Multiple hops in multidimensional activated surface diffusion

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Abstract

Kramers' theory is used to derive simple expressions for the hopping distribution in multidimensional activated surface diffusion. The expressions are tested against one- and two-dimensional numerically exact simulations. The present expressions are valid provided that the average energy loss of the particle as it goes from one barrier to the next is of the order of $k_B T$ or more. The ratio of double hops to single hops is shown to obey an Arrhenius-like behavior, with a prefactor that is proportional to $\sqrt{T}$. The added activation energy is proportional to the average energy loss of the diffusing particle. The magnitude of the energy loss depends on the coupling between modes: the stronger the coupling, the larger the energy loss and the smaller is the multiple hopping probability. The theory is used to analyze recent experiments on the diffusion of the Pt atom on a Pt(110)-(1×2) missing row reconstructed surface.

Keywords: Atomistic dynamics; Computer simulations; Diffusion and migration; Energy dissipation; Equilibrium thermodynamics and statistical mechanics; Friction; Platinum; Surface diffusion

1. Introduction

Linderoth et al. [1] recently reported experimental results for diffusion of Pt atoms on a Pt(110)-(1×2) missing row reconstructed surface. Their central findings were: (a) double hops, between next nearest neighbor sites, participate in the self-diffusion; (b) the rate of double hops follows an Arrhenius law with an activation energy slightly larger than for single hops. In a theoretical discussion, Jacobsen et al. [2] formulated a 'transition path theory' showing that the extra activation energy needed for double hops is given by the minimum energy trajectory which succeeds in the double jump. They also showed that the double hopping probability has a $\sqrt{T}$ prefactor, where T is the temperature.

Multiple hops in surface diffusion were reported previously by Senft and Ehrlich [3] for the diffusion of Pd atoms on a W(211) surface. They have also been noted in various molecular dynamics computations [4–13] and numerical simulations of the one-dimensional Langevin equation [14]. A one-dimensional theory of multiple hops has been worked out in recent years [15–19]. It is based on adaptation of the Kramers model for activated rate processes to the problem of surface diffusion. In this model, the particle moves on a one-dimensional periodic potential and is subjected to a Gaussian random force and a frictional force which are related by the fluctuation dissipation relation. Explicit expressions for the hopping dis-

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tribution, at any value of the damping, have been derived in Ref. [16]. The time dependence of the hopping distribution has been worked out in Ref. [18] and applied successfully to the experiments of Senft and Ehrlich in Ref. [19].

The first purpose of the present paper is to demonstrate that the added activation energy for double hops is predicted from the one-dimensional activated surface diffusion theory of Ref. [16]. In Section 2 we will show that this added activation energy is directly proportional to the average energy loss Δ of the particle to the dissipative environment as it traverses from one barrier to the next. The $\sqrt{T}$ prefactor is a natural outcome of the theory. An extra Arrhenius activation energy for the multiple jumps is predicted to occur whenever $\Delta/(k_B T) > 1$. This condition sets the scale for the characteristic magnitude of the friction coefficient and temperatures at which one can observe Arrhenius-like behavior for multiple jumps. The ratio ($P_{j,1}$) of hops of length $j \geq 2$ to single hops has the simple form

$$P_{j,1} \sim \frac{2(j-1)^{-3/2}}{\sqrt{\pi \Delta/k_B T}} \exp[-(j-1)\Delta/(4k_B T)],$$

$$j \geq 2,\ \Delta > k_B T. \tag{1}$$

The theory, applied successfully to the experimental results of Linderoth et al. [1] demonstrates that there is also a small contribution of triple hops (and longer) to the measured experimental results.

The activated surface diffusion theory of Ref. [16] is a one-dimensional theory. This is an idealization; in reality the adatom is moving on a three-dimensional potential. The multidimensional theory of activated surface diffusion has not been studied extensively. Numerical simulations on model two-dimensional systems described by Langevin equations [20–22], as well as by numerical simulations of realistic systems [4–13], abound. Systematics and a theoretical understanding of multidimensional effects are still not available.

The multidimensional Kramers problem for activated rate processes has been studied extensively [23–35]. When the added degrees of freedom are weakly coupled to the reaction coordinate, the system behaves effectively as a one-dimensional system. However, in the limit of strong coupling of the modes, they act simultaneously to deplete energy from the reactive system; hence the energy loss becomes much larger. The known results for the double well potential are that the magnitude of the energy loss Δ strongly depends on the coupling between the modes of the system. In the limit of strong coupling of n degrees of freedom the energy loss will go as $(\beta E)^n$ [where $\beta = 1/(k_B T)$]. This would seem to imply that in the strong coupling limit the extra activation energy needed for the multiple hops in surface diffusion is not Arrhenius-like in nature.

In principle, one can always use a realistic molecular dynamics computation to obtain rates, hopping distributions, etc. However, such a computation serves in many ways as a black box and one would like to gain further insight. When an atom diffuses on a surface, it is often the case that at most only the three degrees of freedom of the diffusing particle are strongly coupled while the coupling to the crystal atoms is weak. It is therefore of interest to understand how strong coupling between a few degrees of freedom could affect the resulting dynamics. More specifically, the results of Jacobsen et al. [2] were obtained from a full molecular dynamics simulation and they observed only a linear inverse temperature dependence of the energy loss. Does this indicate that in fact they were dealing with a weakly coupled system? To elucidate these questions we have undertaken a study of the effect of coupling of other degrees of freedom on activated surface diffusion.

Instead of estimating the energy loss via perturbation theory about the unperturbed multidimensional trajectory, we will use the stochastic trajectories to evaluate directly the multidimensional energy loss Δ. When the damping is not too weak we find that this energy loss is independent of the temperature and the ratio of multiple to single hops obeys an Arrhenius law. The magnitude of the energy loss is found to be dependent on the coupling between the modes: the stronger the coupling, the larger the energy loss and multiple hops become less probable. The multidimensional theory is presented in Section 3. Numerical examples are obtained using a new and extremely efficient fourth-order integrator for Langevin equations of motion [36]. We end in

Section 4 with a discussion of additional open problems in the multidimensional theory of activated surface diffusion.

2. Multiple hops in one-dimensional activated surface diffusion

2.1. Theory

The starting point for the one-dimensional theory is the generalized Langevin equation (GLE) describing the time evolution of the particle

$$\ddot{q}+\frac{\mathrm{d}w(q)}{\mathrm{d}q}+\int^{t}\mathrm{d}\tau\,\gamma(t-\tau)\dot{q}(\tau)=\xi(t) \tag{2}$$

where $\gamma(t)$ is the time-dependent friction; below we will use the notation $\hat{\gamma}(s)$ to denote its Laplace transform. The potential $w(q)$ is periodic, characterized by the frequencies ω_0, $\omega^{\ddagger}$ at the wells and barriers respectively, with a barrier height $V^{\ddagger}$ and distance l_0 between adjacent wells. The particle with unit mass is assumed to be initially in one of the wells, labelled 0. The boundary conditions are such that the energy of the particle deep down in the zeroth well is thermal ($P(\epsilon)\sim \mathrm{e}^{-\epsilon}$, where $\epsilon\equiv\beta E$ is the reduced energy which is zero at the barrier top). Initially, there are no particles at the bottom of any of the other wells.

