\equiv\Gamma_0\exp(-E_A/k_BT)$, as discussed above. Second, in view of the fact that we are in a regime where friction is important, we can assume, approximately, that an energy equivalent to the height of the barrier is dissipated each time a barrier is crossed. Since the probability of crossing one barrier is proportional to $\exp(-E_A/k_BT)$, then the frequency of a jump taking the adatom to the nth nearest-neighbor site, which we denote Γ_n, must be proportional to $\exp(-nE_A/k_BT)$ (since all sites are equivalent). Since each such nth-nearest-neighbor ''transition'' is attempted at a rate Γ_{0n}, i.e., $\Gamma_n=\Gamma_{0n}\exp(-nE_A/k_BT)$, we have

$$\Gamma=\Gamma_0\exp\left(\frac{-E_A}{k_BT}\right)=\sum_{n=1}^{\infty}n\Gamma_n=\sum_{n=1}^{\infty}n\Gamma_{0n}\exp\left(\frac{-nE_A}{k_BT}\right). \tag{3.1}$$

We can go one step further by noting that the way to escape out of an equilibrium site is the same for all jumps, regardless of the length, and is therefore independent of n, i.e.,

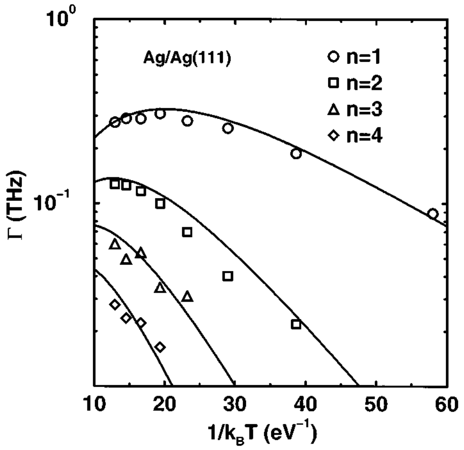

FIG. 4. Comparison between the MD data and the predictions of the correlated-jump model (solid line) for the frequency of jumps of length $n=1$, 2, 3, and 4, for Ag/Ag(111).

$\Gamma_{0n}=\hat{\Gamma}_0$. With this simplification, we can operate the sum in Eq. (3.1) and obtain the following expression for Γ_n:

$$\Gamma_n=\hat{\Gamma}_0\exp\left(\frac{-nE_A}{k_BT}\right)\equiv\Gamma_0\left[1-\exp\left(\frac{-E_A}{k_BT}\right)\right]^2\exp\left(\frac{-nE_A}{k_BT}\right). \tag{3.2}$$

In the limit $E_A \gg k_BT$, the exponential term in the square brackets becomes negligible and $\Gamma_2 \ll \Gamma_1$; i.e., the RW-model expression is recovered, $\Gamma=\Gamma_1=\Gamma_0\exp(-E_A/k_BT)$. For our (111) surfaces, however, as demonstrated above (cf. Fig. 3), the energy barrier is comparable to k_BT and correlated jumps must be taken into account in order to properly describe the diffusion process.

In order to provide a firm basis for the assumptions leading to Eq. (3.2), we compare in Fig. 4 the frequency of jumps of length up to $n=4$ computed from the MD trajectories with the predictions of Eq. (3.2) in the case of Ag/Ag(111). For Γ_0 and E_A, we use the values given in Table I. The criterion we use to define jumps of length n involves the introduction of a characteristic time τ: If two hops occur within the time τ, they are considered to belong to the same jump; a sequence of n such hops leads to a jump of length n, and a jump is considered to terminate when no further hop takes place within a time τ after the previous one. In practice, we have chosen τ in the range $\tau_0-2\tau_0$, where $\tau_0=1/\Gamma_0$ is simply the time between two successive attempts of the adatom to cross the barrier (cf. Table I.) For the data presented in Fig. 4, we have used $\tau=0.7$ ps, about 1.6 times larger than $\tau_0=0.45$ ps. We have verified carefully that our results do not depend in a significant way on the particular choice of τ (within the range above): indeed, for $\tau=0.6$ ps ($\sim 1.3\tau_0$) and $\tau=0.8$ ps ($\sim 1.8\tau_0$), the calculated frequency of jumps remains in excellent agreement with that obtained directly from the MD data, *modulo* the numerical error on the fitted values of Γ_0 and E_A. It is clear, therefore, that within the statistical error inherent to the simulations, especially for longer jumps, the MD results are very well described by the correlated-jump (CJ) model. This comparison thus clearly establishes the validity of Eq. (3.2).

