Theory of Correlated Hops in Surface Diffusion

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Scanning tunneling microscopy observations of long hops in the diffusion of Pb atoms on Ge surfaces are explained by the model of a Brownian particle in a periodic potential. The classical turnover theory for barrier crossing predicts a large correlated hopping probability in the underdamped limit, consistent with experiment and in agreement with simulations. The corresponding quantum theory predicts that in the underdamped limit the rate is dominated by tunneling. This causes the quantum correlated hopping probability to vanish in this limit and may be thought of as a new form of quantum localization.

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The diffusion of adatoms on surfaces is of central importance in epitaxial growth and in catalytic reactions. Recent scanning tunneling microscopy observations [1] of the diffusion of Pb on Ge surfaces show that the Pb atoms can make a surprisingly large number of long jumps. Long jumps have also been observed in computer simulations [2]. In this Letter we suggest that a simple Langevin equation of motion in a periodic potential provides a proper framework for the description of such correlated hopping.

There is a long history of stochastic modeling of surface diffusion and reactivity, which has been comprehensively reviewed in Refs. [3, 4]. Recent work on the diffusion of a classical particle in a periodic potential [5–7] has indicated that correlated hopping could be important. In contrast to previous approaches we will utilize the Kramers turnover theory for activated processes [8–11]. This enables us to address the correlated hopping dynamics of a particle interacting with a quantum bath.

The basic idea is that correlated jumps are the result of competition between energy activation and deactivation of the diffusing particle through its interactions with the bath. In the underdamped regime, the average energy of classical particles crossing the potential barrier between adjacent sites is proportional to the square root of the damping constant (γ) [8, 9, 12–14], whereas the average energy loss of a particle moving from one barrier to the next is linearly proportional to γ [9, 11]. This implies that for sufficiently low damping a classical particle will get activated infrequently but when it does cross a barrier it will usually have more than enough energy to cross the next few barriers before again becoming trapped in a well. A quantum particle may tunnel through the barrier. We will show that even for temperatures above the "crossover temperature," in the underdamped limit, the average energy of the escaping particle is *lower* than the barrier energy [$\sim \ln(\gamma)$] and thus lower than the classical energy. Paradoxically, the quantum tunneling prevents correlated hopping, which is probable only for high particle energies.

In this Letter we present a theory for these correlated hops, valid at temperatures above the crossover temperature between tunneling and thermal activation [15]. The classical limit of the theory is compared with accurate numerical simulations. The predicted correlated hopping probability is in qualitative agreement with the experimental observations.

The particle is assumed to be trapped initially in one of the wells of a one dimensional periodic potential which is generically characterized by a frequency ω at the barriers and wells, barrier height $V^{\ddagger}$, and distance l between adjacent barriers. The specific results presented in this Letter will be for the periodic potential of form

$$w(q) = -\tfrac{1}{2}V^{\ddagger}\cos(2\pi q/l). \tag{1}$$

The time evolution of the particle (with unit mass) is determined by the generalized Langevin equation:

$$\ddot{q} + \frac{dw(q)}{dq} + \int^{t} d\tau\gamma(t-\tau)\dot{q}(\tau) = \xi(t). \tag{2}$$

The quantum rate for hopping out of one of the wells [5] at temperatures above the crossover temperature [15] ($\hbar\beta\omega \leq 2\pi$) may be written as [8, 9, 11, 15, 16]

$$\Gamma = (\omega/\pi)e^{-\beta V^{\ddagger}}(\lambda^{\ddagger}/\omega)\Xi\Upsilon. \tag{3}$$

Here, $\lambda^{\ddagger}$ is the usual Kramers-Grote-Hynes reactive frequency [17],

$$\lambda^{\ddagger}/\omega = [1 + \hat{\gamma}(\lambda^{\ddagger})/\lambda^{\ddagger}]^{-\frac{1}{2}}, \tag{4}$$

where the caret denotes the Laplace transform of the time dependent friction, and $\beta \equiv 1/k_B T$. The ratio of quantum partition functions at the barrier and the well (Ξ) is expressed in terms of the Matsubara frequencies