From Kramers' early work, one knows that the rate of escape from the initial well is dependent on the magnitude of the friction coefficient $\gamma\equiv\hat{\gamma}(0)$ (where the hat notation signifies the Laplace transform). When $\gamma/\omega^{\ddagger}\ll 1$ the rate-limiting step is the diffusion of energy from the bath to the system. When $\gamma/\omega^{\ddagger}\geq 1$ the energy diffusion is typically fast and the rate is limited by the spatial diffusion of the particle over the barrier. In the spatial diffusion limit, the rate is given by the well-known Kramers–Grote–Hynes result [37,38]

$$\Gamma_{\mathrm{sd}}=\frac{\omega_0}{\pi}\,\mathrm{e}^{-\beta V^{\ddagger}}\,\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}. \tag{3}$$

The reactive frequency [37,38] $\lambda^{\ddagger}$ is the positive solution of the equation

$$\lambda^{\ddagger 2}+\lambda^{\ddagger}\hat{\gamma}(\lambda^{\ddagger})=\omega^{\ddagger 2} \tag{4}$$

In the energy diffusion-limited regime, Mel'nikov [39] has shown that the conditional probability that the particle changes its (reduced) energy ($\epsilon\equiv\beta E$) from ϵ to ϵ' as it traverses from one barrier to an adjacent one is a Gaussian

$$P(\epsilon'|\epsilon)=\frac{1}{\sqrt{4\pi\delta}}\exp\left[-\frac{(\epsilon'-\epsilon+\delta)^2}{4\delta}\right]. \tag{5}$$

The reduced energy loss parameter δ is the average energy (in units of $k_{\mathrm{B}}T$) that the particle loses to the bath as it traverses from one barrier to the next. In the weak damping limit ($\gamma/\omega^{\ddagger}\ll 1$), it is given to a good approximation as [39–42]

$$\delta=\frac{\beta}{2}\int_{-\infty}^{\infty}\mathrm{d}t\int_{-\infty}^{\infty}\mathrm{d}t'\,\dot{q}(t)\gamma(t-t')\dot{q}(t') \tag{6}$$

where $q(t)$ is the solution of the unperturbed equation of motion [$\ddot{q}+w'(q)=0$] at the barrier energy, such that at time $t=-\infty$ the particle is initiated at the first barrier and it reaches the second barrier at the time $t=\infty$. For ohmic friction, defined as

$$\gamma(t)=2\gamma\delta(t) \tag{7}$$

the energy loss is simply $\delta=\beta\gamma S$, where S is the action of the orbit.

The hopping probability p_j is defined as the probability that a particle is initiated at the zeroth well, escapes, and is then retrapped for the first time in the jth well, which is a distance jl_0 from the original well. As shown in Refs. [16,40], the (classical) hopping probability depends only on the single reduced parameter δ and is given by the expression

$$\begin{aligned}p_j&\equiv-\frac{\Gamma_j}{\Gamma_0}\\&=-\frac{1}{\pi}\int_0^{2\pi}\mathrm{d}k\,\sin^2\left(\frac{k}{2}\right)\cos(jk)\exp[f(k)]\\&\simeq\frac{\Gamma_j}{\Gamma_{\mathrm{sd}}}\end{aligned} \tag{8}$$

where

$$\begin{aligned}f(k)\equiv&\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\tau\,\frac{1}{\tau^2+\frac{1}{4}}\\&\times\ln\left[\frac{1-P(\tau)^2}{1+P(\tau)^2-2P(\tau)\cos(k)}\right]\end{aligned} \tag{9}$$

and

$$P(\tau) \equiv \exp[-\delta(\tau^2 + \tfrac{1}{4})]. \tag{10}$$

In Eq. (8), Γ_j, $j \neq 0$ is the rate of particles entering the jth well, whereas Γ_0 is the (negative) rate of particles exiting from the zeroth well. For large δ the difference between $-\Gamma_0$ and Γ_{sd} is negligible.

In the limit of large energy loss $\delta \gg 1$ the small parameter of the problem is $b = e^{-\delta/4}$. In this limit, the expression for $f(k)$ [see Eq. (9)] can be simplified. Keeping only the leading order term in b for each power of $\cos(k)$ one may rewrite Eq. (9) as

$$f(k) = f_0 + \sum_{n=1}^{\infty} f_n \cos^n k \tag{11}$$

$$f_n \simeq \frac{2}{\sqrt{\pi\delta}} \frac{2^n}{n^{3/2}} e^{-\delta n/4}$$

where the coefficients f_n are accurate to $o(\delta^{-1} b^n)$. With accuracy $o(b)$ one can rewrite Eq. (8) as

$$p_{j+1} \simeq \frac{1}{4\pi} \int_0^{2\pi} dk \cos(jk)\, e^{f(k)} \tag{12}$$

and the function $g(k) = e^{f(k)}$ can be written as an expansion over powers of $\cos(k)$:

$$g(k) = \sum_{n=0}^{\infty} g_n \cos^n k, \quad g_0 = 1. \tag{13}$$

One can readily derive the recurrence relation between the coefficients g_n and f_n:

$$n g_n = \sum_{m=0}^{n} m f_m g_{n-m}, \quad n = 1, \ldots \tag{14}$$

From Eq. (10) one notes that all terms in Eq. (14) are of the order of b^n and must all be taken into account if one wants exponential accuracy. However, one can show that the main contribution to g_n comes from the last term in Eq. (14):

$$g_n \simeq f_n = \frac{2}{\sqrt{\pi\delta}} \frac{2^n}{n^{3/2}} e^{-\delta n/4}. \tag{15}$$

The first term in the expansion given by Eq. (13) which contributes to p_{j+1} is the jth one [see Eq. (12)]. On the other hand, all terms of order higher than j will contain higher powers of the small parameter b. Taking into account that

$$\int_0^{2\pi} dk \cos(jk) \cos^j k = 2^{1-j}\pi$$

one finds the central result of this section:

$$p_{j+1} = p_{-(j+1)} \simeq \frac{j^{-3/2}}{\sqrt{\pi\delta}} e^{-j\delta/4}, \quad j \geq 1. \tag{16}$$

To order b, the probability for a single hop is $p_1 = p_{-1} = 1/2$. The hopping ratio $P_{j,i}$ for a hop of length j relative to a hop of length i is de*f*ined as

$$P_{j,i} \equiv \frac{p_j}{p_i} \tag{17}$$

and one notes that Eqs. (16) and (17) immediately give Eq. (1).

The formal result found for the multiple jump ratio, given in Eqs. (16) and (17) has a simple physical interpretation. When the damping is weak, but the energy loss is large, the distribution of escaping particles is thermal [39,40]. Therefore, the fraction of particles that start at a barrier and make it to the adjacent barrier is given by (the barrier energy is zero)

$$F_{2,1} \sim \int_0^{\infty} d\epsilon \int_0^{\infty} d\epsilon'\, P(\epsilon|\epsilon') \exp(-\epsilon')$$
$$= \operatorname{erfc}\left(\frac{\sqrt{\delta}}{2}\right) \sim \frac{2}{\sqrt{\pi\delta}} \exp(-\delta/4), \quad \delta \gg 1 \tag{18}$$

and the conditional probability $P(\epsilon|\epsilon')$ has already been defined in Eq. (5). Similarly, the fraction of particles that make it to the barrier which is two lattice lengths distant is

$$F_{3,1} \sim \int_0^{\infty} d\epsilon \int_0^{\infty} d\epsilon' \int_0^{\infty} d\epsilon''\, P(\epsilon|\epsilon') P(\epsilon'|\epsilon'') \exp(-\epsilon'')$$
$$= \tfrac{1}{2}\left[\operatorname{erfc}\left(\sqrt{\frac{\delta}{2}}\right) + \operatorname{erfc}^2\left(\frac{\sqrt{\delta}}{2}\right)\right] \sim \frac{1}{\sqrt{2\pi\delta}} e^{-\delta/2}, \quad \delta \gg 1 \tag{19}$$

and the generalization to longer hops is evident.