We can also consider the relative probability of occurence of jumps of length n; within the present model, this is given by

$$P(n)=\frac{\Gamma_n}{\Sigma_{n=1}^{\infty}\Gamma_n}=\exp\left(\frac{-(n-1)E_A}{k_BT}\right)\left[1-\exp\left(\frac{-E_A}{k_BT}\right)\right]. \tag{3.3}$$

This quantity is plotted in Fig. 5 at three different temperatures and compared to the MD data. Again, the agreement is remarkable. It is of interest to note that in the moderate damping limit, Pollak and co-workers[41] have shown that a plot of $\log P(n)$ versus n is very well described by a straight line; altough this work was concerned with much lower temperatures (compared to the activation barrier), we do observe a similar behavior here.

We thus have, for the diffusion coefficient in the correlated-jump (CJ) model,

$$D_{CJ}=\sum_{n=1}^{\infty}\frac{l_n^2\Gamma_n}{2d}, \tag{3.4}$$

where l_n is the length of the jump to the nth nearest-neighbor site and Γ_n is given by Eq. (3.2). If we assume that correlated jumps take place along the same directions as single hops, which is quite reasonable in view of the above discussion, then the length of a correlated jump can be taken as the maximum length that can be reached with n single hops, and we have

$$l_n^2=\begin{cases} n^2a^2/8 & \text{if } n \text{ is even} \\ (3n^2+1)a^2/24 & \text{if } n \text{ is odd.}\end{cases} \tag{3.5}$$

This implies that the calculated diffusion coefficient will actually be an upper limit to the actual one. If only small-n jumps take place, which is really what we expect at the temperatures considered here (see Fig. 5), then Eq. (3.5) is an excellent approximation (it becomes exact for $n=1$ and 2).

In the case where large-n jumps are present, i.e., $k_BT \gg E_A$, then the concept of thermalization into a site, and therefore jump, is in any case no longer valid. The present model, therefore, does not apply in such situations. Nevertheless, it extends, relative to the RW model, the range of temperatures for which diffusion parameters can be extracted from the static properties—barrier and attemp-to-diffuse frequency. Even if the model fails in the high-temperature limit, we note that the diffusion coefficient [given in Eq. (3.6)] will have a linear dependence on temperature in this limit, as expected for Brownian motion. Of course, the model also fails in cases where the surface undergoes a transformation, e.g., reconstruction or premelting.

Using the expression (3.5), we can now operate the sum in Eq. (3.4) and obtain, for the diffusion coefficient of an adatom on the (111) surface of an fcc lattice,[46]

$$D_{\rm CJ}=\frac{D_{\rm RW}}{(1+e^{-E_A/k_BT})^2}\left\{1+3e^{-E_A/k_BT}+5e^{-2E_A/k_BT}+\frac{6e^{-3E_A/k_BT}}{1-e^{-E_A/k_BT}}\right\}, \tag{3.6}$$

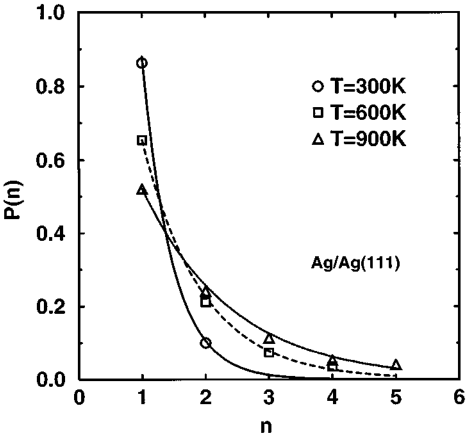

FIG. 5. Comparison between the MD data and the predictions of the correlated-jump model (solid line) for the relative probability of jumps of length $1 \leqslant n \leqslant 5$ at three different temperatures for Ag/Ag(111).