$\tilde{\omega}_n \equiv 2\pi n/\hbar\beta$ and the Laplace transform of the time dependent friction [18]

$$\Xi \equiv \prod_{n=1}^{\infty} \frac{[\omega^2 + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)]}{[-\omega^2 + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)]}. \tag{5}$$

The last factor Υ in Eq. (3) is the "depopulation factor" which has the quantum form

$$\Upsilon = \exp\left[a^{-1}\sin(\frac{\pi}{a})\int_{-\infty}^{\infty} dt \frac{\ln[1-\tilde{P}(t-\frac{i}{2})]}{[\cosh(\frac{2\pi t}{a}) - \cos(\frac{\pi}{a})]}\right], \tag{6}$$

where the quantum parameter $a \equiv 2\pi/\hbar\beta\lambda^{\ddagger}$.

The magnitude of the depopulation factor is mainly determined by the probability kernel $P(E|E')$ which expresses the probability that a particle with energy E' initially in the vicinity of a barrier will reach the next barrier with energy E. The two sided Laplace transform of this kernel which appears in the expression for the depopulation factor is defined as

$$\tilde{P}(is) \equiv \int_{-\infty}^{\infty} d\epsilon e^{-s(\epsilon-\epsilon')} P(\epsilon|\epsilon'). \tag{7}$$

In the classical limit the probability kernel (using the dimensionless energy variable $\epsilon \equiv \beta E$) is a Gaussian function

$$P(\epsilon|\epsilon') = \left(\frac{1}{4\pi\delta}\right)^{\frac{1}{2}} \exp\left[-\frac{(\epsilon+\delta-\epsilon')^2}{4\delta}\right]. \tag{8}$$

The reduced average energy loss of the particle δ as it traverses from one barrier to the next depends on the damping and the particular form of the periodic potential and will be specified below. The depopulation factor simplifies considerably in the classical limit:

$$\Upsilon_{\rm cl} = \exp\left[\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{dy}{1+y^2} \ln(1 - e^{-\delta\frac{(1+y^2)}{4}})\right]. \tag{9}$$

In the underdamped limit, for which the energy loss parameter $\delta \ll 1$, one finds that $\Upsilon_{\rm cl} \simeq \delta$. This reflects the large reduction of the escape rate due to the very slow energy diffusion process. The quantum depopulation factor is *larger* than the classical in the underdamped limit, $\Upsilon \simeq \delta^{1-\hbar\beta\lambda^{\ddagger}/2\pi}$ [16]. In the overdamped limit, the energy relaxation rate is fast and the depopulation factor tends rapidly to unity.

The quantum rate [cf. Eq. (3)] is found by solving a master equation for the population per unit time of particles $f(\epsilon)$ with (reduced) energy ϵ at the top of the barrier. This leads to the integral equation [16]

$$f(\epsilon) = \int_{-\infty}^{\infty} d\epsilon' P(\epsilon|\epsilon') R(\epsilon') f(\epsilon'), \tag{10}$$

where $R(\epsilon)$ is the quantum reflection probability for a parabolic barrier:

$$R(\epsilon) = [1 + \exp(a\epsilon)]^{-1}. \tag{11}$$

The transmission coefficient $T(\epsilon) = 1 - R(\epsilon)$ is determined by unitarity. This integral equation is subject to the boundary condition that deep in the well the distribution $f(\epsilon)$ is in thermal equilibrium. As shown in [16] this integral equation is readily solved using two sided Laplace transforms. The explicit expression for the rate [cf. Eq. (3)] is then found by summing over all particles transmitted per unit time:

$$\Gamma = \int_{-\infty}^{\infty} d\epsilon T(\epsilon) f(\epsilon). \tag{12}$$

Thus far we have reviewed the known results for the escape rate of the particle. The detailed quantum derivation and assumptions are discussed in Ref. [16]. The theory is accurate for large (reduced) barrier heights; practical applications have demonstrated [5, 19] that already for $\beta V^{\ddagger} = 5$ the theory is quantitative.

