Transition-state theory for tunneling in dissipative media

Eli Pollak
Chemical Physics Department, The Weizmann Institute of Science, 76100 Rehovot, Israel
(Received 18 November 1985)

The recently developed theory for tunneling in dissipative systems is rederived using quantal transition-state theory. As predicted by Caldeira and Leggett, we find an exponential damping of the tunneling rate at 0 K. The exponential rate enhancement at low temperatures as well as the crossover temperature are also obtained with this approach. Moreover, the rate enhancement is given explicitly in terms of energy transfer from the bath to the dissociative mode. The present derivation includes memory effects.

I. INTRODUCTION

One of the most useful approximations for obtaining the rate of bimolecular reactions is transition-state theory.[1] The elements of this theory in its classical mechanical version are well known. One finds the lowest saddle point on the potential energy surface which connects reactants to products. At this point—the transition state—one evaluates the total (canonical or microcanonical) flux in products' direction, divides by the density of reactants, and obtains the rate. All the necessary information is given via the partition function of the "internal" degrees of freedom at the transition state and the partition function of reactants.

The theory, which is well defined classical mechanically—it provides a variational upper bound for the classical rate—has also a quantal version. Instead of classical partition functions one evaluates quantal partition functions. However, one must also account for quantal tunneling. The best available prescription is to assume that the motion along the reaction coordinate is separable from the internal degrees of freedom. It is then very easy to incorporate a one-dimensional tunneling probability. In the simplest form, the barrier is taken to be an inverse harmonic oscillator or an Eckart barrier for which the tunneling probability is known analytically. Surprisingly, quantal transition-state theory works remarkably well even in a harmonic version for the tunneling correction. In the limit that the frequency of the internal degrees of freedom is larger than the imaginary frequency of the barrier one expects an adiabatic approximation to be valid. The fast internal degrees of freedom provide an effective potential for the reaction coordinate motion. This assures the separability needed for quantal transition-state theory. It is well known that quantal transition-state theory is exact in the adiabatic limit.[1]

In recent years there has been much interest in determining the effect of dissipation on tunneling. Caldeira and Leggett[2] have provided a thorough analysis using a theoretical machinery which is based on the instanton technique.[3] By integrating out the bath variables they represent the rate in the form of a functional path integral which is then evaluated semiclassically along the instanton trajectory. The main result of their analysis is that at zero temperature, the bath will exponentially dampen the tunneling rate. Caldeira and Leggett obtain explicit formulas for the tunneling rate in the low- and high-friction limits. Chang and Chakravarty[4] evaluated the rate numerically for the entire range of friction coefficient for the case of Ohmic dissipation. Barone and Ovchinnikov[5] estimated an interpolation formula. Grabert, Weiss, and Hänggi[6] have essentially extended the Caldeira-Leggett methodology to estimate the effect of temperature on the tunneling rate. Their main result is that for Ohmic dissipation, increasing the temperature of the bath will (in the low-temperature limit) increase the tunneling rate by a factor of $\exp(AT^2)$. Similar conclusions have been obtained by Larkin and Ovchinnikov[7] and Zwerger.[8] These predictions have been subsequently verified experimentally by Washburn *et al.*[9] in their measurement of the tunneling rate in an isolated Josephson junction.

The quantal theory used to evaluate the tunneling rate is based on modeling the phenomenological Langevin equation that governs the tunneling by an infinite set of harmonic oscillators coupled linearly to the tunneling degree of freedom. It would seem that one should be able to analyze the tunneling rate of such a system by using quantal transition-state theory (TST) instead of the instanton technique. This is the main purpose of this paper. In Sec. II we use the adiabatic formulation of quantal TST to obtain an analytic estimate of the decay rate at zero temperature. We find good agreement with the numerical estimate of Chang and Chakravarty.[4] Moreover, the result is easily generalized to non-Ohmic dissipation. The theory proposed is based on a renormalization of the imaginary frequency of the barrier as a result of the coupling to the bath.[10] The renormalization factor is provided by the "reactive frequency" defined by Grote and Hynes[11] in their classical mechanical study of barrier crossing in dissipative systems.

In Sec. III we proceed to estimate the effect of temperature. The coupling causes a modification of the bath frequencies. If one treats the bath modes adiabatically one finds that temperature will cause a *decrease* in the rate of the order of $\exp(-AT^n)$. However, if one uses a sudden approximation one finds that temperature enhances the rate. At low temperatures one predominantly populates the low-frequency modes. This justifies the sudden ap-

proach and disqualifies the adiabatic result. In agreement with Grabert, Weiss, and Hänggi[6] we find that the power of the exponential temperature dependence is determined by the frequency dependence of the spectral density of the bath. We also find the crossover temperature from tunneling to thermal activation as well as the decay rate at high temperatures. Our analysis leads to the same conclusion reached by Hänggi *et al.*[12] based on the instanton analysis. Finally, in Sec. IV we discuss the implications of our analysis on future work.

II. THE TUNNELING RATE AT 0 K

A. Preliminaries

As discussed in detail by Caldeira and Leggett,[2] we assume that the dissipative system is described phenomenologically by a generalized Langevin equation (GLE) of the form

$$M\ddot{q}+\int_0^t d\tau\,\eta(\tau)\dot{q}(t-\tau)+\frac{\partial V(q)}{\partial q}=F_{\rm ext}(t)\ . \tag{1}$$

Here $\eta(t)$ is the time-dependent friction coefficient, $V(q)$ the potential for the particle of mass M and $F_{\rm ext}(t)$ is the external Gaussian random force. The random force is assumed to be zero centered,

$$\langle F_{\rm ext}(t)\rangle=0\ , \tag{2}$$

and is related to the time-dependent friction via the fluctuation dissipation theorem

$$\eta(t)=\beta\langle F_{\rm ext}(0)F_{\rm ext}(t)\rangle\ . \tag{3}$$

If $\eta(t)=\eta\delta(t)$ then the GLE [Eq. (1)] reduces to the simpler Langevin equation (LE). The average in Eqs. (2) and (3) is over the thermal bath at temperature T ($\beta=1/k_BT$). The potential $V(q)$ is assumed to have the general form shown in Fig. 1. At $q=0$ we assume a minimum in V such that the harmonic frequency around the minimum ω_0 is simply $[V''(0)/M]^{1/2}$. At q^*, V has a maximum V^*, the imaginary frequency at the barrier ω^* is defined as $[-V''(q)/M]^{1/2}$. Note that for a cubic potential $\omega_0=\omega^*$. The length of the tunneling path q_0 is defined by the condition $V(q_0)=0$.