where $D_{\mathrm{RW}} = a^2\Gamma_0 \exp(-E_A/k_BT)/24$. We emphasize that D_{CJ} is expressed *entirely* in terms of two system-dependent parameters, namely, E_A and Γ_0 (or equivalently D_0), which can in principle be extracted from a small number of MD runs. Thus, taking into account correlated jumps does not require additional parameters in comparison to the simple RW model and, as we will see below, leads to a substantially better description of the diffusion coefficients.

The CJ-model diffusion coefficients, $D_{\mathrm{CJ}}(T)$, as determined from Eq. (3.6), are plotted as full lines in Fig. 6 for the two (111) surfaces, together with the data from the MD simulations; we have used for D_{CJ} the values of Γ_0 and E_A obtained from the hop-frequency data (cf. Table I). We find that Eq. (3.6) reproduces extremely well the diffusion MD data for Ag at high temperature, reassuring us of the validity of our model. The agreement for Au, however, is not very good — no better in fact than with the RW model — but the Au(111) surface is a bit peculiar. As we have discussed already, the energy barrier on this surface increases with temperature (due to the combined effects of the finite size of our simulation cell and reconstruction), while Eq. (3.6) assumes E_A to be constant. The values of $D_{\mathrm{CJ}}(T)$ for Au(111) corrected to take into account the variation in temperature of the energy barrier are shown as crosses in Fig. 6(b). The corrected values are now in excellent agreement with the MD data, indicating that the CJ model can describe properly diffusion over a wider range of temperatures than the simple RW model (which is the limit of the CJ model when $E_A \gg k_BT$).

Experimentally, of the two systems studied here, only the value (of the energy barrier) for Ag(111) is, to our knowledge, available. From scanning-tunneling microscopy measurements carried out between 500 and 800 K, a value of 0.15 ± 0.1 eV has been reported.[31] This is in apparent disagreement with our activation energy of 0.055 eV; however, an Arrhenius fit to our MD data in the same temperature range, 500–800 K, gives a barrier of 0.10 eV, in better agreement with experiment. We note, however, that the experimental value suffers a large uncertainty. Further, it has been claimed recently that EAM underestimates the energy barrier when compared to first-principles calculations for Pt/Pt(111) and Ag/Pt(111).[47,48] Considering these results, calculations using more accurate models and/or more accurate low-temperature experiments are needed to resolve the discrepancy.[49]

We have recently carried out a series of *ab initio* calculations for the systems of interest here.[50] The calculated barriers are 0.14 eV for Ag and 0.22 eV for Au, much higher in fact than the ones predicted by EAM. In the EAM model, therefore, because the barriers are underestimated, the contributions of correlated jumps are overestimated. Nevertheless, i.e., in spite of the disagreement between EAM and first principles, the present model is useful, and should be applicable to some systems. In fact, in the case of Al/Al(111), *ab initio* calculations give a diffusion barrier of only 0.04 eV,[51] i.e., about 500 K. We expect correlated-jump contributions to be important on this surface at temperatures above 500 K. It would be of considerable interest that experimental confirmation of this prediction be carried out.

C. (100) surfaces

(100) surfaces differ significantly from (111) surfaces in that their potential-energy surface is much more corrugated (i.e., energy barriers are much larger) so that correlated jumps are not a concern. In addition, since they are more open, mechanisms for diffusion other than jump, namely, exchange, are possible, as mentioned earlier. In our MD simulations, we have also observed more complicated processes — exchanges in which more than two atoms are involved — but their small frequency of occurrence here does not permit a detailed Arrhenius analysis. Such events have already been discussed elsewhere.[52–54] In any event, since more than one process for diffusion are possible, the ''measured'' diffusion coefficient is a sum of exponential contributions, and it is not possible to interpret the results in terms of a single Arrhenius law. We examine, therefore, the various contributions to diffusion via a detailed analysis of their frequencies of occurrence.

