Semiclassical theory of activated diffusion

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(Received 1 June 1993; revised manuscript received 9 February 1994)

A semiclassical theory for the diffusion of a particle moving on a periodic potential, coupled to a dissipative heat bath, is presented. The resulting expressions for the diffusion coefficient, mean squared path length, and hopping length distribution are valid for memory friction and provide a theory which goes uniformly from the underdamped to the strongly damped limit. In the underdamped limit, quantum tunneling and reflection cause the quantum diffusion coefficient to be lower than the classical, leading to an inverse isotope effect; the diffusion of D atoms should be faster than the diffusion of H atoms.

PACS number(s): 05.40.+j, 68.35.Fx, 82.20.−w, 66.30.−h

I. INTRODUCTION

The theory of activated rate processes has been developed extensively during the past decade [1]. The standard model is that of a classical particle trapped in a potential well, separated by a barrier from a different well or a continuum. The particle is coupled to a bath which exerts upon it a (time dependent) frictional and random force. The equation of motion is the generalized Langevin equation (GLE). In the weak damping limit, the escape rate is limited by energy diffusion from the bath to the particle. When the damping is strong, it is limited by the spatial diffusion across the barrier. A unified theory which is valid for all values of the damping and arbitrary memory friction has been developed [2, 3]. Quantum effects may also be treated [1, 4]. Quantum tunneling will cause the quantum rate to be *larger* than the classical.

Experimental measurement of the diffusion of hydrogen and deuterium on tungsten [5] and nickel [6] surfaces has revealed an inverse isotope effect. The diffusion of hydrogen atoms was found to be slower than deuterium or tritium atoms. Recent scanning tunneling microscopy (STM) experiments [7] have provided direct observation of diffusion of an activated particle on a surface. Pb atoms, chemically bound to a Ge surface, have been observed to undergo large correlated hops as they move from one site to the other. Correlated hops were observed in a variety of numerical simulations [8–13]. These observations have revived interest in the classical theory of activated rate processes [12, 15–18] and the escape dynamics of a particle moving on an infinite periodic potential. Such a model may be applied to diverse phenomena, ranging from atomic and molecular diffusion in solids to rotational relaxation and reorientation in the condensed phase [14].

In the spatial diffusion limit, the particle might escape from a well, get trapped in an adjacent well, and after a long time escape with equal probability in either direction. The diffusion coefficient D is proportional to the product of the (spatial diffusion) rate Γ_{sd} and the distance squared (l_0^2) between wells [19]. Since the quantum escape rate is greater than the classical, the quantum diffusion coefficient will also be greater than the classical.

In the underdamped limit, the average energy of a particle that escapes above a barrier is proportional to the square root of the damping ($\sqrt{\gamma}$) [20]. As the particle moves from one barrier to the next, it will, on the average, lose energy to the bath. The energy loss is proportional to γ [2, 3]. Therefore the particle will undergo large correlated hops before becoming retrapped. Kozhushner *et al.* [21] have used a phonon model to demonstrate that the underdamped limit is applicable to surface diffusion of metal atoms on metal surfaces.

It has recently been shown [22] that the classical correlated hopping probability, which gives the probability that an escaping particle will *not* be immediately reflected by the next barrier, is of the order of unity in the classical underdamped limit. The quantum correlated hopping probability was found to be *smaller* than the classical. The reason, paradoxically, has to do with quantum tunneling which causes a *lowering* of the average energy of quantum particles crossing the barrier. This reduces the number of particles whose energy is greater than the barrier height and prevents correlated hopping. These observations suggested that the quantum diffusion coefficient could be smaller than the classical in the underdamped limit. This is a central result of the present paper. It implies an inverse isotope effect which should be considered in theoretical interpretations of diffusion in solids and on surfaces.

The second, equally important, result of the present work is the derivation of relatively simple expressions for experimentally measurable quantities, such as the diffusion coefficient, the mean squared path length, and the hopping length distribution. We will provide a solution for the quantum dynamics (above crossover) of the GLE in which the particle is moving on a periodic potential. Explicit solutions for the rate of escape (Γ), the probability P_j of being retrapped after moving a distance jl_0, the mean squared path length $\langle l^2 \rangle$, and the diffusion coefficient D will be presented. The solutions are valid for all values of the damping and for arbitrary memory friction. The resulting expressions go uniformly from the energy

diffusion to the spatial diffusion limited regimes. They extend previous results derived by Mel'nikov [23, 24] for motion on a tilted potential in the presence of Ohmic friction.