At this point we adapt the theory to account for correlated hops. A correlated hop is one in which the particle, upon crossing the first barrier, proceeds immediately to cross the next (second) barrier without first getting trapped in the well separating the two barriers. The fraction of particles P_1 immediately crossing the second barrier is determined by the flux distribution $f_1(\epsilon) = f(\epsilon)$ of particles at the top of the first barrier and the probability kernel for energy change upon traversing from the first barrier to the second one:

$$P_1 = \frac{1}{\Gamma}\int_{-\infty}^{\infty} d\epsilon T(\epsilon) \int_{-\infty}^{\infty} d\epsilon' P(\epsilon|\epsilon') T(\epsilon') f_1(\epsilon'). \tag{13}$$

Since the solution of the integral equation [cf. Eq. (10)] is known (cf. Appendix A of Ref. [16]), it becomes a matter of straightforward but rather lengthy algebra to find the central result of this Letter, which is an explicit expression for the correlated hopping probability P_1:

$$P_1 = a^{-1}\sin\left(\frac{\pi}{a}\right)\frac{1}{\Upsilon^{\frac{1}{2}}}\int_{-\infty}^{\infty} dt \frac{\tilde{P}(t-\frac{i}{2})[1-\tilde{P}(t-\frac{i}{2})]^{\frac{1}{2}}}{[\cosh(\frac{2\pi t}{a}) - \cos(\frac{\pi}{a})]} \cos\left\{\frac{1}{4\pi}\int_{-\infty}^{\infty} dw \frac{1}{w} \ln\left(\frac{1-\tilde{P}[(t-w)-\frac{i}{2}]}{1-\tilde{P}[(t+w)-\frac{i}{2}]}\right)\left[\frac{\pi w}{a}\coth\left(\frac{\pi w}{a}\right)\right]\right\}. \tag{14}$$

In the classical limit ($a \to \infty$) the expression for the correlated hopping probability simplifies considerably,

$$P_1^{\rm cl} = \Upsilon_{\rm cl}^{-\frac{1}{2}}\frac{1}{2\pi}\int_{-\infty}^{\infty} dt \frac{e^{-\delta(t^2+\frac{1}{4})}[1-e^{-\delta(t^2+\frac{1}{4})}]^{\frac{1}{2}}}{t^2+\frac{1}{4}} \cos\left[\frac{1}{4\pi}\int_{-\infty}^{\infty} dw \frac{1}{w}\ln\left(\frac{1-e^{-\delta[(w-t)^2+\frac{1}{4}]}}{1-e^{-\delta[(w+t)^2+\frac{1}{4}]}}\right)\right], \tag{15}$$

and is a function of only the energy loss parameter δ. In the quantum mechanical case it is a function also of $\hbar$ through the parameter $a = 2\pi/\hbar\beta\lambda^{\ddagger}$. Below we are mainly interested in the weak to moderate damping regime where

for all practical purposes one may replace the renormalized barrier frequency by the bare one.

To simplify, the theory will be applied to the case of Ohmic friction,

$$\gamma(t) = 2\gamma\delta(t); \tag{16}$$

later studies [20] will also include memory friction. The classical correlated hopping probability is plotted in Fig. 1 as a function of the energy loss δ. In the underdamped limit $P_1^{\rm cl} \to 0.6944$; in the large damping limit, the correlated hopping probability becomes exponentially small, $P_1 \simeq 2(\delta\pi)^{-1/2} e^{-\delta/4}$. Also shown in Fig. 1 are the results of a numerical Langevin simulation [21] for the correlated hopping probability using the periodic potential given in Eq. (1), in the presence of Ohmic friction, for the reduced barrier height $\beta V^{\ddagger} = 5$. An adequate expression relating the energy loss δ to the damping constant γ is [5] $\delta = \gamma \int_{-l/2}^{l/2} dq[-2w(q)]^{1/2} = 4\beta V^{\ddagger}\gamma/\omega$. As seen from Fig. 1, the theoretical expression is in quantitative agreement with the numerical simulation.