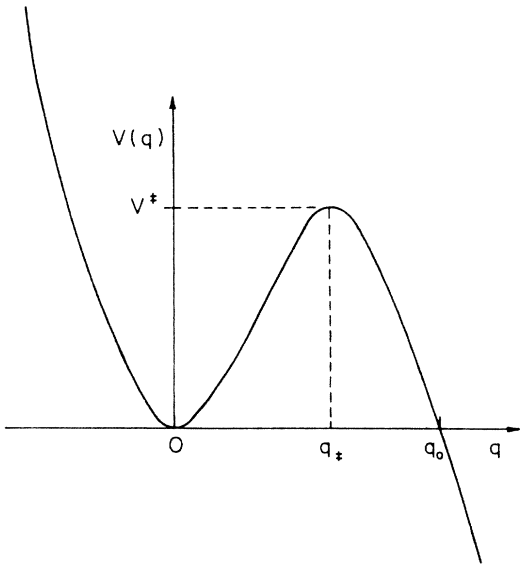

FIG. 1. Schematic diagram of the potential-energy surface of the metastable system.

If there is no friction then Eq. (1) reduces trivially to a one-dimensional conservative equation of motion. The tunneling rate at 0 K is given within the WKB approximation as[13]

$$\Gamma_0=\frac{\omega_0}{2\pi}\exp(-B_0/\hbar) \tag{4}$$

where we have assumed that the "ground state" of the oscillator at $q=0$ is well approximated as harmonic. B_0 in the exponent is the tunneling-action integral and is defined as

$$B_0=2\int dq\{2M[V(q)-\hbar\omega_0/2]\}^{1/2}\ . \tag{5}$$

Note that the expression used in Eqs. (4) and (5) differs slightly from the one used by Caldeira and Leggett[2] and derived by Callan and Coleman.[3,14] Equations (4) and (5) are derived by the standard WKB method using the well-known connection formulas. As shown by Miller,[15] the Callan and Coleman result is the $\hbar\to0$ limit of Eq. (4). In any case, since we are dealing mainly with a large barrier, we will assume that $\hbar\omega_0\ll V^*$. This implies that B_0 is for all practical purposes the instanton action.

To evaluate the decay rate in the presence of friction one models the GLE via a harmonic bath.[2] The total Hamiltonian is of the form

$$H=\frac{1}{2M}p_q^2+V(q)+\sum_{j=1}^{N}\left[\frac{p_j^2}{2m_j}+\frac{m_j}{2}\left[\omega_j x_j+\frac{C_j}{m_j\omega_j}q\right]^2\right]. \tag{6}$$

Here (p_j,x_j) are the momenta and coordinates of the jth bath oscillator whose mass and frequency are m_j,ω_j, respectively. C_j couples the system to the bath. It is well known[16] that the equations of motion for the system (p_q,q) may be written in the form of a GLE where the time-dependent friction is identified as

$$\eta(t)=\sum_j\frac{C_j^2}{m_j\omega_j^2}\cos(\omega_j t)\ . \tag{7}$$

The external force is given in terms of the initial conditions of the bath variables (x_j^0,p_j^0) as

$$F_{\rm ext}(t)=\sum_j C_j\left[\left[x_j^0+\frac{C_j}{m_j\omega_j^2}q(0)\right]\cos(\omega_j t)+\frac{p_j^0}{m_j\omega_j}\sin(\omega_j t)\right]. \tag{8}$$

The Hamiltonian H may be decomposed as

$$H=H_{\rm sys}+H_{\rm bath},\quad H_{\rm sys}=\frac{1}{2M}p_q^2+V(q)\ . \tag{9}$$

If we assume that at time $t=0$ the bath is in thermal (or microcanonical) equilibrium such that the distribution of

initial states is given as

$$P(\underline{x}^0,\underline{p}_x^0)=e^{-\beta H_{\rm bath}}/{\rm Tr}(e^{-\beta H_{\rm bath}}) , \tag{10}$$

then one can easily show that

$$\langle F_{\rm ext}(t)\rangle \equiv {\rm Tr}[P(\underline{x}^0,\underline{p}_x^0)F_{\rm ext}(t)]=0 , \tag{11}$$

and that

$$\langle F_{\rm ext}(t)F_{\rm ext}(0)\rangle = \frac{1}{\beta}\eta(t) . \tag{12}$$

The trace operation is over the bath phase-space variables $(\underline{x},\underline{p}_x)$.

The spectral density of the bath $J(\omega)$ is[2]

$$J(\omega)=\frac{\pi}{2}\sum_j \frac{C_j^2}{m_j\omega_j}\delta(\omega-\omega_j) . \tag{13}$$

The time-dependent friction [Eq. (7)] may be expressed in terms of the spectral density

$$\eta(t)=\frac{2}{\pi}\int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega}\cos(\omega t) . \tag{14}$$

For future use we also define the Laplace transform of $\eta(t)$,

$$\hat{\eta}(\epsilon)=\int_0^\infty e^{-\epsilon t}\eta(t)dt=\frac{2}{\pi}\int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega}\frac{\epsilon}{\epsilon^2+\omega^2} . \tag{15}$$

Finally the condition

$$J(\omega)=\eta\omega\Theta(\omega) \tag{16}$$

implies that for positive time $\eta(t)=\eta\delta(t)$—that is, we regain the LE. In Eq. (15), $\Theta(\omega)$ is the Heaviside unit step function.

B. A normal mode analysis

To obtain the tunneling rate we study the properties of the Hamiltonian in the vicinity of the well and barrier of $V(q)$. For small q the system Hamiltonian is approximately harmonic,

$$V(q)\simeq\tfrac{1}{2}M\omega_0^2 q^2 . \tag{17}$$

This implies that by an orthogonal transformation the Hamiltonian may be written in separable form as the sum of $N+1$ harmonic oscillators. This is achieved in standard fashion[17] by first transforming to mass weighted coordinates

$$q'=\sqrt{M}q,\quad x_j'=\sqrt{m_j}x_j , \tag{18}$$

and then diagonalizing the $(N+1)\times(N+1)$ force constant matrix $\underset{\sim}{K}$ defined by the second derivatives of the total potential energy surface evaluated at $q'=x_j'=0$; $j=1,N$. Let λ^2 denote the eigenvalues; then the solution of the secular equation $\det(\underset{\sim}{K}-\lambda^2\underset{\sim}{I})=0$ may be written as

$$\prod_{i=1}^{N}(\omega_i^2-\lambda^2)[\omega_0^2(\Gamma^2+1)-\lambda^2] = \sum_{i=1}^{N}\frac{C_i^2}{m_iM}\prod_{j(\neq i)}(\omega_j^2-\lambda^2) . \tag{19}$$

Here

$$\Gamma^2=\frac{1}{M\omega_0^2}\sum_{j=1}^{N}\frac{C_j^2}{m_j\omega_j^2} . \tag{20}$$

Obviously, the coupling of the system to the bath modifies both the system and the bath frequencies. We will assume that the coupling to each of the bath modes is weak. This is justified since implicitly we are assuming that the main effect of the bath is changing the system and not vice versa. Thus, using first-order perturbation theory we find that the new bath frequencies λ_j may be written as

$$\lambda_j\simeq\omega_j\left[1+\frac{C_j^2}{2m_jM\omega_j^2(\omega_j^2-\omega_0^2)}\right],\quad j=1,2,\ldots,N . \tag{21}$$

Note that for bath frequencies less than the system frequencies, the coupling causes a *decrease* in frequency.

