Quantum Theory of Activated Events in Presence of Long-Time Memory

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The temperature dependence of kinetic processes involving activation over a potential barrier is studied in the temperature range where quantum effects are important. Deviations form the Arrhenius law are determined and a simple formula for the dominant quantum corrections is obtained. The dissipative coupling to the environment is explicitly taken into account and the role of long-time memory is emphasized.

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The Arrhenius law $\Gamma=\omega_a \exp(-V_b/k_BT)$ governs the classical kinetics of many processes in physical and chemical sciences. Here, the preexponential factor ω_a is an attempt frequency and V_b is the height of the potential barrier which should be surmounted by the kinetic process. The Arrhenius law predicts a vanishing rate Γ as the temperature T approaches absolute zero. However, quantum mechanics allows for tunneling through the potential barrier and leads to a finite rate at zero temperature. The crossover between classical and quantum behavior was observed for phenomena as diverse as diffusion of atoms on surfaces,[1] ligand migration in bimolecules,[2] decay of the zero-voltage state in current-biased Josephson junctions,[3] and domain-wall motion in ferromagnets,[4] to name only a few.

A simple criterion that characterizes the crossover temperature T_0 below which tunneling transitions are predominant over thermally activated Arrhenius-type transitions was given by Gol'danskii.[5] For parabolic barriers he found

$$T_0=\hbar\omega_b/2\pi k_B, \tag{1}$$

where $M\omega_b^2=-V_b''$ is the curvature of the potential at the barrier top and M is the mass of the tunneling particle. The Gol'danskii criterion, however, entirely disregards the environmental influence upon the tunneling rate. Recently, it has been shown that tunneling rates are indeed strongly influenced by dissipation[6] and thermal fluctuations[7] which are present whenever the tunneling system is part of a macroscopic system.

For dissipative systems the transition between thermal hopping and quantum tunneling has recently been studied by means of a functional integral approach.[8,9] At high temperatures the rate Γ is found to be affected by the fluctuation modes about the metastable minimum and the barrier top, respectively. When the temperature is lowered one of the eigenvlaues of the fluctuation modes about the barrier top decreases and reaches zero at a temperature T_0. There a new saddle-point solution of the functional integral, the so-called bounce trajectory associated with quantum tunneling,[6,7] appears. Hence, T_0 is the crossover temperature below which quantum tunneling dominates thermal hopping.[8]

For a system with long-time memory, the critical eigenvalue is given by $\lambda_1=\nu^2-\omega_b^2+\nu\hat{\gamma}(\nu)$, where $\nu=2\pi k_BT/\hbar$, and where $\hat{\gamma}(\omega)$ denotes the Laplace transform of the friction kernel $\gamma(t)$ (see below). λ_1 vanishes at the crossover temperature T_0 given by

$$T_0=\hbar\omega_R/2\pi k_B, \tag{2}$$

where ω_R is a dissipation-renormalized frequency which is given by the *largest positive* solution of the equation

$$\omega_R^2+\omega_R\hat{\gamma}(\omega_R)=\omega_b^2. \tag{3}$$

This relation holds independent of the detailed shape of the potential provided that it is parabolic in the vicinity of the barrier top. Hence, the result (2),(3) gives the dissipation- and memory-renormalized crossover temperature for transitions between two bound states as well as for decay into a continuum. Amazingly, the relation (3) was previously encountered in studies of classical activation rates for systems

with frequency-dependent damping. In the presence of memory effects the classical hopping rate reads[10]

$$\Gamma_{\rm cl}=\frac{\omega_0}{2\pi}\frac{\omega_R}{\omega_b}\exp\left(-\frac{V_b}{k_BT}\right), \tag{4}$$

where ω_0 is the frequency of small oscillations about the metastable minimum while ω_R and ω_b are defined as above. It is now readily seen that the factor ω_R/ω_b which gives the difference between the transition-state result and the correct classical rate (4) also determines the deviation of the crossover temperature T_0, Eq. (2), from the simple estimate (1).