II. SEMICLASSICAL THEORY OF DIFFUSION

The GLE describing the time evolution of the particle is

$$\ddot{q} + \frac{dw(q)}{dq} + \int^t d\tau \gamma(t-\tau)\dot{q}(\tau) = \xi(t), \tag{2.1}$$

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 $\omega_0, \omega^\ddagger$ at the wells and barriers respectively, with a barrier height $V^\ddagger$ and distance l_0 between adjacent wells. The particle is assumed to be initially in one of the wells, labeled 0. The boundary conditions are such that the energy of the particle deep down in the zeroth well is thermal ($\sim e^{-\epsilon}$, where $\epsilon \equiv \frac{E}{k_B T}$ is the reduced energy and is 0 at the barrier top) and no particles will be found at the bottom of any of the other wells.

In the spatial diffusion limit, the quantum rate for hopping out of the well at temperatures above the crossover temperature is well known [25]:

$$\Gamma_{sd} = \frac{\omega_0}{\pi} e^{-\beta V^\ddagger} \frac{\lambda^\ddagger}{\omega^\ddagger} \Xi. \tag{2.2}$$

The reactive frequency [26] $\lambda^\ddagger$ is the solution of the equation $\lambda^{\ddagger 2} + \lambda^\ddagger \hat{\gamma}(\lambda^\ddagger) = \omega^{\ddagger 2}$. The ratio ($\Xi$) of the quantum partition functions at the barrier and well is expressed in terms of the Matsubara frequencies $\tilde{\omega}_n \equiv 2\pi n/\hbar\beta$ as

$$\Xi \equiv \prod_{n=1}^{\infty} \frac{[\omega_0^2 + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)]}{[-\omega^{\ddagger 2} + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)]}. \tag{2.3}$$

The starting point for the evaluation of the quantum mechanical escape rate is an equation for the stationary flux of particles exiting each well at either barrier. We will denote the number of particles per unit energy and per unit time hitting the right (left) barrier of the jth well with positive (negative) velocity by f_j^+ (f_j^-); cf. Fig. 1. The transmission probability through the barrier $T(\epsilon)$ is taken as the parabolic barrier result:

$$T(\epsilon) = e^{a\epsilon} R(\epsilon) = \frac{e^{a\epsilon}}{1+e^{a\epsilon}}, \qquad a \equiv \frac{2\pi}{\hbar\beta\lambda^\ddagger}, \tag{2.4}$$

where R is the reflection coefficient. The reflection symmetry of the potential and the boundary conditions about the zeroth well implies that $f_j^\pm(\epsilon) = f_{-j}^\mp(\epsilon)$.

As the particle traverses from one barrier to the next it changes its energy. The conditional probability kernel $P(\epsilon|\epsilon')$ that the particle changes its energy from ϵ' to ϵ is determined by the energy loss parameter δ and the quantum parameter a defined in Eq. (2.4). Explicit expressions for the quantum kernel were derived in Refs. [23, 27]. The steady state equation for the fluxes, which gives the fundamental integral equation which must be solved, is

$$f_j^+(\epsilon) = \int_{-\infty}^{\infty} d\epsilon' P(\epsilon|\epsilon')[R(\epsilon') f_j^-(\epsilon') + T(\epsilon') f_{j-1}^+(\epsilon')]. \tag{2.5}$$

The boundary conditions for the fluxes are

$$f_j^\pm(\epsilon) \simeq \delta_{j0} \frac{C}{2\pi\hbar\beta} e^{-\epsilon}, \qquad \epsilon \to -\infty \tag{2.6}$$

where δ_{j0} is the Kronecker delta function and C is the equilibrium ratio of partition functions around the barrier and the bottom of the well: [$C = 2(\omega_0/\omega^\ddagger)\sin(\frac{\pi}{a})\Xi e^{-\beta V^\ddagger}$].

The number of particles per unit time that are trapped in the jth well (Γ_j) is given by the difference between the incoming and outgoing fluxes of the jth well:

$$\Gamma_j = \int_{-\infty}^{\infty} d\epsilon T(\epsilon)[f_{j-1}^+(\epsilon) + f_{j+1}^-(\epsilon) - f_j^-(\epsilon) - f_j^+(\epsilon)]. \tag{2.7}$$