To find the new system frequency λ_0 we first note that Eq. (19) may be rewritten as

$$\lambda_0^2=\frac{\omega_0^2}{1+\frac{1}{M}\sum_{i=1}^{N}\frac{C_i^2}{m_i\omega_i^2}\frac{1}{\omega_i^2-\lambda_0^2}} . \tag{22}$$

Use of Eq. (13) gives the desired result

$$\lambda_0^2=\frac{\omega_0^2}{1+\frac{2}{\pi}\frac{1}{M}\int_{-\infty}^{\infty}d\omega\frac{J(\omega)}{\omega}(\omega^2-\lambda_0^2)^{-1}} , \tag{23}$$

and it is understood that λ_0^2 must be real and positive. In Sec. II C we will provide some explicit solutions for Eq. (23).

One can repeat the same type of analysis also in the vicinity of the barrier. Here, we assume that

$$V(q)\simeq V_0-\tfrac{1}{2}M(\omega^*)^2(q-q^*)^2 . \tag{24}$$

The only change in the secular equation [Eq. (19)] is that the expression $\omega_0^2(\Gamma^2+1)$ on the left-hand side must be replaced by $(\omega^*)^2[(\Gamma^*)^2-1]$ where

$$(\Gamma^*)^2=\frac{1}{M(\omega^*)^2}\sum_{j=1}^{N}\frac{C_j^2}{m_j\omega_j^2} . \tag{25}$$

Using first-order perturbation theory we find that the new bath frequencies are

$$\lambda_j^*\simeq\omega_j\left[1+\frac{C_j^2}{2Mm_j\omega_j^2}\frac{1}{\omega_j^2+(\omega^*)^2}\right],\quad j=1,N . \tag{26}$$

Similarly the new imaginary barrier frequency λ_0^* is given by the analog of Eq. (23)

$$(\lambda_0^*)^2=\frac{(\omega^*)^2}{1+\frac{2}{\pi}\frac{1}{M}\int_{-\infty}^{\infty}d\omega\frac{J(\omega)}{\omega}[\omega^2+(\lambda_0^*)^2]^{-1}} . \tag{27}$$

Here it is understood that $(\lambda_0^*)^2$ is real and positive. Equation (27) may be recast into an illuminating form by use of the Laplace transform of the time-dependent friction [cf. Eqs. (14) and (15)]. One may write

$$\lambda_0^* = \frac{(\omega^*)^2}{\lambda_0^* + \frac{1}{M}\hat{\eta}(\lambda_0^*)} . \tag{28}$$

Equation (28) is identical to Eq. (4.28) derived by Grote and Hynes,[11] with the identification that their reactive frequency λ_r is identical to λ_0^*. As discussed elsewhere,[10] this implies that the reactive frequency of Grote and Hynes may be interpreted as an effective barrier frequency. Instead of considering the motion in the q direction subject to friction and a random force we may think of the bath as providing a renormalized barrier whose height has not changed but whose direction in configuration space and whose imaginary frequency is determined by the coupling to the bath.

C. Dissipative tunneling at 0 K

To obtain the tunneling rate we must know the imaginary action B. In the spirit of transition-state theory we will use a harmonic approximation around the barrier to evaluate B. First, though, one must evaluate the effective barrier height E_0. As done in quantal transition-state theory one makes an adiabatic approximation for the bath modes. Since we are dealing with tunneling from the ground state of the bath, the adiabatic barrier height will be the sum of the static barrier height V_0 and the difference in zero-point energies of all modes at the barrier and at the well. Explicitly,

$$\begin{aligned} E_0 &= V_0 - \tfrac{1}{2}\hbar\lambda_0 + \sum_{i=1}^{N} \frac{\hbar}{2}(\lambda_i^* - \lambda_i) \\ &= V_0 - \tfrac{1}{2}\hbar\lambda_0 + \frac{\hbar}{2\pi M}\int_{-\infty}^{\infty} d\omega\, J(\omega)\{[\omega^2 + (\omega^*)^2]^{-1} \\ &\qquad - (\omega^2 - \omega_0^2)^{-1}\} , \end{aligned} \tag{29}$$

where to obtain the second line we have made use of Eqs. (13), (21), and (26). B is well known for tunneling through a harmonic barrier so that our final expression for the tunneling rate is the simple analog of Eq. (4)

$$\Gamma = \frac{\lambda_0}{2\pi}\exp\left[-\frac{2\pi E_0}{\hbar\lambda_0^*}\right] . \tag{30}$$

To assess the accuracy of this approximation we shall consider first Ohmic dissipation [Eq. (16)] and a cubic potential for the tunneling mode

$$V(q) = \tfrac{1}{2}M\omega_0^2\left[q^2 - \frac{q^3}{q_0}\right] . \tag{31}$$

For this potential $\omega^* = \omega_0$ and $q^* = \frac{2}{3}q_0$. The height of the barrier $V_0 = \frac{2}{27}M\omega_0^2 q_0^2$. With this choice it is easy to see [cf. Eq. (29)] that

$$E_0 = V_0 - \tfrac{1}{2}\hbar\lambda_0 . \tag{32}$$

Also $\eta(\lambda_0^*) = \eta$ so that from Eq. (28) we find that

$$\lambda_0^* = \omega^*[(1+\alpha^2)^{1/2} - \alpha] \equiv \frac{\omega^*}{b(\alpha)}, \quad \alpha = \frac{\eta}{2M\omega_0} . \tag{33}$$

The remaining parameter to be evaluated is λ_0 [Eq. (23)]. For pure Ohmic dissipation it is easy to see that $\lambda_0 = \omega_0$, the bath does not affect the well frequency. The decay rate for the cubic potential is then simply

$$\Gamma = \frac{\omega_0}{2\pi}\exp\left[-2\pi\frac{V_0 - \frac{1}{2}\hbar\omega_0}{\hbar\omega_0}b(\alpha)\right] . \tag{34}$$