The temperature range accessible with MD on the (100) surfaces is much more narrow than on the (111) surfaces, due to the higher corrugation and lower stability of the former upon the creation of adatom-vacancy pairs. We have thus studied Au between 400 and 600 K and Ag between 650 and 750 K, which is sufficient, in view of the high diffusion barriers, to obtain a detailed understanding of their dynamics. Arrhenius plots of the frequency of occurrence of the two main processes (jump and exchange) as a function of temperature are presented in Fig. 7. The MD data are shown as points, and the Arrhenius fits as full lines; the corresponding parameters E_A and Γ_0 are listed in Table I.

We find that diffusion is ''easier'' on Au than on Ag. On the former, the predominant mechanism is the exchange while on the latter, diffusion proceeds more readily by jumps. This has also been observed by other authors using different models.[9,30,55,56] While the two systems have very similar barriers for diffusion by jumps (0.48 eV for Ag versus 0.49 eV for Au), the ones for exchange are very different (0.78 versus 0.26). In view of the exponential dependence of the frequencies on the activation energy, it could be concluded from this that diffusion by exchanges on Ag(100) should be almost unobservable in comparison to Au(100). However, as can be seen in Table I, the prefactors Γ_0, i.e.,

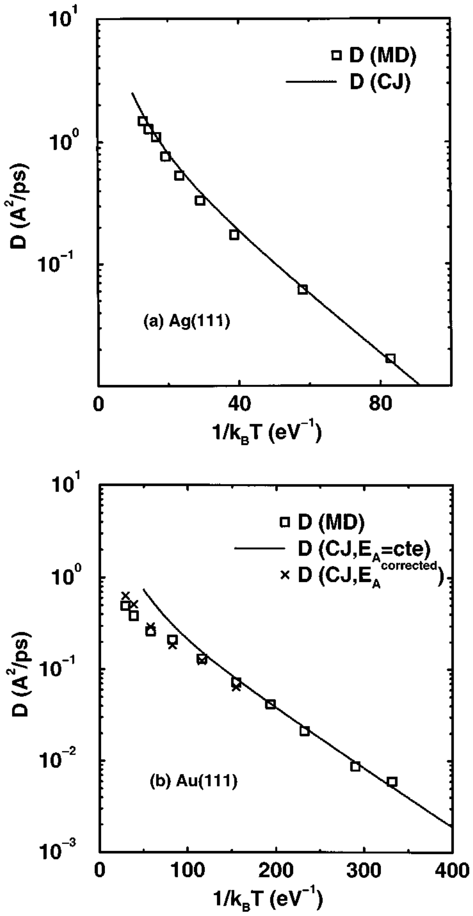

FIG. 6. Comparison between the MD data and the predictions of the correlated-jump model for the diffusion coefficient for (a) Ag/Ag(111) and (b) Au/Au(111). In (b), the corrected CJ model (see text) is indicated by crosses.

the frequencies at which the processes are attempted, are *much* higher on Ag than on Au (390 versus 14 THz), compensating largely for the larger activation barrier. When translated into diffusion prefactors, we obtain $D_0 = 1631$ and 58 Å^2/ps for Ag and Au, respectively. While D_0 for Au is in line with the usual value of 10 Å^2/ps, the value for Ag is 2 orders of magnitude larger. In fact, we also find for jump diffusion on Au(100) a value of D_0—156 Å^2/ps—which largely exceeds the commonly accepted value.

The above results find a natural explanation in the Meyer-Neldel rule, also referred to as the compensation law. We have recently demonstrated,[15] through a detailed analysis of diffusion data on Pd(100), Ni(100), as well as the present surfaces, that there exists a correlation between the prefactor (attempt-to-diffuse frequency) and the height of the barrier for diffusion: the rate at which diffusion events are attempted, Γ_0 or D_0, increases when E_A increases so as to ''compensate'' for the increased difficulty in overcoming the energy barrier. The Meyer-Neldel rule, in fact, probably also provides an explanation for the experimental observation of a high prefactor for exchange on Ir(100) ($E_A = 0.87$ eV — Ref. 10), much larger than on Pt(100) ($E_A = 0.47$ eV — Ref. 11).