One must distinguish between the probability for a long jump p_j and the experimentally measured time-dependent distribution of the particle. Typically, at time $t = 0$ the particle is found to be

at some location on the surface. At some fixed later time t, one measures the probability of finding the particle at the jth lattice site away from the initial point. This time-dependent distribution $p_j(t)$ is governed by a master equation that may be solved, as shown in Ref. [18]. The result is again a function of the reduced energy loss δ and the spatial diffusion rate Γ_{sd} only. The explicit result was found to be [18,19]

$$p_l(t)=\frac{1}{2\pi}\int_0^{\infty} \mathrm{d}k\, \mathrm{e}^{-\hat{\Gamma}(k)t}\, \mathrm{e}^{-\mathrm{i}kl} \tag{20}$$

where the function $\hat{\Gamma}(k)$ is the Fourier transform of the transition rates between different wells and is given by

$$\frac{\hat{\Gamma}(k)}{\Gamma_{sd}}=2\sin^2\left(\frac{k}{2}\right)\exp\left(\frac{1}{\pi}\int_0^{+\infty} \mathrm{d}s\, \frac{\ln\{1-\exp[-2\delta(s^2+\frac{1}{4})]\}/(s^2+\frac{1}{4})}{1+\exp[-2\delta(s^2+\frac{1}{4})]-2\cos(k)\exp[-\delta(s^2+\frac{1}{4})]}\right) \tag{21}$$

In the limit of large δ the leading contribution is from single and double jumps only and one recovers Eq. (1) of Ref. [1], which was used by Linderoth et al. to fit their experimental distribution.

2.2. Experimental application

Linderoth et al. [1] measured the single and double jump rates for Pt on Pt(110). They fit the experimental results for the single jump rate to an Arrhenius form:

$$\Gamma_1/\mathrm{s}^{-1}=10^{10.7}\exp\left[\frac{-0.81\ \mathrm{eV}}{k_B T}\right]. \tag{22}$$

Using Eq. (8) and the reduced energy loss δ as a fitting parameter, we find an excellent fit to their experimental results for $\delta=0.19\ \mathrm{eV}/k_B T$, see Fig. 1. This value of the energy loss implies that δ varies between 5.8 and 7.4 over the temperature range studied in the experiment. In this range, the time-dependent distribution is sufficiently sensitive to the magnitude of the energy loss. Using this value for the energy loss, we obtain also excellent agreement with the experimental time-dependent

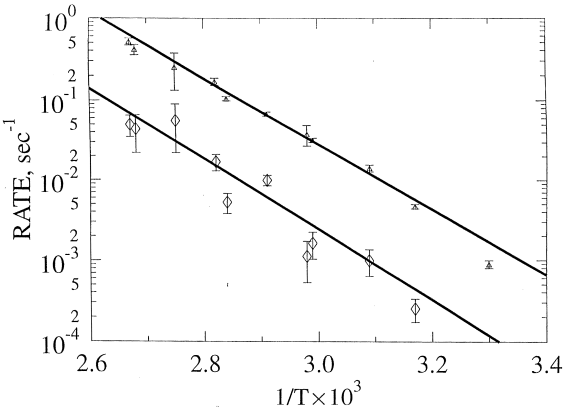


Fig. 1. Arrhenius plot of the single and double hopping rates of Pt on the Pt(110)-(1×2) reconstructed surface. Triangles and diamonds with error bars are the experimental results of Ref. [1]. The solid lines are the fits based on Eq. (16). The fitted parameters are $\Gamma_{sd}=0.64\ \mathrm{s}^{-1}$ (at $T=375$ K), $V^{\ddagger}=0.81$ eV and $\Delta=0.19$ eV.

distribution (at $T=375$ K) as shown in Fig. 2, using the value of $\Gamma_{sd}=0.64\ \mathrm{s}^{-1}$.

At $T=375$ K, the ratio of hopping probabilities we find is: $P_{2,1}=0.080$, $P_{3,1}=0.010$ and longer hops are smaller. Our fit to the experimental data is as good as that of Ref. [1], but our $P_{2,1}$ is somewhat lower than their estimate of $P_{2,1}=0.095$. Linderoth et al. [1] used a fitting procedure in which each hopping ratio is treated

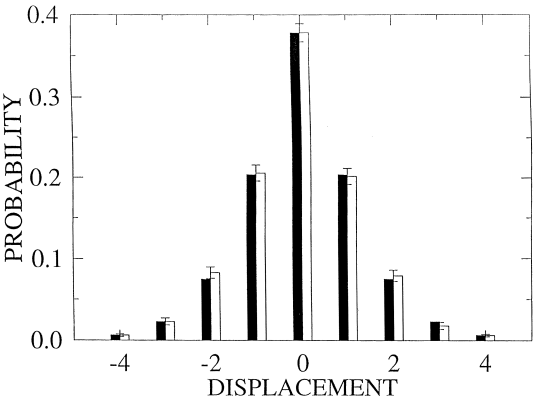


Fig. 2. Distribution of displacements after 2.3 s for the diffusion of Pt on the Pt(110)-(1×2) reconstructed surface at $T=375$ K. White bars are the experimental results of Ref. [1], black bars are the theoretical fit, based on Eqs. (20) and (21). The fit parameters are the same as used in Fig. 1.

as an independent parameter. Eq. (21) shows that the hopping ratios are dependent and the whole distribution should be describable in terms of the two parameters δ and Γ_{sd}. This leads to some differences between the hopping ratios we get and those of Linderoth et al. The same happens at other temperatures, e.g. at $T=294$ K we find $P_{2,1}=0.051$, $P_{3,1}=0.004$ compared with $P_{2,1}=0.056$ obtained in Ref. [1].

The magnitude of the energy loss is large enough to justify use of only the leading term in the expansion of the jump rates with respect to δ. Using Eq. (1) one notes that this implies that the difference in activation energy ($\delta/4$) between single and double jumps is ~ 0.05 eV. This is within the error bounds of the experiment as reported in Ref. [1] (see Fig. 1). The agreement of the fit with the experimental results supports the contention of Linderoth et al. [1] that the diffusion of Pt on Pt(110) is effectively one-dimensional and that coupling to other surface degrees of freedom is rather weak.

The magnitude of the energy loss may also be estimated from physical properties of the adatom and the surface. In Ref. [18] we showed the following.

- Phonon friction is the major energy loss mechanism for metal atom diffusion on metal surfaces.
- Phonon friction is ohmic [see Eq. (7)]. (We note here, that this result is controversial. Sethna and coworkers [43,44] claim that the friction is superohmic, whereas Refs. [18,45–47] claim that it is ohmic. Even if the friction is superohmic, the quantitative effect on the energy loss will be small and so this is not expected to change the conclusions delineated below.)
- Typically, the friction coefficient $\gamma/\omega^{\ddagger} \sim 0.01$–$0.1$ i.e. the damping constant is small.
- The typical energy loss $\delta > 1$ owing to the relatively large activation energies when compared with room temperature or lower.
- One can obtain reasonable estimates for the magnitude of the friction coefficient γ and the energy loss in terms of physical properties of the crystal and measured activation energies.

Specifically, the potential $w(q)$ may be approximated as a periodic cosine potential:

$$w(q) = V^{\ddagger} \cos^2\left(\pi \frac{q}{a}\right) \tag{23}$$

where a is the distance between adjacent wells and $V^{\ddagger}$ is the activation barrier height. The barrier and well frequencies are identical:

$$\omega^2 = \frac{2\pi^2 V^{\ddagger}}{ma^2} \tag{24}$$

where m is the mass of the adatom. The friction coefficient may be estimated using

$$\frac{\gamma}{\omega} = \frac{m\omega^3}{6\pi\rho c_t^3} \tag{25}$$

where ρ is the crystal density and c_t is the sound velocity in the crystal. The barrier height may be inferred from the measured temperature dependence for the single jump rate. The energy loss for the potential given in Eq. (24) is then

$$\Delta = 4\frac{\gamma}{\omega} V^{\ddagger}. \tag{26}$$

The constants for Pt on Pt(110) are given in Table 1. One finds that the frequency of the particle in the well, as obtained from Eq. (24), is a factor of 30 larger than the frequency obtained from the experimental prefactor of $\sim 10^{11}\ s^{-1}$. This is seemingly a huge discrepancy. We believe that this results mainly from the difficulty in predicting accurately the prefactor from temperature-dependent results. To demonstrate this, we show in Fig. 3 what we believe is as reasonable a fit to the

Table 1
Physical parameters for the diffusion of Pt on Pt(110)

Parameter	Magnitude	Dimensions	Reference
a	2.78×10^{-8}	cm	[1]
$V^{\ddagger}$	0.81	eV	[1]
ρ	21.4	g/cm^3	[49]
c_t	1.73×10^5	cm/s	[49]
m	195	a.m.u.	[49]
ω	1.0×10^{13}	s	Eq. (24)
γ/ω	0.154	dimensionless	Eq. (25)
Δ	0.50	eV	Eq. (26)