Equation (34) may be recast into a more illuminating form by use of the following notation. The barrier height V_0 may be expressed in terms of a harmonic tunneling length Δq as

$$V_0 \equiv \tfrac{1}{2}M(\omega^*)^2\left[\frac{\Delta q}{2}\right]^2 , \tag{35}$$

such that Δq is the length of the tunneling path through the harmonic barrier. If we assume that $V_0 \gg \frac{1}{2}\hbar\omega_0$ then Eq. (34) may be written as

$$\Gamma(\alpha) = \frac{\omega_0}{2\pi}\exp\left[-\frac{\pi}{2}\left[\frac{M\omega_0(\Delta q)^2}{2\hbar}\right]b(\alpha)\right] . \tag{36}$$

The effect of the dissipation on the decay rate may be expressed in terms of a correction to the undamped decay rate,

$$\Gamma(\alpha) = \Gamma(0)\exp\left[-\frac{\Delta B}{\hbar}\right] , \tag{37}$$

and

$$\begin{aligned} \Delta B &\equiv \tfrac{1}{2}M\omega_0(\Delta q)^2[\Delta b(\alpha)] , \\ \Delta b(\alpha) &= \frac{\pi}{2}[b(\alpha) - b(0)] . \end{aligned} \tag{38}$$

It is of interest to compare the dimensionless damping constant $\Delta b(\alpha)$ found from the present TST approach and the corresponding $\Delta b_{\rm ins}(\alpha)$ found via instanton methods. First we note that

$$\Delta b(\alpha) \sim \begin{cases} \frac{\pi}{2}\alpha + O(\alpha^2) & \text{as } \alpha \to 0 \\ \pi\alpha - \frac{\pi}{2} + \frac{\pi}{4}\frac{1}{\alpha} + O\left[\frac{1}{\alpha^2}\right] & \text{as } \alpha \to \infty . \end{cases} \tag{39}$$

Using instanton methods one finds[2]

$$\Delta b_{\rm ins}(\alpha) \sim \begin{cases} 1.86\alpha + O(\alpha^2) & \text{as } \alpha \to 0 \\ \frac{8\pi\alpha}{9} - \frac{16}{15} + \frac{2\pi}{9}\frac{1}{\alpha} + O\left[\frac{1}{\alpha^2}\right] & \text{as } \alpha \to \infty . \end{cases} \tag{40}$$

In Fig. 2 we compare our estimate for $\Delta b(\alpha)$ as given in Eqs. (33) and (38) with the numerical results of Chang and Chakravarty,[4] an interpolation formula of Barone and Ovchinnikov,[5] and the result of Riseborough *et al.*[18] It is reassuring to see that two very different approximations for the decay rate agree so well.

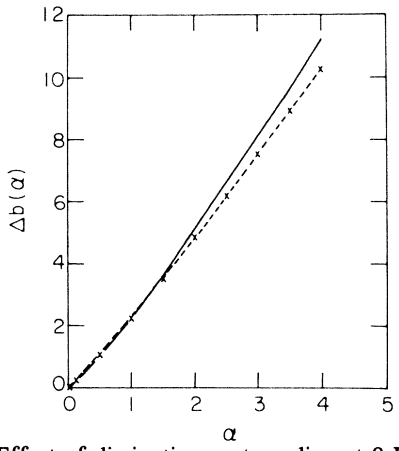

FIG. 2. Effect of dissipation on tunneling at 0 K. $\Delta b(\alpha)$ is defined in Eq. (38). The solid line is the TST result based on Eqs. (33) and (38). The dashed line is the interpolation formula of Ref. 5. The crosses are the exact numerical results of Ref. 4. The result of Ref. 18 is identical to the corresponding result of Ref. 4.

D. Memory effects

Having shown that the TST approach provides a reasonable picture, one can proceed to use this simplified approximation to analyze memory effects in dissipative tunneling.[12] From Eq. (30) one sees that the main effect of the bath is the change caused to the imaginary-barrier frequency. It is easy to show that any dissipation will always decrease λ_0^* relative to the bare-barrier frequency ω^*. Since $J(\omega)$ is by definition a positive quantity, it follows that for any positive ϵ, $\hat{\eta}(\epsilon)$ is also positive. Equation (28) may be rewritten as

$$(\lambda_0^*)^2=(\omega^*)^2-\frac{\lambda_0^*}{M}\hat{\eta}(\lambda_0^*)\ , \tag{41}$$

which proves the claim.

A more interesting aspect is a comparison of Ohmic dissipation to dissipation of a frequency-dependent bath. As an example we will consider the Drude form for the spectral density

$$J(\omega)=\frac{\eta\omega}{1+\omega^2\tau_D^2}\Theta(\omega)\ . \tag{42}$$

It follows that [cf. Eq. (15)]

$$\hat{\eta}(\epsilon)=\eta(\epsilon\tau_D+1)^{-1}\ . \tag{43}$$

The time-dependent friction may be obtained by taking the inverse Laplace transform of Eq. (43). One finds

$$\eta(t)=\frac{\eta}{\tau_D}e^{-t/\tau_D}\ . \tag{44}$$

Insertion of Eq. (43) into Eq. (28) and rearrangement gives a cubic equation for the reactive frequency

$$(\delta^*)^3\theta+(\delta^*)^2+(2\alpha-\theta)\delta^*-1=0\ , \tag{45}$$

where we used the reduced notation

$$\delta^*=\frac{\lambda_0^*}{\omega^*},\quad \theta=\omega^*\tau_D,\quad \alpha=\frac{\eta}{2M\omega^*}\ . \tag{46}$$

It is easy to see that for small values of θ

$$\delta^*(\theta)\simeq\delta^*(0)\left[1+\frac{1-[\delta^*(0)]^2}{2[\delta^*(0)+\alpha]}\theta\right], \tag{47}$$

where $\delta^*(0)$ is the value of the reduced reactive frequency for Ohmic dissipation. Equation (47) implies that short memory will increase the reactive frequency and so will cause an increase of the decay rate. For long memory ($\theta\rightarrow\infty$) one finds

$$\delta^*(\theta)\simeq 1-\frac{\alpha}{\theta}\ , \tag{48}$$

so that one returns (as expected) to the bare-barrier decay rate. It is easy to see that

$$\frac{d\delta^*}{d\theta}=\frac{\delta^*[1-(\delta^*)^2]}{3(\delta^*)^2\theta+2\delta^*+2\alpha-\theta}>0\ , \tag{49}$$

since the denominator must be positive and $0<\delta^*<1$. In other words, memory effects can only increase the tunneling rate relative to an Ohmic bath.