The rate of escape from the zeroth well Γ is

$$\Gamma = -\Gamma_0. \tag{2.8}$$

The probability of being trapped at the jth well is $P_j = \frac{\Gamma_j}{\Gamma}$ such that the mean squared path length is

$$\langle l^2 \rangle = l_0^2 \sum_{j=-\infty}^{\infty} j^2 P_j. \tag{2.9}$$

The diffusion coefficient for the one dimensional problem is just the rate of escape multiplied by half the mean squared path length [12, 28]:

$$D = \frac{1}{2}\Gamma\langle l^2 \rangle = \frac{1}{2} l_0^2 \sum_{j=-\infty}^{\infty} j^2 \Gamma_j. \tag{2.10}$$

The periodicity of the potential implies that one can solve the integral equations by Fourier transforms. The notation

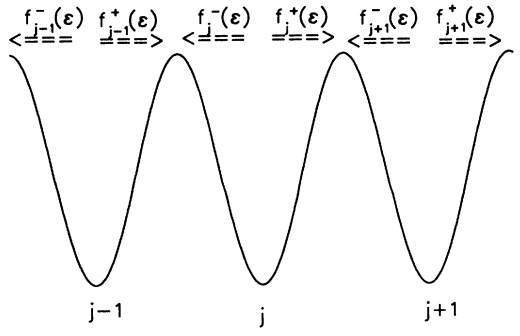

FIG. 1. Schematic diagram of stationary fluxes leaving each well.

$$N(\epsilon,k) \equiv R(\epsilon)\sum_{j=-\infty}^{\infty} e^{i(j+\frac{1}{2})k} f_j^+(\epsilon)$$
$$\equiv N_r(\epsilon,k) + iN_{im}(\epsilon,k) \tag{2.11}$$

is used for the Fourier transformed distribution, weighted by the reflection coefficient. The two-sided Laplace transform of a function will be denoted

$$\tilde{g}(is) \equiv \int_{-\infty}^{\infty} d\epsilon e^{s\epsilon} g(\epsilon). \tag{2.12}$$

The system of integral equations [Eq. (2.5)] is Fourier and Laplace transformed and rearranged:

$$\tilde{N}_{im}[i(s-a),k] = -G(is,k)\tilde{N}_{im}(is,k), \tag{2.13}$$

where G is

$$G(is,k) \equiv \frac{1-\tilde{P}^2(is)}{1+\tilde{P}^2(is)-2\tilde{P}(is)\cos(k)} \tag{2.14}$$

and $\tilde{P}(is)$ is the two-sided Laplace transform of the kernel $P(\epsilon|\epsilon')$. Only the imaginary part of the function $N(\epsilon,k)$ is needed to determine the rates.

The solution of the integral equation [Eq. (2.13)], with the appropriate boundary conditions, is obtained by using the method described in the Appendix of Ref. [27]. The result for the partial rates is

$$\Gamma_j = -\Gamma_{sd}\frac{1}{\pi}\int_0^{2\pi} dk \sin^2\left(\frac{k}{2}\right)\cos(jk)$$
$$\times\exp\left[\frac{\sin(\frac{\pi}{a})}{a}\int_{-\infty}^{\infty} d\tau \frac{\ln[G(\tau-\frac{i}{2},k)]}{\cosh(\frac{2\pi\tau}{a})-\cos(\frac{\pi}{a})}\right]. \tag{2.15}$$

The expression for the diffusion coefficient simplifies considerably because of the infinite summation:

$$\frac{D}{D_{sd}} = \Upsilon^{-1}\exp\left[\frac{\sin(\frac{\pi}{a})}{a}\int_{-\infty}^{\infty} d\tau \frac{\ln[1+\tilde{P}(\tau-\frac{i}{2})]}{\cosh(\frac{2\pi\tau}{a})-\cos(\frac{\pi}{a})}\right], \tag{2.16}$$

where $D_{sd} \equiv \frac{1}{2}l_0^2\Gamma_{sd}$ is the diffusion coefficient in the spatial diffusion limit and is independent of the energy loss δ. The "depopulation factor" Υ is [27]

$$\Upsilon = \exp\left[\frac{\sin(\frac{\pi}{a})}{a}\int_{-\infty}^{\infty} d\tau \frac{\ln[1-\tilde{P}(\tau-\frac{i}{2})]}{\cosh(\frac{2\pi\tau}{a})-\cos(\frac{\pi}{a})}\right]. \tag{2.17}$$

Equations (2.15)–(2.17) are the central result of this paper. They provide a uniform expression for the partial rates, the decay rate, and the diffusion coefficient in terms of the energy loss δ, the quantum parameter a, and the rate expression in the spatial diffusion limit. The mean squared traversal distance may be obtained directly from the rate and the diffusion coefficient via Eq. (2.10).