In the case of frequency-independent damping, i.e., $\hat\gamma(\omega)=\gamma_0$, one has

$$\omega_R=(\omega_b^2+\gamma_0^2/4)^{1/2}-\gamma_0/2. \tag{5}$$

However, several recent experiments[11] on classical activation rates have shown a failure of a simple approach based on frequency-independent damping. This is due to the fact that barrier frequencies, ω_b, are often of the order 10^{12}–10^{14} sec^{-1}, and environmental forces are likely to be correlated on this time scale, thereby giving rise to memory effects. On the other hand, these memory effects will likewise be important for the determination of the transition between classical hopping and quantum tunneling. In this Letter we shall address this problem.

Let us first consider a specific model henceforth referred to as model A. A particle of mass M moving in a multistable potential $V(x_0)$ is coupled to a doubly infinite harmonic chain of particles of mass m with nearest-neighbor interactions. The Hamiltonian of the system reads

$$H=\tfrac{1}{2}M\dot x_0^2+V(x_0)+\tfrac{1}{2}m\sum_{\substack{i=-\infty\\ i\neq 0}}^{+\infty}\dot x_i^2+\tfrac{1}{2}K\sum_{i=-\infty}^{+\infty}(\delta x_i-\delta x_{i-1})^2, \tag{6}$$

where δx_i denotes the displacement of the ith particle from its equilibrium position in the absence of V. For $V(x_0)=0$, model A just coincides with the free Brownian motion model of Rubin.[12] The equations of motion read

$$M\ddot x_0=K(\delta x_1+\delta x_{-1}-2\delta x_0)-\partial V/\partial x_0, \tag{7a}$$

$$m\ddot x_i=K(\delta x_{i+1}+\delta x_{i-1}-2\delta x_i), \qquad \text{for } i\neq 0. \tag{7b}$$

Considering $K\,\delta x_0(t)$ as a given "external force," Eqs. (7b) may be solved for $x_1(t)$ and $x_{-1}(t)$. Substituting the result into (7a) and performing an average over initial conditions, one arrives at a classical equation of motion for $x(t)=x_0(t)$ of the form

$$\ddot x(t)=-M^{-1}\partial V/\partial x-\int_0^t ds\,\gamma(t-s)\dot x(s), \tag{8}$$

where

$$\gamma(t)=r\omega_L J_1(\omega_L t)/t \tag{9}$$

is a damping kernel. Hereby $r=m/M$ is the mass ratio, $\omega_L=2(K/m)^{1/2}$ is a typical frequency of the harmonic lattice, and $J_1(z)$ is a Bessel function of the first kind. Note that $\gamma(t)$ describes a dissipative mechanism with long-time memory since

$$\gamma(t)\sim r(2\omega_L/\pi)^{1/2}\sin(\omega_L t-\pi/4)t^{-3/2}$$

for $t\to\infty$.

We assume now that the potential $V(x)$ has a metastable minimum at x_0 and an adjacent barrier at x_b. For model A the temperature T_0 below which quantum tunneling through the barrier dominates over thermal hopping can be evaluated in closed form. Since the Laplace transform of (9) reads

$$\hat\gamma(\omega)=r\omega_L^2/[\omega+(\omega^2+\omega_L^2)^{1/2}], \tag{10}$$

we obtain from (3)

$$\frac{\omega_R}{\omega_b}=\begin{cases}\left(\dfrac{(1-r)+\kappa^2/2-[r^2+\kappa^2(1-r)+\kappa^4/4]^{1/2}}{(1-2r)}\right)^{1/2}, & \text{for } r\neq\frac{1}{2}\\ (1+\kappa^2)^{-1/2}, & \text{for } r=\frac{1}{2},\end{cases} \tag{11}$$

where $\kappa=r\omega_L/\omega_b$. The crossover temperature T_0 follows immediately by virtue of (2).

The memory correlation time is characterized by

$$\tau_c=\int_0^\infty dt\,t\gamma(t)/\gamma_0, \tag{12}$$

where $\gamma_0=\int_0^\infty dt\,\gamma(t)$ denotes the noise strength. For model A one has $\tau_c=\omega_L^{-1}=r/\gamma_0$ and $\gamma_0=\kappa\omega_b$. For fixed noise strength we can take the limit $r\to 0$ leading to memoryless damping. In this limit the previous ous result (5) is recovered. On the other hand, for $r\to\infty$ the frequency ω_R approaches the undamped value ω_b. We find that for given noise strength the crossover temperature T_0 increases monotonically with increasing r, that is, increasing memory correlation time (Fig. 1). Hence, the suppression of tunneling events by dissipation[6–9] is less effective in the presence of long-time memory.