To complete the analysis for the Drude form of the spectral density one must evaluate the effective barrier height E_0 [cf. Eq. (29)] and the well frequency λ_0 [cf. Eq. (23)]. One finds

$$E_0(\tau_D)=V_0-\frac{\hbar\lambda_0(\tau_D)}{2}+\frac{\hbar\eta}{4\pi M}\left[\frac{\ln[(\omega^*)^2\tau_D^2]}{(\omega^*)^2\tau_D^2-1}+\frac{\ln(\omega_0^2\tau_D^2)}{\omega_0^2\tau_D^2+1}\right], \tag{50}$$

$$\lambda_0^2(\tau_D)=\frac{\eta}{2M\tau_D}+\frac{\omega_0^2}{2}-\frac{1}{2\tau_D^2}+\left[\left[\frac{\eta}{2M\tau_D}+\frac{\omega_0^2}{2}-\frac{1}{2\tau_D^2}\right]^2+\frac{\omega_0^2}{\tau_D^2}\right]^{1/2}. \tag{51}$$

From Eq. (51) it is evident that

$$\lambda_0(\tau_D)\sim\begin{cases}\omega_0(1-2\alpha^3\omega_0\tau_D) & \text{as } \tau_D\rightarrow 0\\ \omega_0(1+\alpha/\omega_0\tau_D) & \text{as } \tau_D\rightarrow\infty\ .\end{cases} \tag{52}$$

In other words, memory only weakly affects the effective well frequency. Similarly, it is easy to see that for short and long memory the third term on the right-hand side of Eq. (50) vanishes. To first order, the main effect of any memory in the system is the alteration of the reactive frequency λ_0^*.

III. TEMPERATURE EFFECTS

A. Introduction

It has been predicted by several researchers,[7,8] most notably by Grabert, Weiss, and Hänggi,[6] that thermal heating of the bath will enhance the tunneling rate. The enhancement is dependent on the spectral density of the bath but generally has the form of a power law in the ex-

ponent. It is a triumph of the theory that the $\exp(AT^2)$ dependence predicted for Ohmic dissipation has been verified experimentally.[9] The "physical" origin of the rate enhancement may be understood in terms of the instanton approach. At finite temperature, the imaginary time trajectory is no longer an infinite time trajectory; rather, it is periodic with period $\hbar\beta$. As a result, its action becomes smaller and so one has exponential enhancement of the rate. As temperature is further increased the period becomes shorter, till there are no imaginary time trajectories (except the trivial one that sits on top of the barrier forever). This temperature is then defined as the crossover temperature from quantum tunneling to thermal activation.[7,12] At higher temperatures the system behaves essentially classically, the rate-determining step is thermal activation to energies above the barrier height.

In this section we will analyze the temperature effect using the methodology of transition-state theory. At first glance we find a surprising result. Instead of an exponential increase we find an exponential *decrease* of the rate. The reason for this decrease may be understood in terms of adiabatic transition-state theory. Here one assumes that the time scales of all the bath modes are faster than those of the reactive mode. This assumption breaks down though for the low-frequency modes. This in turn leads us to consideration of a sudden transition-state theory[19] where one assumes that the time scale of the reactive mode is much faster than that of the bath.[20] As might be expected, the sudden theory predicts the same exponential power-law increase of the rate in agreement with the instanton analysis.

B. Adiabatic transition-state theory

The adiabatic assumption for the bath modes implies that if initially the jth bath oscillator is in its n_jth vibrational state, it will stay in this state forever. If at the well its frequency is λ_j and at the barrier λ_j^* then as the system moves from the well to the barrier it will have to overcome (or gain) the energy difference $(n+1/2)\hbar(\lambda_j^*-\lambda_j)$. In the adiabatic approximation, the bath modes provide an effective potential for the tunneling mode.[19] Within the adiabatic approximation, if the system is in the ground state and the bath is in state $\underline{n}$, that is n_1 quanta in mode 1, n_2 in mode 2, etc., then the tunneling rate from this state will be

$$\Gamma_0(\underline{n})=\frac{\lambda_0}{2\pi}\exp\left[-\frac{2\pi}{\hbar\lambda_0^*}\left[E_0+\hbar\sum_{i=1}^{N}n_i(\lambda_i^*-\lambda_i)\right]\right] . \tag{53}$$

Here E_0 is the ground-state barrier height, as defined in Eq. (29).

The thermal rate averaged over the bath is defined as

$$\Gamma_0(\beta)=\frac{\sum_{\underline{n}} e^{-\beta\hbar\underline{n}\cdot\underline{\lambda}}\Gamma_0(\underline{n})}{\sum_{\underline{n}} e^{-\beta\hbar\underline{n}\cdot\underline{\lambda}}} . \tag{54}$$

Here $\beta=1/k_BT$, the summation for the ith oscillator is from $n_i=0,\infty$ and the zero-point energy contribution appears in both numerator and denominator and so is already canceled. With a bit of manipulation, Eq. (54) may be brought to the form

$$\Gamma_0(\beta)=\frac{\lambda_0}{2\pi}\exp\left[-\frac{2\pi}{\hbar\lambda_0^*}E_0\right]\times\prod_{i=1}^{N}\frac{1-e^{-\beta\hbar\lambda_i}}{1-e^{-\beta\hbar\lambda_i}\exp[(2\pi/\lambda_0^*)(\lambda_i-\lambda_i^*)]} . \tag{55}$$

Denoting

$$\Gamma_0(\beta)\equiv\Gamma_0(\infty)\exp[\Delta S(\beta)] , \tag{56}$$

we find that for low temperatures (large β)

$$\Delta S(\beta)\simeq\sum_{i=1}^{N}\left[\exp\left[\frac{2\pi}{\lambda_0^*}(\lambda_i-\lambda_i^*)\right]-1\right]e^{-\hbar\beta\lambda_i} . \tag{57}$$

The frequency difference $(\lambda_i-\lambda_i^*)$ is small so that the exponent in Eq. (57) may be expanded. Using Eqs. (13), (21), and (26) we find

$$\Delta S(\beta)\simeq\frac{2}{M\lambda_0^*}\int_{-\infty}^{\infty}d\omega\,J(\omega)e^{-\hbar\beta\omega}\{(\omega^2-\omega_0^2)^{-1}-[\omega^2+(\omega^*)^2]^{-1}\} . \tag{58}$$

For Ohmic dissipation [Eq. (16)] and large β one finds

$$\Delta S(\beta)\simeq-\frac{2\eta}{M\lambda_0^*}\left[\frac{1}{\omega_0^2}+\frac{1}{(\omega^*)^2}\right]\left[\frac{1}{\hbar\beta}\right]^2<0 . \tag{59}$$

As mentioned, within the adiabatic approximation, thermal excitation of the bath leads to an exponential decrease of the rate.