III. AN INVERSE ISOTOPE EFFECT

In this section we will demonstrate that in the underdamped limit, the quantum diffusion coefficient may be lower than the classical. This implies that the diffusion of D atoms on a surface may be faster than the diffusion of H atoms. It is appropriate here to note that there are other mechanisms which may lead to inverse isotope effects in surface diffusion. Auerbach *et al.* [29] suggested that the lower D atom frequency leads to a more efficient exchange of energy with the bath, thus leading to a larger escape rate. Rick *et al.* [30] have suggested that the lower zero point energy associated with a D atom may lead to a lowering of the effective barrier so that the escape rate of a D atom will be larger than that of an H atom. The major difference between these approaches and the present work is that in our mechanism, the escape rate of the D atom is *slower* than that of an H atom. One may still be able to observe an inverse isotope effect for the diffusion coefficient however, because the mean squared path length of a D atom will be substantially longer than that of an H atom in the underdamped limit.

Analysis of Eq. (2.16) leads to the conclusion that $\frac{D}{D_{sd}} \simeq \frac{N}{\Upsilon}$, where the numerical constant N is of the or-

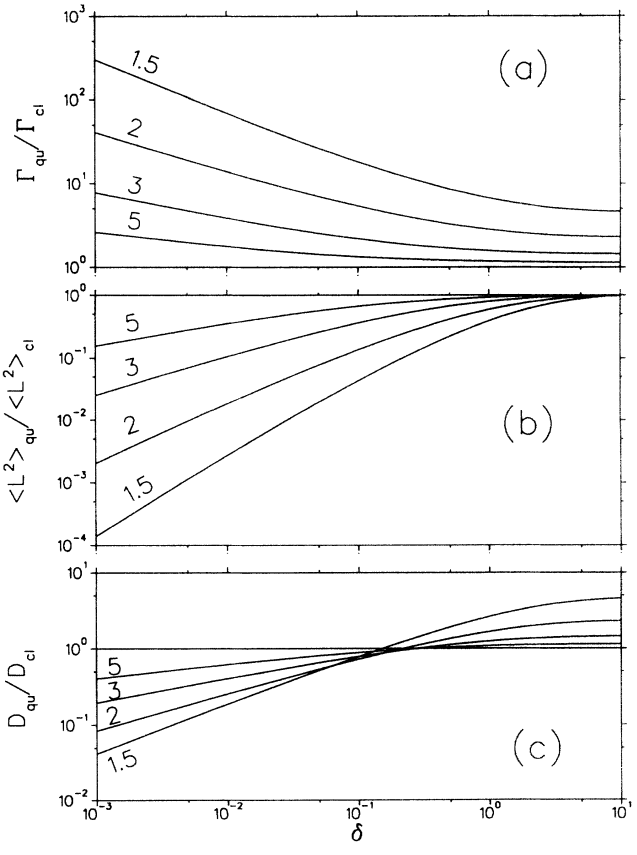

FIG. 2. (a) The rate, (b) mean squared path length, and (c) diffusion coefficient as a function of the energy loss (δ) for a few values of the quantum parameter $a = 2\pi/\hbar\beta\lambda^{\ddagger}$. Results are presented for the periodic cosine potential [cf. Eq. (16)]. The rate is normalized by the standard one dimensional TST rate ($\Gamma_{TST} = \frac{\omega_0}{\pi}e^{-\beta V^{\ddagger}}$); the diffusion coefficient is normalized by the TST value ($D_{TST} = \frac{1}{2}\Gamma_{TST}l_0^2$). The numbers on each line denote the respective values of the quantum parameter a.

der of unity for any value of the energy loss δ in both the quantum and classical cases. The dependence of the diffusion coefficient on the damping is thus easily obtained by studying the dependence of the depopulation factor on the damping. In the underdamped limit ($\delta \ll 1$) the quantum depopulation factor is small $\Upsilon_q \sim \delta^{1-\frac{1}{a}}$, but larger than the classical ($\Upsilon_{cl} \sim \delta$) [31]. Since the diffusion coefficient is *inversely* proportional to the depopulation factor one finds that in the underdamped limit the quantum diffusion coefficient is *smaller* than the classical, $\frac{D_q}{D_{cl}} \sim \frac{\Upsilon_{cl}}{\Upsilon_q} \sim \delta^{\frac{1}{a}}$. When the energy loss is large ($\delta \gg 1$), the depopulation factor becomes unity. In this spatial diffusion limit, the quantum diffusion coefficient is *larger* than the classical because of quantum tunneling through the barrier. The ratio $\frac{D_q}{D_{cl}}$ will be less than unity for weak damping, but will be greater than unity in the spatial diffusion limit.