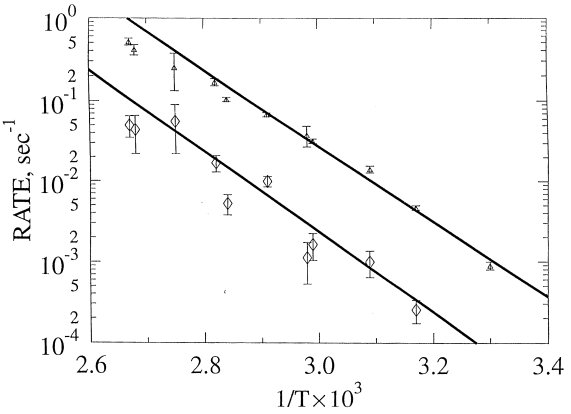


Fig. 3. Arrhenius plot of the single and double hopping rates of Pt on the Pt(110)-(1 × 2) reconstructed surface. The fits (solid lines) are based on two independent parameters only: the activation energy for single jumps and the energy loss Δ. The prefactor is assumed to be ω/π where the frequency ω is estimated via Eq. (24). (In Fig. 1 the prefactor is also treated as an independent parameter.) The fitted parameters are $V = 0.93$ eV and $\Delta = 0.19$ eV.

experimental results as shown in Fig. 1, but which is based on the estimate that,

$$\Gamma_1 = 10^{12.5} \exp\left[\frac{-0.93\ \text{eV}}{k_B T}\right] \text{s}^{-1} \tag{27}$$

which by construction gives a frequency of 1.0×10^{13} s, in agreement with the estimate given in Table 1. The increase in the prefactor is compensated for by a small $\sim 14\%$ increase in the activation energy. Owing to the limited range of temperatures, the experiment is not really able to distinguish between the two representations. The fit to the rate of double jumps is obtained using the same energy loss parameter as in Fig. 1.

The estimate for the friction coefficient, based on Eq. (25), using the frequency ω obtained from Eq. (24) leads via Eq. (26) to an energy loss $\Delta = 0.50$ eV, a value which is 2.5 times larger than the value estimated from the fits to the experimental data. At $T = 375$ K this is equivalent to the dimensionless energy loss $\delta = 15$. Eqs. (24)–(26) provide only a rough estimate of the friction coefficient. A lowering of the well frequency by 35% would suffice to bring the theoretical estimate of the energy loss into agreement with the fitted result (0.19 eV), since the magnitude of the friction coefficient goes as the fourth power of the frequency [see Eq. (25)]. The assumption of a cosine potential as in Eq. (23), which assumes equal frequencies at the barriers and wells of the periodic potential, is a rough guess. All this implies that Eqs. (23)–(26) provide a ballpark estimate for the friction coefficient and the energy loss. The fact that the crude estimate gives an energy loss that is larger than the experimental suggests that indeed phonon friction is the main source for the energy loss mechanism. Any additional frictional mechanism would even further increase the energy loss.

2.3. Numerical application

The validity of the approximate expression for the hopping distributions given in Eqs. (14)–(18) was tested by comparison with numerically exact results for the Langevin equation with the periodic potential given in Eq. (23) and ohmic friction. The parameters used were $a = 2\pi$ and $V^{\ddagger} = 1$. The numerical solution of the Langevin equation was obtained with the fourth-order Runge–Kutta integrator described in Ref. [36]. The added accuracy of the integrator enabled the computation of extremely small hopping ratios and thus provides a stringent test of the approximate expressions.

In Fig. 4 we compare the dependence of the numerically exact ratio of double jumps to single jumps $P_{2,1}$ on the magnitude of the reduced energy loss δ with the theoretical expressions [Eqs. (1) and (18)] for a large range of temperatures and friction coefficients.

3. Multiple hops in multidimensional activated surface diffusion

3.1. Theory

For the sake of simplicity we will restrict ourselves to a system with two degrees of freedom; the generalisation to more degrees of freedom is straightforward. The discussion will also be limited to ohmic frictions; the generalisation to memory friction follows the discussion in Refs. [33–35,42].

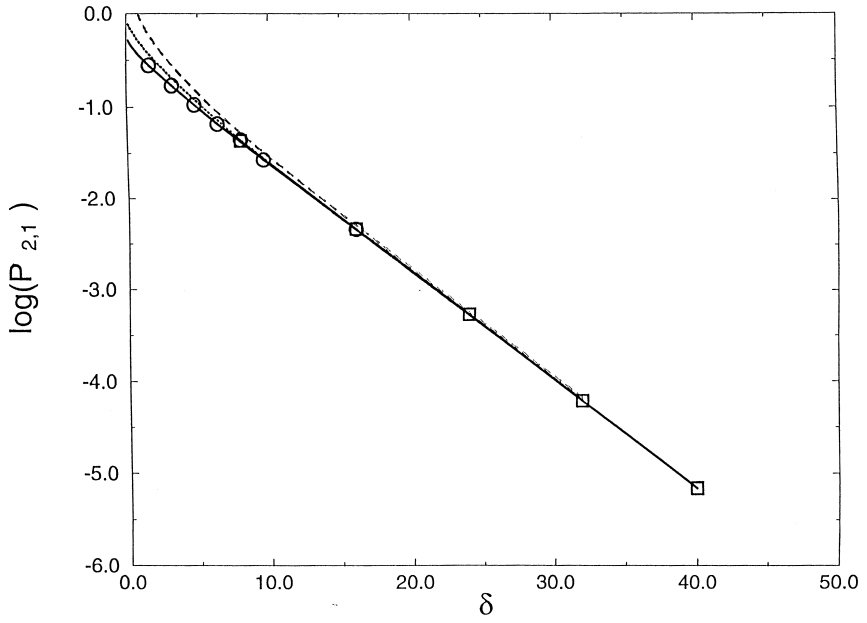


Fig. 4. Dependence of the ratio of double jumps to single jumps $P_{2,1}$ on the magnitude of the reduced energy loss δ for one-dimensional diffusion. The open squares and open circles show the numerically exact results for the Langevin equation with the potential of Eq. (24). The squares are for $\gamma = 10^{-3}$, the circles for $\gamma = 10^{-2}$. The solid line is the exact analytic result, based on Eq. (8). The dotted line is the function $\mathrm{erfc}(\sqrt{\delta}/2)$, valid for $\delta > 1$; the dashed line is the asymptotic expansion of the erfc function, see Eq. (18).

The equations of motion take the form

$$\ddot{q} + \frac{\partial w(q, z)}{\partial q} + \gamma_q \dot{q} = \xi_q(t) \tag{28}$$

$$\ddot{z} + \frac{\partial w(q, z)}{\partial z} + \gamma_z \dot{z} = \xi_z(t). \tag{29}$$

The Gaussian random forces $\xi_i(t)$; $i = q, z$ have zero mean and obey the usual fluctuation dissipation relations $\langle \xi_i(t)\xi_j(t')\rangle = \delta_{ij} 2k_B T \gamma_i \delta(t-t')$. The potential $w(q, z)$ is assumed to be periodic with wells and barriers. In all computations we used the following potential:

$$w(q, z) = \tfrac{4}{9}[\cos(3q) - 1] + \tfrac{1}{2}\left[\omega_z z + \frac{C}{\omega_z}\sin(3q)\right]^2 + \tfrac{1}{4} f z^4 \tag{30}$$

choosing $\omega_z = 1.5$ and $f = 3$. The quartic term was added to localise the motion in the z direction. Contour plots of the potential for different values of the coupling coefficient ($C = 0.1$, $1/3$, $2/3$) are shown in Fig. 5.