The reason for the decrease is easily understood. The coupling of the bath modes to the system causes a shift of frequencies. At the well, one will always find that the coupling will lower the bath frequencies that are less than ω_0 and increase those that are above. The same holds true at the barrier, except that here the lowest eigenvalue is $(-\omega^*)^2$ so that *all* the bath frequencies are increased. The net result is that the adiabatic barrier height becomes larger for the low-frequency modes. However, at low enough temperature, one predominantly excites the low-frequency modes and the net result is an exponential decrease of the rate.

The only fallacy in the adiabatic theory is the adiabatic assumption. We just saw that the main effect at low temperatures comes from the bath modes for which $\omega_j<\omega_0$. These modes are moving slowly relative to the system so that the adiabatic assumption fails[21,22] and one must resort to a sudden approximation.

C. Sudden transition-state theory

In Sec. III B we assumed that the dissociative motion was slow. Here we assume that it is practically instantaneous. This implies that the initial bath coordinate x_j

does not have time to change. As a result, at the transition state the bath will not be in an eigenstate of the normal-mode Hamiltonian of the barrier. Instead, it will be a superposition of barrier normal-mode states. In other words, if at the well, the ith oscillator is in the n_ith state, there will be a finite transition probability from this state to the $n_i \pm 1$, $n_i \pm 2$, etc., corresponding normal-mode state of the barrier. Such transitions can effectively reduce the tunneling barrier and so increase the decay rate.

To estimate the increase one must know the transition probability. First we note that the "true" eigenstates of the Hamiltonian at the well are not eigenstates of the bath Hamiltonian as defined in Eq. (9). However, to obtain the GLE we have assumed that the bath eigenstates are in thermal equilibrium. This means that an initial state described by n_i quanta in the ith bath mode, etc., has the following wave function:

$$\psi_{\underline{n}} = \prod_{j=1}^{N} \phi_{n_j}(x_j', \omega_j) \ . \tag{60}$$

Here ϕ_{n_j} are the harmonic oscillator wave functions of an oscillator whose frequency is the unperturbed bath frequency ω_j, and whose coordinate is that of the bath mode in the prescence of the system. x_j' and q' are the mass-weighted coordinates [cf. Eq. (18)].

To obtain the transition probability one must project this wave function onto the eigenfunctions of the normal-mode Hamiltonian at the barrier. Denote the (mass-weighted) coordinate of the jth normal mode at the barrier by y_j^*. At the barrier

$$y_j^* = x_j' + \frac{C_j}{(m_j M)^{1/2}} \frac{q_*'}{\omega_j^2} \ , \tag{61}$$

where q_*' is the (mass-weighted) location of the barrier [cf. Eq. (24)]. The oscillator wave functions at the barrier are $\phi_{n_j}(y_j^*, \lambda_j^*)$. The overlap of the mth bath-mode wave function with the nth barrier wave function is then simply

$$S_{nm}^j \equiv \int_{-\infty}^{\infty} dy_j^* \, \phi_{m_j}\left[y_j^* - \frac{C_j}{(m_j M)^{1/2}\omega_j^2} q_*', \omega_j \right] \times \phi_{n_j}(y_j^*, \lambda_j^*) \left[\frac{\lambda_j^*}{\hbar} \right]^{1/2} . \tag{62}$$

Since we are assuming that the coupling of the bath modes to the system is weak, we may evaluate S_{nm}^j by perturbation theory. To first order in C_j^2 one finds

$$\begin{aligned} |S_{nn}^j|^2 &= 1 + \frac{1}{4}\frac{C_j^2}{M m_j \omega_j^2}[\omega_j^2 + (\omega^*)^2]^{-1} \\ &\quad - \frac{1}{2\hbar}\frac{C_j^2}{M m_j \omega_j^3}(q_*')^2(2n+1) \ , \\ |S_{nn-1}^j|^2 &= \frac{1}{2\hbar}\frac{C_j^2}{M m_j \omega_j^3}(q_*')^2 n \ , \\ |S_{n,n+1}^j|^2 &= \frac{1}{2\hbar}\frac{C_j^2}{M m_j \omega_j^3}(q_*')^2(n+1) \ . \end{aligned} \tag{63}$$

All other overlaps are of the order of C_j^4 and higher. Accordingly, the decay rate from the ground state of the system and the $\underline{n}$th state of the bath will be

$$\Gamma_0(\underline{n}) = \frac{\lambda_0}{2\pi} \exp\left[-\frac{2\pi}{\hbar\lambda_0^*}(V_0 - \tfrac{1}{2}\hbar\lambda_0) \right] \exp\left[-\frac{2\pi}{\hbar\lambda_0^*} \sum_i (n_i + \tfrac{1}{2})\hbar(\lambda_i^* - \omega_i) \right] \times \left\{ \prod_{i=1}^{N} |S_{nn}^i|^2 + \sum_{j(\neq i)} |S_{nn}^j|^2 \left[\exp\left[-\frac{2\pi}{\hbar\lambda_0^*}\hbar\lambda_i^* \right] |S_{n,n+1}^i|^2 + \exp\left[\frac{2\pi}{\hbar\lambda_0^*}\hbar\lambda_i^* \right] |S_{n,n-1}^i|^2 \right] \right\} . \tag{64}$$

To obtain the thermal rate at low temperatures one only needs the rate from the ground-bath state ($\underline{n} = \underline{0}$) and the first excited state, in which one bath state is excited ($n_j = 1$) and all others are in the ground state. From Eqs. (63) and (64) one infers that

$$\Gamma_0(\underline{n}' = 0, n_j = 1) = \Gamma_0(\underline{0}) \exp[-(2\pi/\lambda_0^*)(\lambda_j^* - \omega_j)] \left[1 + \frac{C_j^2 (q_*')^2}{\hbar M m_j \omega_j^3} \{ \cosh[2\pi(\lambda_j^*/\lambda_0^*)] - 1 \} \right] . \tag{65}$$

Following the same considerations as in Eqs. (54)–(57) one finds

$$\Delta S(\beta) \simeq \sum_{i=1}^{N} \left[\exp[(2\pi/\lambda_0^*)(\omega_i - \lambda_i^*)] \left[1 + \frac{(q_*')^2}{\hbar M}\frac{C_i^2}{m_i \omega_i^3} [\cosh(2\pi\lambda_i^*/\lambda_0^*) - 1] \right] - 1 \right] e^{-\hbar\beta\omega_i} . \tag{66}$$