To demonstrate this behavior we have studied the dependence of the escape rate, the mean squared path length, and the diffusion coefficient for the periodic cosine potential

$$w(q) == -\frac{V^{\ddagger}}{2}\cos\left(\frac{2\pi q}{l_0}\right) \tag{3.1}$$

in the presence of Ohmic friction $\gamma(t) = 2\gamma\delta(t)$. Explicit expressions for the Laplace transformed quantum kernel $[\tilde{P}(\tau - \frac{i}{2})]$ have been derived in Ref. [22]. The energy loss is linearly proportional to the damping ($\delta = 4\beta V^{\ddagger}\gamma/\omega^{\ddagger}$). The quantum rate, mean squared path length, and diffusion coefficient are obtained by numerical integration of the relevant integrals [cf. Eqs. (2.15)–(2.17)] and are presented in Fig. 2. The quantum escape rate is always larger than the classical; this is due to quantum tunneling. However, the quantum mean squared path length is much smaller than the classical in the underdamped limit, hence the *lower* quantum diffusion coefficient.

Both quantum tunneling and quantum above barrier reflection are responsible for the suppression of the quantum diffusion coefficient. Long jumps are obtained if the energy is greater than the barrier height. Quantum tunneling lowers the average energy of escaping particles, reducing the probability for a long hop. If the energy of the particle is greater than the barrier, quantum reflection will reduce the diffusion coefficient by reducing the length of the correlated hop relative to the classical. That the two effects are equally important may be shown by replacing the harmonic tunneling probability [Eq. (2.4)] with either the simple semiclassical estimate $T(\epsilon) = e^{a\epsilon}$, $\epsilon < 0$; $T(\epsilon) = 1$, $\epsilon > 0$, thus eliminating quantum reflection, or one may allow for only above barrier reflection by a similar replacement in which the transmission probability is zero below the barrier. Such an exercise confirms that both quantum below barrier transmission as well as above barrier reflection suppress the quantum diffusion coefficient.

The suppression of the quantum diffusion coefficient in the underdamped limit implies an inverse isotope effect. For a given potential and damping, the energy loss is inversely proportional to $\sqrt{m}$, where m is the mass of the diffusing atom. The barrier frequency goes as $m^{-\frac{1}{2}}$. Assuming unit mass for the hydrogen atom, denoting δ as the energy loss for the H atom and $a = 2\pi/\hbar\beta\omega^{\ddagger}$ as the quantum parameter for the H atom, one finds that for an atom with mass m relative to H, the ratio of the diffusion coefficients in the underdamped limit goes as $\frac{D_{mH}}{D_H} \sim \delta^{\frac{1}{a}(\frac{1}{\sqrt{m}}-1)}$, verifying the inverse isotope effect. This implies that any consideration of diffusion of light atoms in which tunneling is observed should include the possibility that inverse isotope effects are caused by weak damping of the diffusing particle.

IV. DISCUSSION

We have presented a theory for quantum and classical diffusion on a periodic potential, valid for memory friction and all values of the damping. The results for the mean squared path length are of practical interest. STM measurement of the mean squared path length, the escape rate, as well as the diffusion coefficient are possible as evidenced by the results of Ref. [7]. Elsewhere [32] we will show how the model employed by Kozhushner *et al.* [21] may be used to determine the friction coefficient γ from experimental parameters. A combination of such a model with the present theory and experimental determination of the activation energy allows to predict whether the diffusion process occurs via single hops or correlated hops.

The quantum theory presented in this paper is limited to temperatures above the crossover temperature ($a \geq 1$). This limitation may be removed by allowing for a quadratic energy dependence of the tunneling action around crossover as shown by Hänggi and Hontscha [33]. A somewhat different approach, using an anharmonic one dimensional tunneling coefficient in Eq. (2.4) and numerical integration of the integral equations (2.5), is presented in Ref. [34].

The present paper has dealt with one dimensional diffusion. In many cases, diffusion must be treated with at least two and sometimes three dimensions. Elsewhere [35] we are developing a multidimensional generalization of the Kramers turnover theory, which could be combined with the approach presented here to develop the multidimensional theory of activated diffusion.

ACKNOWLEDGMENTS

We are grateful to Professor A.M. Berezhkovskii, Professor B.J. Berne, Professor V.I. Mel'nikov, Professor I. Rips, Professor G.A. Voth, and Dr. J. Bader for stimulating discussions. This work has been supported by a grant from the Minerva foundation.

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