The force constant matrix at a barrier (well) is denoted as $\boldsymbol{K}^{\ddagger}$ ($\boldsymbol{K}_0$). The spatial diffusion rate constant, which gives the escape rate out of a well, in the limit that the (reduced) energy loss δ is sufficiently larger than unity is [23]

$$\Gamma_{\mathrm{sd}} = \frac{1}{\pi}\left[\frac{\det(\boldsymbol{K}_0)}{\det(\boldsymbol{K}^{\ddagger})}\right]^{1/2} \lambda^{\ddagger} \exp(-\beta V^{\ddagger}). \tag{31}$$

The reactive frequency $\lambda^{\ddagger}$ is the positive solution of the equation [23]

$$\det(\lambda^{\ddagger 2}\boldsymbol{I} + \lambda^{\ddagger}\underline{\gamma} + \boldsymbol{K}^{\ddagger}) = 0 \tag{32}$$

where $\boldsymbol{I}$ is the 2×2 identity matrix and $\underline{\gamma}$ is a diagonal matrix whose elements are γ_i; $i = q, z$. The multidimensional turnover theory for the rate is a straightforward generalization of the one-dimensional theory [33,34] based on the assumption of a Gaussian energy transfer probability distribu-

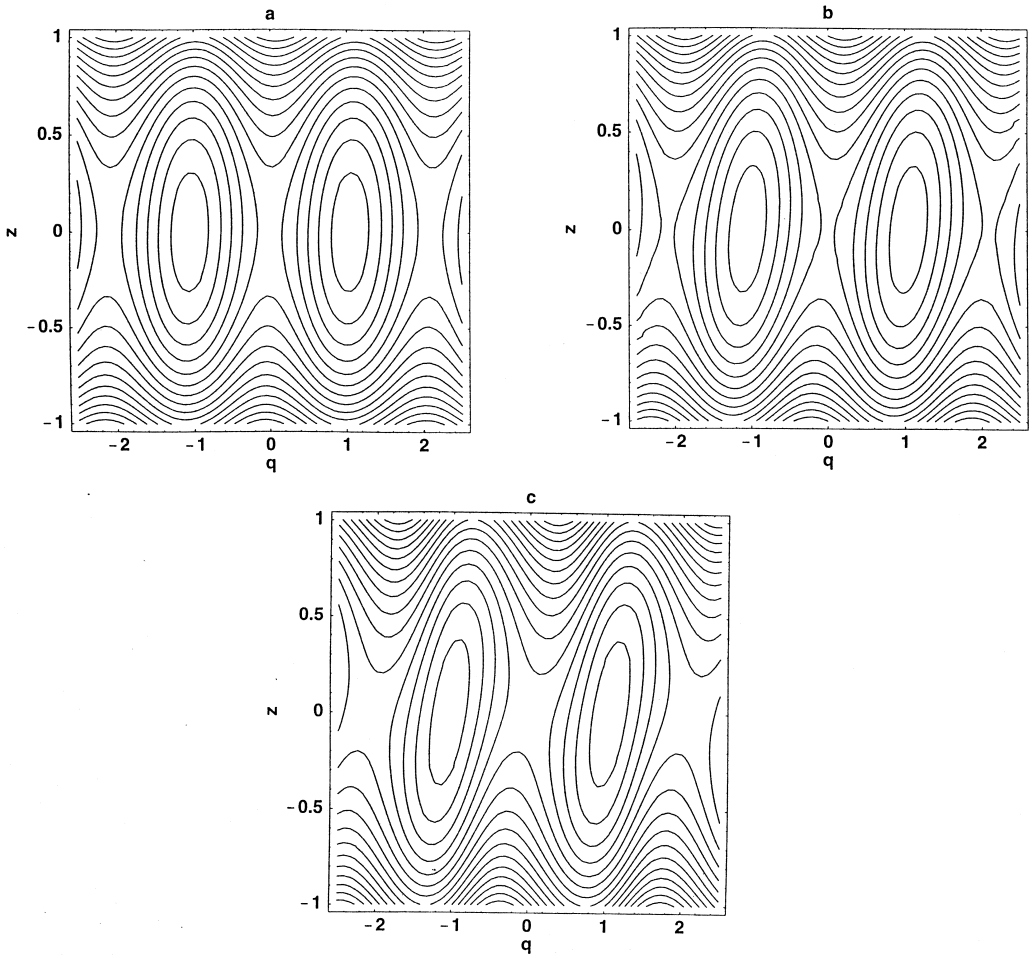


Fig. 5. Contour plots of the two-dimensional periodic potential. (a)–(c) are for $C=0.3$, 1/3 and 2/3 respectively; see also Eq. (32).

tion:

$$P(E'|E;\beta)=\frac{\beta}{4\pi\Delta E(\beta)}\exp\left\{-\frac{\beta[E'-E+\Delta E(\beta)]^2}{4\pi\Delta E(\beta)}\right\} \tag{33}$$

where E is the initial kinetic energy of the unstable mode at the (first) barrier and E' is the final kinetic energy of the unstable mode at the next barrier averaged over all trajectories initiated at the first barrier with a thermal distribution of energy in the perpendicular stable mode. $\Delta E(\beta)$ is the temperature-dependent average energy loss of the particle as it traverses from one barrier to the next. With these definitions, the Gaussian kernel obeys a detailed balance, that is $e^{-\beta E}P(E'|E;\beta)=e^{-\beta E'}P(E|E';\beta)$.

The assumption of a Gaussian probability kernel then implies that the hopping distribution is given as in the one-dimensional case. For a fixed value of the reduced energy loss $\delta(\beta)=\beta\Delta E(\beta)$ one may use Eq. (8) or the simpler result for $\delta>1$ given in Eq. (18) to predict the hopping ratio. The only difference is in the definition of Γ_{sd} which is now given by Eq. (31).

The central object that must be calculated is the average energy lost by a trajectory initiated at the barrier. In previous applications of the multidimensional theory this energy loss was computed using perturbation theory about the trajectories

moving without friction. This perturbation theory which is valid for one-dimensional systems may become suspect in the multidimensional case, where the intramode coupling may cause the trajectory to take a 'long time' as it goes from one barrier to the next, long enough to invalidate the use of the classical perturbation theory. A different approach would be to use a perturbation theory in which the unperturbed trajectory is the zero temperature one. In this case the theory would be valid for low enough temperatures [42,48]. There is though a second problem which occurs in the multidimensional theory. It is necessary to identify in a quantitative manner what one means by 'reaching the barrier' when considering trajectories which are reflected by the adjacent barrier. The added degree of freedom and the nonseparability of the different degrees of freedom make the concept somewhat ambiguous.

To overcome these difficulties we used an approach based on computation of the numerically exact trajectories which are initiated at the first barrier and reach the adjacent barrier for the first time. If the energy transfer probability is truly Gaussian then one finds that the energy transfer distribution for trajectories initiated at a barrier with a thermal distribution reaching the adjacent one is

$$\begin{aligned} P(E=E'-E'';\beta) &= \frac{\int_0^\infty \mathrm{d}E' \int_0^\infty \mathrm{d}E''\, P(E'|E'')\, \mathrm{e}^{-\beta E''}\, \delta(E-E'+E'')}{\int_0^\infty \mathrm{d}E' \int_0^\infty \mathrm{d}E''\, P(E'|E'')\, \mathrm{e}^{-\beta E''}} \\ &= \frac{\mathrm{e}^{-\Delta E(\beta)/4-\beta E^2/[4\Delta E(\beta)]}}{\sqrt{4\pi\Delta E(\beta)/\beta}\,\mathrm{erfc}[\sqrt{\beta\Delta E(\beta)}/2]} \\ &\quad \times [\mathrm{e}^{-\beta E/2}\,\theta(E)+\mathrm{e}^{\beta E/2}\,\theta(-E)]. \end{aligned} \tag{34}$$

Detailed balance assures that this distribution is symmetric about $E=0$.