In the experiment, the diffusion of Pb on the Ge(111)-$c(2\times 8)$ surface is anisotropic. 56% of all hops were along the 1-4 direction, and 47% of *all* hops were correlated. It is plausible to assume that correlated hops are more probable along the 1-4 axis, and that the true percentage of correlated hops in this direction is larger than 47%. Using Fig. 1 one can invert the experimental hopping probability (Pb is sufficiently massive to justify the classical limit) to estimate the energy loss δ. A correlated hopping probability in the 1-4 direction larger than 0.5 (and approaching the underdamped limit of 0.7) would imply a very small δ, a small depopulation factor, and thus would help explain the very small prefactor measured for the rate. Furthermore, one can view diffusion along the 1-4 axis as effectively one dimensional, justifying our one dimensional approach.

Our model is also consistent with the experimental observation of correlated hops which are substantially longer than one site. Even the simplified approximation (valid in the moderate damping limit) that the probability for at least n correlated hops is $(P_1)^n$ leads to the conclusion that longer hops are quite likely. We term $P(n)$ the probability that an activated particle starting at barrier 0 will reverse its velocity for the first time while traveling from barrier n to $n+1$. As shown in Fig. 2, especially in the underdamped limit, the distribution $P(n)$ has a very long tail, leading to an even higher probability for long hops.

The quantum kernel [cf. Eq. (7)] is determined:

$$\tilde{P}(t - \tfrac{1}{2}i) \equiv \exp[-r(t)], \tag{17}$$

where the exponent is

$$r(t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} d\lambda \frac{I(\lambda)\tilde{F}(\lambda)[\cosh(\frac{1}{2}\hbar\beta\lambda) - \cos(t\hbar\beta\lambda)]}{\sinh(\frac{1}{2}\hbar\beta\lambda)}. \tag{18}$$

Here, $I(\lambda)$ is the "spectral density of normal modes" (cf. [16]) which in the case of Ohmic friction and weak to moderate damping is well approximated as

$$I(\lambda) \simeq \gamma\lambda/(\lambda^2 + \omega^2)^2. \tag{19}$$

It is also necessary to obtain the power spectrum of the force $[F(t) = dw/dq + \omega^2(q - q^{\ddagger})]$ that the system exerts on the bath. The time dependence is determined by the trajectory at energy $E = V^{\ddagger}/2$ that starts asymptotically at $t = -\infty$ at the first barrier and ends at $t = \infty$ at the second barrier:

$$\sin[\omega q/(2V^{\ddagger})^{\frac{1}{2}}] = \tanh(\omega t). \tag{20}$$

The power spectrum of the force may now be found using an integration by parts and tabular integrals:

$$\tilde{F}(\lambda) \equiv \left|\int_{-\infty}^{\infty} dt e^{i\lambda t} F(t)\right|^2 = \frac{2\pi^2 V^{\ddagger}}{\omega^2}\frac{(\omega^2+\lambda^2)^2}{\lambda^2}\frac{1}{\cosh^2(\frac{\pi\lambda}{2\omega})}. \tag{21}$$

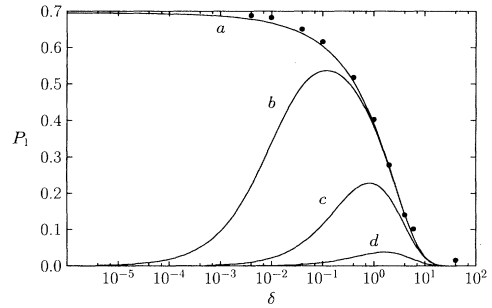

FIG. 1. The classical correlated hopping probability, P_1, as a function of the energy loss parameter δ. The line denoted a is the classical ($\hbar\beta\omega \to 0$) result and is compared with stochastic simulations (solid circles) for $\beta V^{\ddagger} = 5$. In the simulations, P_1 is defined as the fraction of trajectories whose momentum does not reverse as they cross adjacent barriers. Quantum results are shown for three values of the quantum parameter $\hbar\beta\omega$. The lines denoted b, c, and d correspond to $\hbar\beta\omega = 0.2\pi$, π, and 1.8π, respectively.