Thus, it is clearly not sufficient to compare activation-energy values to determine the relative importance of the various mechanisms for diffusion, or of the same mechanism on different surfaces: prefactors may differ greatly for the various mechanisms and for different materials, and cannot be assumed to be constant. Taking these into account, in fact, can change significantly the barrier extracted from the measurement of the diffusion coefficient at a single temperature, especially if the barrier is high.

D. Transition-state theory

As noted earlier, in either the RW or the CJ model, the diffusion coefficient can be determined completely from a knowledge of two essential parameters, the attempt-to-diffuse frequency Γ_0 and the activation energy E_A (other parameters are ''structural''). The most direct way of determining these coefficients is to carry out a detailed dynamical calculation of the diffusion coefficient at different temperatures and to fit the expression for D to these data, as we have done above. This procedure is tedious and time consuming, however, and it is desirable to obtain the parameters from a simpler approach. In particular, it would be of considerable interest if they could be determined from purely static properties. The transition-state theory provides such a link; further, it is known to be valid in the moderate-friction regime,[42] and therefore appropriate to our MD results. We investigate now the ability of the classical harmonic approximation to the TST to describe diffusion for our different surfaces and mechanisms.

Within the framework of TST, in the classical harmonic approximation, the energy barrier (or activation energy) is $E_A = E^{\mathrm{TS}} - E^{\mathrm{ES}}$, where E^{TS} is the energy of the system with the adatom at the transition site and E^{ES} is the energy of the system with the adatom at the equilibrium site. The frequency of diffusion events is $\Gamma_0 = n\nu$, where n is the number of equivalent paths to escape out of an equilibrium state and ν is given by[16]

$$\nu = \frac{\prod_{i=1}^{3N} \nu_i}{\prod_{i=1}^{3N-1} \nu_i'} . \tag{3.7}$$

The ν_i's are the frequencies of the normal modes of the system in the equilibrium state; there are $3N$ such modes, with N the total number of atoms. The ν_i''s are the normal modes for the transition state; since the adatom is on a saddle point in this case, there is one imaginary frequency, and thus the product contains only $3N-1$ terms. The normal-mode frequencies in both equilibrium and transition states are the eigenvalues of the corresponding dynamical matrices (see, e.g., Ref. 57). For the usual jump mechanism, we can go one step further and use the adiabatic approximation, which considers only the frequencies of vibration of the adatom; thus, we have $\nu = \nu_1 \nu_2 \nu_3 / \nu_1' \nu_2'$ (though the substrate is, of course, fully relaxed). It should be stressed that this approximation is not appropriate for the exchange process because of the large distortions of the lattice that the adatom generates in the transition state.

The parameters of the TST — E_A and ν — were obtained from static, zero-temperature, relaxation of the slabs described in Sec. II. (This procedure for minimizing the total energies of the systems is often referred to as molecular stat-