The second moment of the distribution is found to be

$$\beta\langle\langle E^2\rangle\rangle_0 = \delta^2+2\delta-\frac{2\delta^{3/2}\,\mathrm{e}^{-\delta/4}}{\sqrt{\pi}\,\mathrm{erfc}(\sqrt{\delta}/2)} \tag{35}$$

where the double brackets serve to remind that the average is over the initial and final energies and the 0 subscript notes that only positive energies are considered. This equation is readily solved for a given value of the second moment. In Fig. 6 we plot the dependence of the second moment on the reduced energy loss parameter δ. Asymptotically for very large δ the second moment approaches the value of 8, for very small energy loss it goes as 2δ. But in the range of $1<\delta<20$, typically relevant for surface diffusion, one must solve the equation numerically.

3.2. Numerical results

The purpose of the numerical study was to answer the following questions.

1. Does strong intramode coupling affect the Arrhenius behavior of the double to single hop ratio ($P_{2,1}$) as a function of temperature?
2. Can the $P_{2,1}$ ratio be described quantitatively in terms of the multidimensional Kramers theory?
3. Does one get a 'good' estimate for the energy loss from the second moment of the energy transfer distribution and does it agree with the observed activation energy found in the $P_{2,1}$ ratio?
4. How does the energy loss depend on the intramode coupling strength and the magnitude of the friction coefficient?
5. How does one reconcile the quadratic (inverse) temperature dependence of the energy loss in the underdamped limit with the observed linear (inverse) temperature dependence?

All computations were performed with the efficient fourth-order integrator of Hershkovitz [36]. In Fig. 7 we show Arrhenius plots of the numerical (solid circles) $P_{2,1}$ ratio as a function of temperature for different values of the intramode coupling coefficient C, see Eq. (30). As is evident from the figure, for all values of the coupling coefficient, the ratio has an Arrhenius-like behavior. Moreover, the slope depends on the coupling. This is seen more clearly in Fig. 8, where we show the dependence of the Arrhenius activation energy on the intramode coupling coefficient. It is clear that the activation energy increases as C increases from zero. The reduction of the activation energy as the

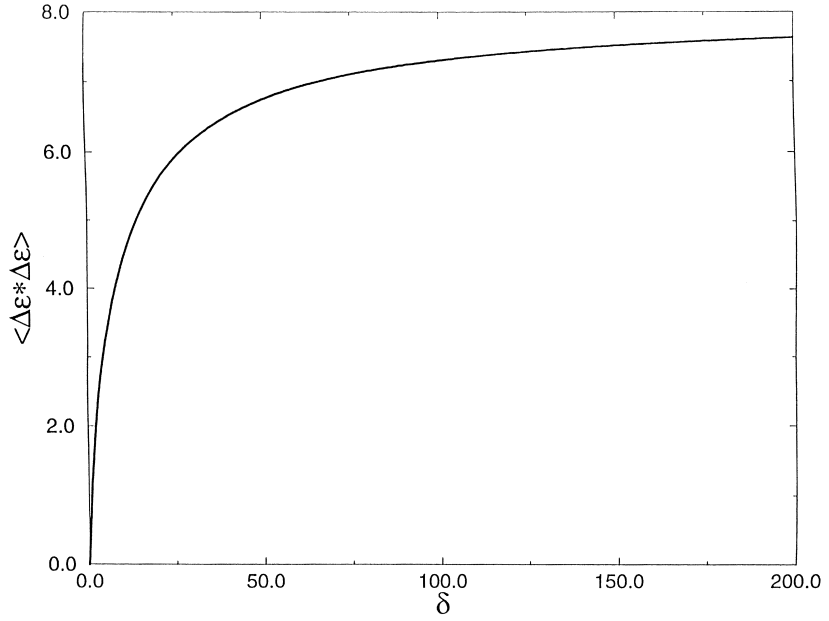


Fig. 6. The dependence of the second moment ($\langle \Delta\epsilon^2 \rangle$) of the energy transfer distribution [cf. Eqs. (34) and (35)] on the reduced energy loss and assuming a Gaussian energy transfer kernel for the multidimensional case. Reduced units are used throughout ($\epsilon = \beta E$).

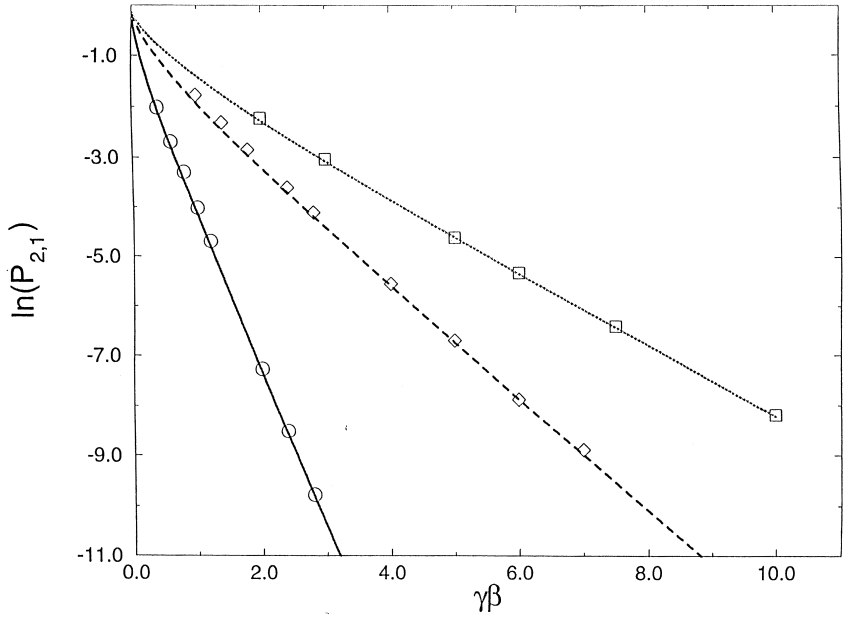


Fig. 7. Arrhenius plot of the ratio of double to single hops as a function of temperature and coupling between the system degrees of freedom. The open symbols are the numerically exact results, the lines are based on the theoretical prediction $\mathrm{erfc}(\sqrt{\delta}/2)$ [see Eq. (18)] using the value of the energy loss parameter obtained from the Arrhenius slope of the double to single hopping ratio. For $C =$ 0.1 (squares), 0.167 (diamonds) and 0.333 (circles) the reduced energy loss parameter is 2.95, 4.8 and 13 respectively. The value of the friction coefficient used for all plots is $\gamma = 10^{-2}$.

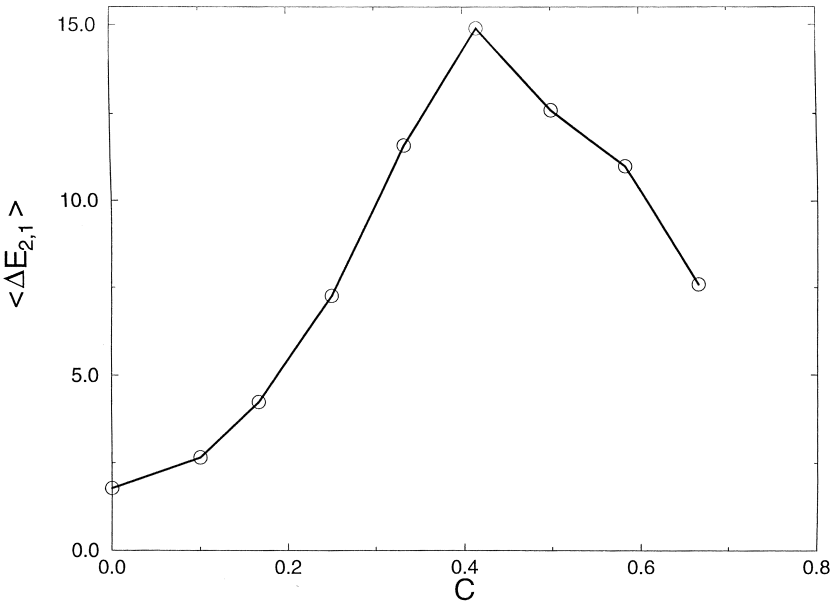


Fig. 8. Dependence of the double jump to single jump added activation energy ($\Delta E_{2,1}$) on the intramode coupling coefficient C. All results are obtained with $\gamma = 10^{-2}$.

coupling coefficient grows beyond $C \approx 0.45$ remains a puzzle which we do not understand.