Again, the frequency difference $(\omega_i - \lambda_i^*)$ is small. Expanding to first order in the C_i^2 terms and using Eqs. (13) and (26) we find

$$\Delta S(\beta) \simeq -\frac{2}{\lambda_0^* M} \int_{-\infty}^{\infty} d\omega \, J(\omega) \frac{e^{-\hbar\beta\omega}}{\omega^2 + (\omega^*)^2} + \frac{2}{\pi}\frac{(q_*')^2}{\hbar M} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) e^{-\hbar\beta\omega}}{\omega^2} \{ \cosh[2\pi(\omega/\lambda_0^*)] - 1 \} . \tag{67}$$

The first term on the right-hand side (rhs) provides a negative contribution which has the same origin as the negative term in the adiabatic case. However, the second term on the rhs which includes the nonadiabatic terms gives a positive contribution that overwhelms the negative contribution. Specifically using the harmonic approximation $V_0=\frac{1}{2}(\omega^*)^2(q'_*)^2$, and for an Ohmic bath, one finds that for low temperatures

$$\Delta S(\beta)\simeq\frac{2\eta}{M\lambda_0^*}(\hbar\beta\omega^*)^{-2}\left[4\pi\frac{V_0}{\hbar\lambda_0^*}-1\right]. \tag{68}$$

For the cubic oscillator potential, $V_0\gg\hbar\omega_0$, so that the rhs of Eq. (68) is positive—the nonadiabatic contribution is, as expected, the dominant factor. Moreover, by noting that for the cubic oscillator $q=\frac{2}{3}q_0$ and by assuming that $\pi/3\simeq 1$ one can easily show that Eq. (68) is just a constant factor of $2\pi^2/27\simeq 0.73$ smaller than the analogous expression [Eqs. (4.28) and (4.29) of Ref. 6(b)] obtained by Grabert and Weiss. It is also clear from Eq. (67) that if $J(\omega)\sim\omega^n$ for low frequencies then $\Delta S\sim T^{n+1}$, also in agreement with the predictions of Ref. 6.

To complete the analysis one should also consider thermal excitation of the system at the well. However, at low enough temperatures, the probability of excitation of even one quantum of $\hbar\omega_0$ will be exponentially small[6] and so would not effect the decay rate to any appreciable extent.

D. High temperatures

Thus far we have only considered the decay rate in the tunneling region. As one raises the temperature, the probability that the system will have energy greater than the barrier height becomes larger than the tunneling rate. As a result there is a crossover from tunneling to thermal activation. If the barrier height is E_0 then the probability of activation to the barrier height goes as $e^{-\beta E_0}$ while the tunneling rate goes as $\exp[-(2\pi/\hbar\lambda_0^*)E_0]$. We immediately find that the crossover temperature T_0 is given as

$$T_0=\frac{\hbar\lambda_0^*}{2\pi k_B}. \tag{69}$$

This result has been derived previously,[12,33] the only addition being that by using the transition-state theory approach we retrieve the simple derivation[24] and have no need to use functional integration.

For temperatures greater than T_0 (Ref. 25) we use the well-known transition-state-theory expression. That is, the rate is the ratio of partition functions at the transition state and at reactants. At the transition state we have N oscillators with frequencies λ_i^*; $i=1,2,\ldots,N$ and one imaginary frequency oscillator with imaginary frequency λ_0^*. The quantal partition function for the N real oscillators and the one imaginary oscillator at the transition state is

$$Z^*=\left[\prod_{i=1}^{N}[2\sinh(\hbar\beta\lambda_i^*/2)]^{-1}\right]\times\frac{\hbar\beta\lambda_0^*}{2}[\sin(\hbar\beta\lambda_0^*/2)]^{-1}e^{-\beta E_0}. \tag{70}$$

The quantal partition function at the well is given similarly as

$$Z_0=\left[\prod_{i=1}^{N}[2\sinh(\hbar\beta\lambda_i/2)]^{-1}\right][2\sinh(\hbar\beta\lambda_0/2)]^{-1}. \tag{71}$$

The thermal decay rate is

$$\Gamma(\beta)=\frac{kT}{h}\frac{Z^*}{Z_0}=e^{-\beta E_0}\frac{\lambda_0^*}{2\pi}\frac{\sinh(\hbar\beta\lambda_0/2)}{\sin(\hbar\beta\lambda_0^*/2)}\times\prod_{i=1}^{N}\frac{\sinh(\hbar\beta\lambda_i/2)}{\sinh(\hbar\beta\lambda_i^*/2)}. \tag{72}$$

In the limit of high temperatures this expression reduces to

$$\Gamma(\beta)\simeq\frac{\lambda_0}{2\pi}e^{-\beta E_0}\prod_{i=1}^{N}\frac{\lambda_i}{\lambda_i^*}\quad\text{as }\beta\to\infty. \tag{73}$$

Note, however, as shown in Ref. 10, that at the well the determinant of the force-constant matrix $\underset{\sim}{K}$ is

$$\det\underset{\sim}{K}\,|_{\text{well}}=\lambda_0^2\prod_{i=1}^{N}\lambda_i^2=\omega_0^2\prod_{i=1}^{N}\omega_i^2. \tag{74}$$

Similarly at the barrier

$$\det\underset{\sim}{K}\,|_{\text{barrier}}=-(\lambda_0^*)^2\prod_{i=1}^{N}(\lambda_i^*)^2=(-\omega^*)^2\prod_{i=1}^{N}\omega_i^2, \tag{75}$$

and we therefore regain the classical limit

$$\Gamma(\beta)\simeq\frac{\omega_0}{2\pi}\frac{\lambda_0^*}{\omega^*}e^{-\beta E_0}\quad\text{as }\beta\to\infty. \tag{76}$$

The derivation of Eq. (76) from Eq. (73) has been discussed in detail elsewhere;[10] here we just stress that Eq. (76) is identical to the well-known high-viscosity Kramers-Grote-Hynes expression[11] for the decay rate.