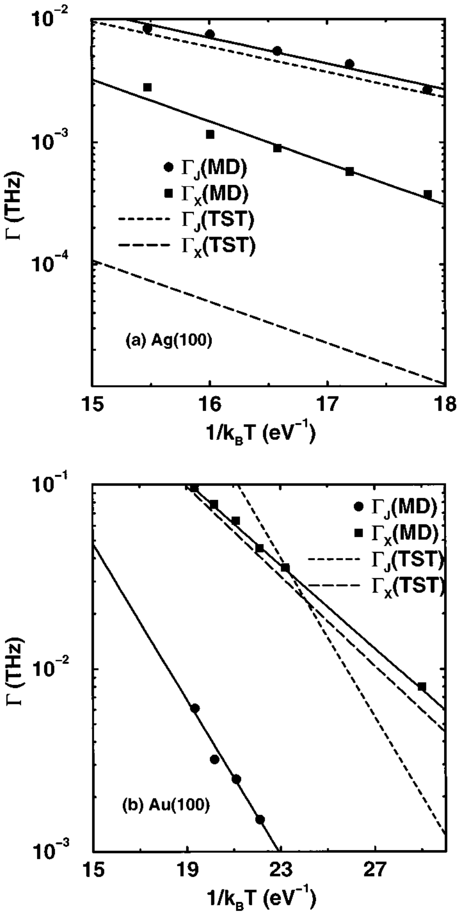

FIG. 7. Arrhenius plot of the exchange and jump frequencies for (a) Ag/Ag(100) and (b) Au/Au(100). The solid lines are Arrhenius fits to the MD data. The dashed and dotted lines are the predictions of TST.

ics.) The results are listed in Table I; in Figs. 1 and 7 we give (as dotted and dashed lines), for comparison with the MD data, the resulting Arrhenius laws. It is immediately clear from the table that the static (TST) barriers are equal, within error, to the activation energies deduced from the dynamical simulations. Thus, the dynamics of the substrate influences only very little the activation energy of the diffusion process. This result is of great importance: Activation energies can be determined accurately from static first-principles calculations; dynamic, or Car-Parrinello,[58] first-principles simulations are beyond the capabilities of present-day computers for problems such as those considered here.

For the attempt-to-diffuse frequencies, Γ_0, the agreement with the dynamical values is at best qualitative; however, considering the approximations used (harmonic and static), interesting observations can be made. In most cases, we find a value for Γ_0 that is within the error bar of the MD data (see Fig. 1 and Fig. 7). Notable exceptions are exchange on Ag(100) and jump on Au(100). For these two cases, we have found relaxation of the substrate in the transition state is very substantial; for instance, in the case of Au(100), the adatom nearly incorporates into the top layer of the slab, leading to significant rearrangements of the neighboring surface atoms. To properly describe such situations, it would be necessary to go beyond the simple harmonic and static approximations used here, while these approximations are appropriate in cases where relaxation is small.[59]

We have also tested the adiabatic approximation for the jump process. As noted earlier, this is not applicable to Au(100) because of the particular transition state described earlier and no such approximation is possible for exchange since a surface atom is directly involved in the process. The values for the other cases are listed in parentheses in Table I. We find that this further approximation accounts reasonably well for the ‘‘exact’’ prefactors, i.e., obtained from a full diagonalization of the dynamical matrices, at a much reduced computing cost.

IV. SUMMARY AND CONCLUDING REMARKS

We have studied the homodiffusion of single adatoms on the flat Ag and Au (100) and (111) surfaces using molecular dynamics and the semiempirical embedded-atom-method potentials, with a view of understanding more clearly the relationship between static and dynamic energy barriers, as well as the deviations at high temperatures from the Arrhenius behavior.

We find that diffusion by jumps can no longer be associated to a random walk when the thermal energy of the atoms becomes comparable to the height of the diffusion barrier. At this point, correlated jumps start to contribute significantly to the diffusion process, resulting in a non-Arrhenius dependence of the diffusion coefficient on temperature. We have presented a simple model taking those correlated jumps into account, and which agrees very well with the MD data, at no additional cost over the random-walk model. On the more corrugated (100) surfaces, where two important mechanisms contribute to diffusion — jump and exchange — our results indicate that knowledge of the energy barriers alone is not sufficient to determine the predominant mechanism, since the prefactors, or attempt-to-diffuse frequencies, can vary substantially. In fact, we have observed a correlation between the prefactor and the barrier height, which can be explained in terms of the Meyer-Neldel compensation law.[15]

We have also performed molecular-statics energy-minimization calculations to assess the ability of a simple harmonic approximation to the transition-state theory to describe diffusion on these surfaces. We find that the diffusion barriers are, in general, very well accounted for by the theory; it also does quite well at predicting the prefactors, except in cases where relaxation of the substrate is substantial. This suggests that energy barriers, and even prefactors, in the moderate-friction regime, can be extracted with confidence from more accurate first-principles approaches.

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