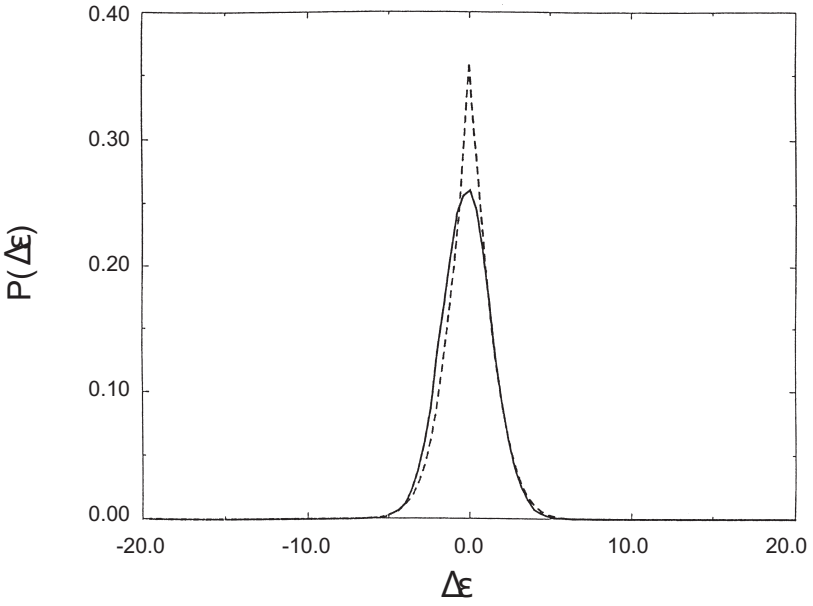
One of the main goals of this study was to establish the connection between the Arrhenius activation energy for the jump ratio and the energy loss of the particle as it moves from one barrier to the next. In Fig. 9, we plot the energy loss distribution for different coupling between the modes. The numerically computed distribution (solid line) is compared with the theoretical prediction given in Eq. (34) (dashed line) which has no free parameters. It is based on the assumption of a Gaussian energy transfer kernel for which the energy loss parameter is taken to be four times the jump ratio activation energy.

It is rather expensive to compute the energy loss parameter from the second moment of the energy loss distribution, especially for large values of δ. The slope at large δ (see Fig. 6) significantly magnifies any error in the second moment. To overcome this, we plot in Fig. 10 the numerical value of the second moment obtained from trajectory computations versus the value of the second moment predicted from Eq. (35). The value of the energy loss parameter is taken from the slope of the Arrhenius plot of the hopping ratio obtained for the same conditions. The unit slope of the figure demonstrates that the Arrhenius activation energy is just 1/4 the energy loss of the particle as it goes from one barrier to the next.

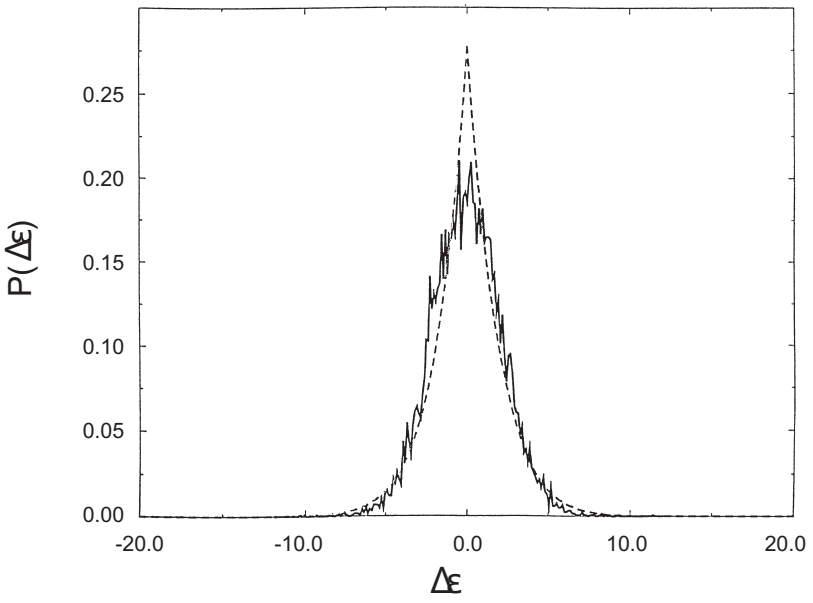
The slope of the Arrhenius plot can now be used in conjunction with Eq. (18) to obtain the hopping ratio from Kramers' theory. The resulting theoretical prediction (solid lines) is compared with the numerically exact hopping ratios in Fig. 7. The good agreement, verifies the correctness of the multidimensional Kramers theory for the system studied. It also justifies the interpretation of the Arrhenius activation energy in terms of the energy loss of the particle as it traverses from one barrier to the next. The good agreement, obtained for different values of the coupling coefficient C also verifies that the intramode coupling dependence of the energy loss is well represented by Fig. 8.

4. Discussion

A simple result was derived for the hopping distribution in surface diffusion. The result is valid



(9a)



(9b)

Fig. 9. Comparison of numerical and theoretical energy loss distributions for different values of the intramode coupling coefficient. The solid lines are from stochastic trajectory computations, the dashed lines are the theoretical prediction, based on Eq. (34). (a) Weak intramode coupling ($C=0.1$) and $\beta=200$. (b) Strong intramode coupling ($C=1/3$) and $\beta=120$.

as long as the damping is weak but the reduced energy loss from the system to the surrounding is of the order of $k_B T$ or larger. Kramers' theory for the hopping distribution leads to the conclusion that the ratio of double hops to single hops will have an Arrhenius form. The added activation

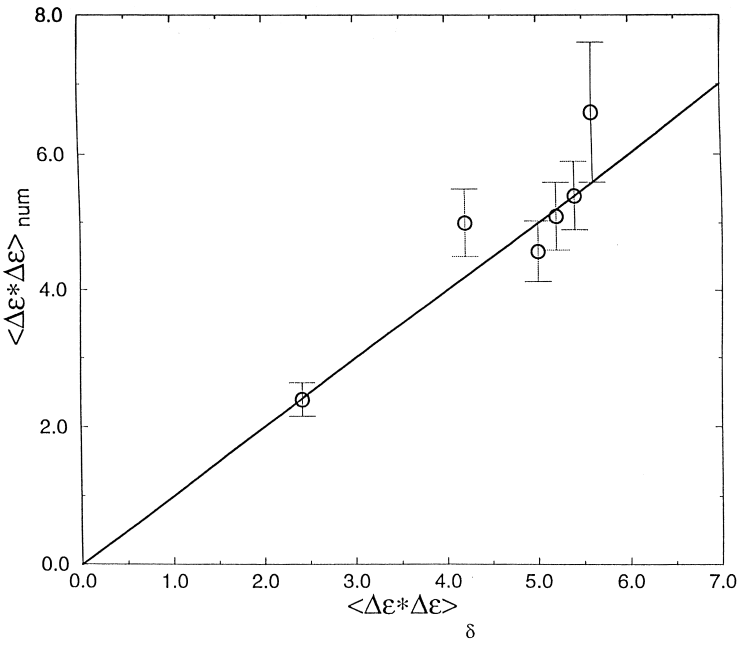


Fig. 10. The numerically computed second moment of the energy transfer distribution is plotted versus the prediction of Eq. (35) using the value of the energy loss parameter δ obtained from the Arrhenius plot of the hopping ratio. The solid line has unit slope.

energy is directly related to the average energy loss of the particle to the bath as it traverses from one barrier to the next. This result was found to be correct for one- and two-dimensional surface diffusion. The prefactor of the hopping ratio is determined by the energy loss, and leads to a $\sqrt{T}$ dependence, as found also by Jacobsen et al. [2].