If one expands Eq. (72) in powers of $\hbar$ to lowest order, one finds the following result:

$$\Gamma(\beta)=\frac{\omega_0}{2\pi}\frac{\lambda_0^*}{\omega^*}e^{-\beta E_0}\times\left[1+\frac{\hbar^2\beta^2}{24}\left[\lambda_0^2+(\lambda_0^*)^2+\sum_{i=1}^{N}[\lambda_i^2-(\lambda_i^*)^2]\right]\right]. \tag{77}$$

However, the trace of the $\underset{\sim}{K}$ matrix is invariant to an orthogonal transformation so that at the well one finds

$$\mathrm{Tr}(\underset{\sim}{K})\,|_{\text{well}}=\lambda_0^2+\sum_{i=1}^{N}\lambda_i^2=\omega_0^2+\sum_{i=1}^{N}\left[\frac{C_i^2}{m_iM\omega_i^2}+\omega_i^2\right]. \tag{78}$$

Similarly, at the barrier

$$\mathrm{Tr}(\underset{\sim}{K})\,|_{\text{barrier}} = -(\lambda_0^*)^2 + \sum_{i=1}^{N} (\lambda_i^*)^2$$
$$= (-\omega^*)^2 + \sum_{i=1}^{N} \left[\frac{C_i^2}{m_i M \omega_i^2} + \omega_i^2 \right] . \quad (79)$$

Combining these results and inserting into Eq. (77) leads to

$$\Gamma(\beta) = \frac{\omega_0}{2\pi} \frac{\lambda_0^*}{\omega^*} e^{-\beta E_0} \left[1 + \frac{\hbar^2\beta^2}{24} [\omega_0^2 + (\omega^*)^2] \right] , \quad (80)$$

which is exactly the Wigner-type correction term derived by Hänggi *et al.* in Ref. 12.

Equations (76) and (80) are actually not too surprising. In Refs. 12 and 23 they are derived from Wolynes's expression[25] for tunneling at high temperatures. Wolynes uses a path-integral evaluation of the reactive flux-correlation function. Elsewhere[26] we show, using properties of the $\underset{\sim}{K}$ matrices at the well and barrier, that Eq. (72) is identical to Wolynes's expression [Eq. (7) of Ref. 25]. Thus the high-temperature results derived here are necessarily identical to the high-temperature limit of the Wolynes expression.

IV. DISCUSSION

The main message of this paper is that one can evaluate quantal rates of reaction in dissipative media by first solving for the dynamics of the discrete case and then taking the continuum limit. In the present paper we used an approximate solution for the discrete dynamics—the quantal transition-state theory. Undoubtedly, this approximation is somewhat simplistic especially at very low temperatures where a harmonic approximation for the barrier is not very good. However, we showed that it does account for the main qualitative effect—the exponential damping at 0 K and the $\exp(AT^2)$ enhancement at low temperature. Moreover, we have given a clear physical picture for the source of the enhancement. It is simple energy transfer from the bath to the dissociative mode.

The present study raises several interesting questions. For a discrete system one can, using numerical methods, find the "exact" decay rate. Basically, this involves finding a complex eigenvalue of a matrix. With present-day computing techniques it is possible to find eigenvalues of very large matrices. Presumably one should be able to make the matrix large enough so that it will approximate the continuum reasonably well. In fact, this is a crucial question with application even to gas-phase reactions—how many states does one need to effectively approximate the continuum?

Another related question has to do with the sudden and adiabatic approximations. As stressed in Sec. III, one should treat the low-frequency modes using a sudden approximation while the high-frequency modes should be treated adiabatically. For an accurate theory, though, one must know more about the transition from sudden to adiabatic dynamics. This problem is today still unresolved.[21,22,27]

ACKNOWLEDGMENTS

I would like to thank Professor P. Hänggi, Professor W. H. Miller, Professor U. Smilansky, and Professor U. Weiss for stimulating discussions and correspondence. This work has been supported by a grant of the Minerva Foundation (Munich, Germany).

[1]P. Pechukas, Annu. Rev. Phys. Chem. **32**, 159 (1981).
[2]A. O. Caldeira and A. J. Leggett, Ann. Phys. **149**, 374 (1983).
[3]S. Coleman, Phys. Rev. D **15**, 2929 (1977). The instanton methodology was also derived, in different form, by W. H. Miller, J. Chem. Phys. **61**, 823 (1974); **62**, 1899 (1975).
[4]L. D. Chang and S. Chakravarty, Phys. Rev. B **29**, 130 (1984).
[5]A. Barone and Y. N. Ovchinnikov, J. Low Temp. Phys. **55**, 297 (1984).
[6](a) H. Grabert, U. Weiss, and P. Hänggi, Phys. Rev. Lett. **52**, 2193 (1984); (b) H. Grabert and U. Weiss, Z. Phys. B **56**, 171 (1984).
[7]A. I. Larkin and Yu. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. **86**, 719 (1984) [Sov. Phys.—JETP **59**, 420 (1984)].
[8]W. Zwerger, Phys. Rev. A **31**, 1745 (1985).
[9]S. Washburn, R. A. Webb, R. F. Voss, and S. M. Faris, Phys. Rev. Lett. **54**, 2712 (1985).
[10]E. Pollak, J. Chem. Phys. (to be published).
[11]R. F. Grote and J. T. Hynes, J. Chem. Phys. **73**, 2715 (1980).
[12]P. Hänggi, H. Grabert, G. L. Ingold, and U. Weiss, Phys. Rev. Lett. **55**, 761 (1985).
[13]J. N. L. Connor and A. D. Smith, Mol. Phys. **45**, 149 (1982); S. Levit, J. W. Negele, and Z. Paltiel, Phys. Rev. C **22**, 1979 (1980).
[14]C. G. Callan, Jr. and S. Coleman, Phys. Rev. D **16**, 1762 (1977).
[15]W. H. Miller, in *Semiclassical Descriptions of Atomic and Nuclear Collisions,* edited by J. Bang and J. De Boer (Elsevier, New York, 1985), p. 9.
[16]E. Cortes, B. J. West, and K. Lindenberg, J. Chem. Phys. **82**, 2708 (1985), and references therein.
[17]E. B. Wilson Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
[18]P. S. Riseborough, P. Hänggi, and E. Freidkin, Phys. Rev. A **32**, 489 (1985).
[19]E. Pollak, J. Chem. Phys. **82**, 106 (1985).
[20]P. M. Jacobs and U. Smilansky, Phys. Lett. **127B**, 313 (1983).
[21]M. Buttiker and R. Landauer, Phys. Rev. Lett. **49**, 1739 (1982).
[22]E. Pollak, J. Chem. Phys. **83**, 1111 (1985).
[23]H. Grabert and U. Weiss, Phys. Rev. Lett. **53**, 1787 (1984).
[24]V. I. Gol'danskii, Dokl. Akad. Nauk SSSR **124**, 1261 (1959); **127**, 1037 (1959).
[25]P. G. Wolynes, Phys. Rev. Lett. **47**, 968 (1981).
[26]E. Pollak, Chem. Phys. Lett. (to be published).
[27]E. Pollak and R. E. Wyatt, Chem. Phys. Lett. **110**, 340 (1984).