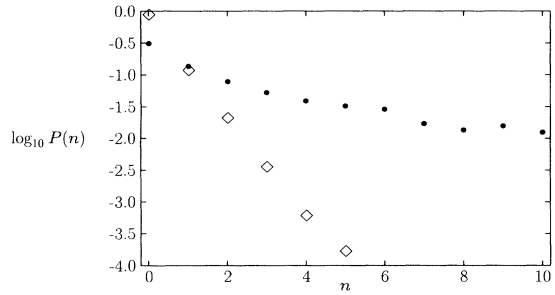

FIG. 2. The classical correlated hopping distribution on a logarithmic scale. $P(n)$ is the probability that an activated particle starting at barrier 0 will reverse its velocity for the first time while it is moving from barrier n to $n+1$. The distributions obtained from numerical simulation are shown for moderate ($\delta = 4$, open diamonds) and weak ($\delta = 0.004$, solid circles) damping. Note the long tail of the distribution in the underdamped case. For moderate damping the distribution is adequately described by a single exponent.

Combining Eqs. (18)–(21) one finds that the exponent $r(t)$ has the specific form

$$r(t) = \frac{\pi\delta}{4\hbar\beta\omega}\int_{-\infty}^{\infty} d\lambda \left[\frac{\cosh(\frac{1}{2}\hbar\beta\lambda) - \cos(t\hbar\beta\lambda)}{\lambda \sinh(\frac{1}{2}\hbar\beta\lambda)\cosh^2(\frac{\pi\lambda}{2\omega})}\right]. \quad (22)$$

One can now evaluate the quantum correlated hopping probability. In contrast to the classical P_1, which is a monotonically decreasing function of the energy loss, the quantum correlated hopping probability is a bell shaped function which vanishes in both the underdamped and overdamped limits. The quantum results (obtained by numerical integration) as a function of the energy loss δ for a few different values of the quantum parameter $\hbar\beta\omega$ are also presented in Fig. 1. The classical probability for correlated hopping is always larger than the quantum probability.

The seemingly counterintuitive quantum result may be understood by inspection of the quantum average energy of particles crossing the barrier:

$$\langle\epsilon\rangle \equiv \frac{\int_{-\infty}^{\infty} d\epsilon \epsilon T(\epsilon) f(\epsilon)}{\int_{-\infty}^{\infty} d\epsilon T(\epsilon) f(\epsilon)} = \frac{\pi}{a}\left[\cot\left(\frac{\pi}{a}\right) + \frac{1}{a}\int_{-\infty}^{\infty} dx \ln\left[1 - \tilde{P}\left(x - \frac{i}{2}\right)\right]\frac{[1 - \cosh(\frac{2\pi x}{a})\cos(\frac{\pi}{a})]}{[\cosh(\frac{2\pi x}{a}) - \cos(\frac{\pi}{a})]^2}\right]. \quad (23)$$

This result is a generalization of the classical limit expression derived by Mel'nikov [8,9]. In the underdamped limit, the quantum average energy becomes increasingly negative, $\langle\epsilon\rangle \sim \ln\delta$. This implies that although the temperature is above the so-called crossover temperature between tunneling and thermal activation, the major quantum mechanism for particle escape is via tunneling. Because of the very weak coupling to the bath the probability for tunneling at an energy below the barrier height is greater than the probability that the particle will gain enough energy to cross above the barrier. Moreover, the quantum depopulation factor is *larger* than the classical depopulation factor [16]. The quantum deactivation of particles as they travel between adjacent barriers is larger than the classical deactivation. The net result of both of these factors is that in the underdamped limit the quantum particle will not undergo a correlated hopping.

In summary, we have presented a quantum theory of correlated hopping valid above the crossover temperature. We predict that quantum correlated hops are less likely than classical correlated hops, implying a quantum localization. The theory takes into account quantum tunneling between adjacent sites but does not allow for coherent multiple well quantum tunneling. The coherent process is very important for low temperatures (below the crossover temperature) but will not significantly affect the results presented here, valid for "high" temperature only.

The analytic theory has been reported only for the hopping probability to an adjacent site (P_1). The same formalism may be used to obtain probabilities for longer jumps, thus also estimating the diffusion coefficient [20]. In this Letter we described results only for Ohmic friction. The formalism of Ref. [11] allows extension of the theory to include memory friction. Based on previous experience, one expects that in the presence of memory the effective damping is decreased [11], leading to a larger range of damping parameters for which correlated hopping may be important.

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