An analysis of the experiments of Linderoth et al. [1] has been presented. Using only two parameters (the activation energy and the energy loss) we find that their results are consistent with the one-dimensional Kramers theory provided that the activation energy is somewhat higher than obtained by their fitting procedure, which is based on three parameters (the prefactor for the rate, the activation energy and the ratio of double hops to single hops). Increasing the activation energy, causes the prefactor to increase and only then gives a frequency which agrees well with the estimate based on the geometrical structure of the surface. This change was found to be consistent within the error bars of the experiment. The use of Kramers' theory also gives the probability for hops of length greater than two, since the distribution is determined by a single parameter: the reduced energy loss δ. We found that the experiment implies a somewhat larger probability for hops of length three and longer than concluded by Linderoth et al. [1].

A study of two-dimensional diffusion showed that the hopping ratio depends on the coupling between the two modes. Stronger coupling leads to a larger energy loss, a larger activation energy and thus a smaller multiple hopping probability. A numerical study of the energy loss distribution shows that the Gaussian energy transfer probability kernel, which lies at the heart of the theory, is a good approximation to the true distribution.

The parameter range studied is the typical one found in the experiments. That is, the reduced friction parameter is $\sim 10^{-2}$ and the reduced energy loss is in the range of 1–20. For this parameter range, Kramers' theory is satisfactory. Jacobsen et al. [2] studied the double to single hopping ratio over a very large range of temperatures. Their prefactor, when taken over such a large range, differs from the one predicted by the Kramers theory by roughly a factor of two.

However, when taken over the characteristic experimental energy range the expression used in this paper fits their numerical results rather well. We note that, in principle, the energy loss is not completely temperature independent, since it is the energy loss taken for a thermal distribution of the perpendicular (stable) degrees of freedom. Changing the temperature, changes this initial distribution and may also slightly change the energy loss. A more careful study of the energy loss is needed to determine this added temperature dependence. As noted though, within the typical experimentally accessible temperature ranges, this weak dependence is negligible.

Finally, the present study dealt exclusively with large energy losses, such that the distribution of particles at the barrier is thermal. If one reduces the friction parameter considerably, the reduced energy loss will become substantially less than unity and then the average energy of escaping particles is no longer thermal, but much smaller, proportional to $\sqrt{\delta}$ [39]. At this smaller energy, the particle is typically much closer to the barrier top and so will spend a much longer time in the interaction region before reaching the next barrier. When the modes are strongly coupled, this added time will increase the energy loss and it will reach the two-dimensional limit where it is proportional to β^2. In this limit though, the hopping distribution is no longer given by Eq. (1), i.e. the ratio of double hops to single hops does not obey the simple Arrhenius law. The smooth transition from the large energy loss to the underdamped limit for multidimensional surface diffusion has not been studied in this paper and remains a challenge for future work.

Acknowledgements

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References

[1] T.R. Linderoth, S. Horch, E. Lægsgaard, I. Stensgaard, F. Besenbacher, Phys. Rev. Lett. 78 (1977) 4978.
[2] J. Jacobsen, K.W. Jacobsen, J.P. Sethna, Phys. Rev. Lett. 79 (1997) 2843.
[3] D.C. Senft, G. Ehrlich, Phys. Rev. Lett. 74 (1995) 294.
[4] J.C. Tully, G.H. Gilmer, M. Shugard, J. Chem. Phys. 71 (1979) 1630.
[5] G. DeLorenzi, G. Jacucci, V. Pontikis, Surf. Sci. 116 (1982) 391.
[6] M.R. Mruzik, G.M. Pound, J. Phys. F: 11 (1981) 1403.
[7] G. DeLorenzi, G. Jacucci, Surf. Sci. 164 (1985) 526.
[8] A.F. Voter, J.D. Doll, J. Chem. Phys. 82 (1985) 80.
[9] J.D. Doll, A.F. Voter, Annu. Rev. Phys. Chem. 38 (1987) 413.
[10] K.D. Dobbs, D.J. Doren, J. Chem. Phys. 97 (1992) 3722.
[11] D.E. Sanders, A.E. DePristo, Surf. Sci. 264 (1992) L169.
[12] Z. Zhang, K. Haug, H. Metiu, J. Chem. Phys. 93 (1990) 3614.
[13] K. Haug, H. Metiu, J. Chem. Phys. 94 (1991) 3251.
[14] R. Ferrando, R. Spadacini, G.E. Tommei, Phys. Rev. E: 48 (1993) 2437.
[15] E. Pollak, J. Bader, B.J. Berne, P. Talkner, Phys. Rev. Lett. 70 (1993) 3299.
[16] Y. Georgievskii, E. Pollak, Phys. Rev. E: 49 (1994) 5098.
[17] J.S. Bader, B.J. Berne, E. Pollak, J. Chem. Phys. 102 (1995) 4037.
[18] Y. Georgievskii, M.A. Kozhushner, E. Pollak, J. Chem. Phys. 102 (1995) 6908.
[19] Y. Georgievskii, E. Pollak, Surf. Sci. 355 (1996) L366.
[20] G. Caratti, R. Ferrando, R. Spadacini, G.E. Tommei, Phys. Rev. E: 54 (1996) 4708.
[21] G. Caratti, R. Ferrando, R. Spadacini, G.E. Tommei, Chem. Phys. 235 (1998) 157.
[22] L.Y. Chen, M.R. Baldan, S.C. Ying, Phys. Rev. B 54 (1996) 8856.
[23] J.S. Langer, Ann. Phys. (N.Y.) 54 (1969) 258.
[24] A. Nitzan, J. Chem. Phys. 86 (1987) 2734.
[25] A. Nitzan, Adv. Chem. Phys. 70 (1988) 489.
[26] R.F. Grote, J.T. Hynes, J. Chem. Phys. 74 (1981) 4465.
[27] R.F. Grote, J.T. Hynes, J. Chem. Phys. 75 (1981) 2191.
[28] B.J. Matkowsky, Z. Schuss, E. Ben-Jacob, SIAM J. Appl. Math 42 (1982) 835.
[29] B.J. Matkowsky, Z. Schuss, C. Tier, SIAM J. Appl. Math. 43 (1983) 673.
[30] B.J. Berne, Chem. Phys. Lett. 107 (1984) 131.
[31] M. Borkovec, B.J. Berne, J. Chem. Phys. 82 (1985) 794.
[32] J. Straub, B.J. Berne, J. Chem. Phys. 85 (1986) 2999.
[33] E. Pollak, E. Hershkovitz, Chem. Phys. 180 (1994) 191.
[34] E. Hershkovitz, E. Pollak, J. Chem. Phys. 106 (1997) 7678.
[35] S.K. Reese, S.C. Tucker, Chem. Phys. 235 (1988) 171.
[36] E. Hershkovitz, J. Chem. Phys. 108 (1998) 9253.
[37] H.A. Kramers, Physica 7 (1940) 284.
[38] R.F. Grote, J.T. Hynes, J. Chem. Phys. 73 (1980) 2715.
[39] V.I. Melnikov, S.V. Meshkov, J. Chem. Phys. 85 (1986) 1018.

[40] V.I. Melnikov, Phys. Rep. 209 (1991) 1.
[41] E. Pollak, H. Grabert, P. Hänggi, J. Chem. Phys. 91 (1989) 4073.
[42] A.N. Drozdov, J.J. Brey, Chem. Phys. 235 (1998) 147.
[43] J.P. Sethna, Phys. Rev. B 24 (1981) 698.
[44] A.A. Louis, J.P. Sethna, Phys. Rev. Lett. 74 (1995) 1363.
[45] B.N.J. Persson, R. Ryberg, Phys. Rev. B 32 (1985) 3586.
[46] M.A. Kozhushner, A.S. Prostnev, M.O. Rozovskii, B.R. Shub, Phys. Status Solidi B: 136 (1986) 557.
[47] R. Tsekov, E. Ruckenstein, J. Chem. Phys. 100 (1994) 1450.
[48] A.N. Drozdov, Phys. Rev. E, in press.
[49] R.C. Weast (Ed.), Handbook of Chemistry and Physics, 67th editionCRC Press, Boca Raton, FL, 1986.