As a second model, called B, we consider the archetype of a phenomenological description of memory effects, namely, the exponential memory

$$\gamma(t)=(\gamma_0/\tau_c)\exp(-t/\tau_c). \tag{13}$$

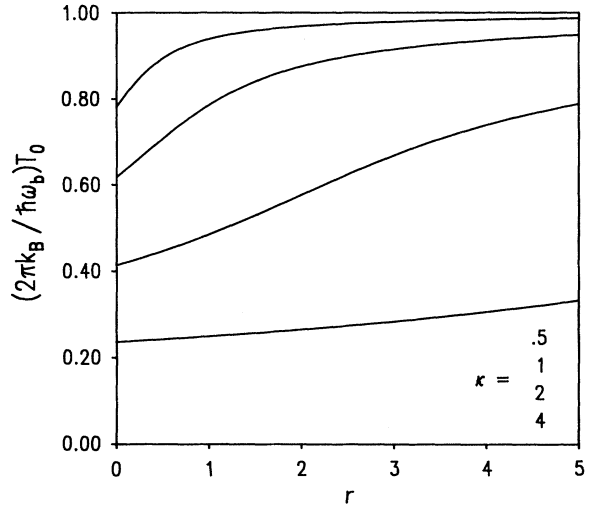

FIG. 1. The dimensionless crossover temperature $(2\pi k_B/\hbar\omega_b)T_0=\omega_R/\omega_b$ for model A depicted as a function of the mass ratio r for various values of the dimensionless noise strength $\kappa=\gamma_0/\omega_b$.

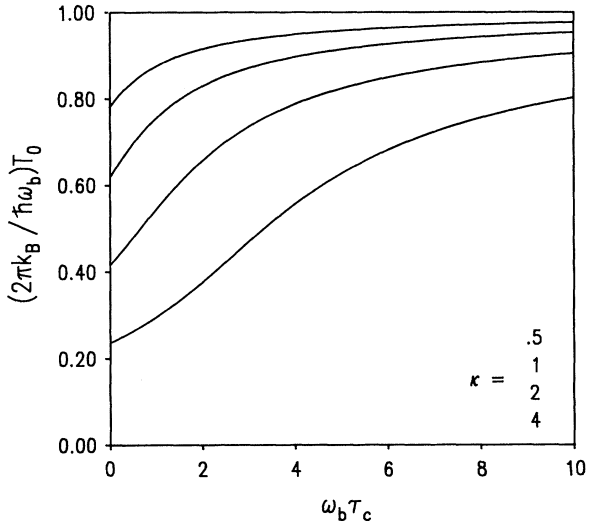

FIG. 2. Same as Fig. 1 for model B. The crossover temperature is depicted as a function of the dimensionless memory time $\omega_b\tau_c$ for various values of the noise strength $\kappa=\gamma/\omega_b$.

Now, (3) leads to a cubic equation which can be shown to possess exactly one positive solution ω_R. Again one finds that $T_0(\tau_c)$ is monotonically increasing from the memoryless Ohmic value for $\tau_c=0$ towards the undamped value (1) for $\tau_c\rightarrow\infty$ (Fig. 2).

For weakly damped systems, the transition between thermal hopping and quantum tunneling is rather sharp,[8] and the crossover temperature T_0 is readily visible on an Arrhenius plot of the rate.[1,2,4] Particularly, this is true for all molecular systems which generally are not damped by an Ohmic heat bath. A determination of T_0 gives valuable information about the form of the barrier top and the damping mechanism. More detailed information, however, can be obtained from the observation of deviations of the rate Γ from the classical value (4).

The rate Γ may be written

$$\Gamma=q\Gamma_{\rm cl}, \tag{14}$$

where $\Gamma_{\rm cl}$ is the classical rate (4) while q describes quantum effects. For $T>T_0$ one finds[8,13]

$$q=\prod_{n=1}^{\infty}\frac{n^2\nu^2+\omega_0^2+n\nu\hat{\gamma}(n\nu)}{n^2\nu^2-\omega_b^2+n\nu\hat{\gamma}(n\nu)}, \tag{15}$$

where $\nu=2\pi k_BT/\hbar$. The factor q approaches unity for $T\gg T_0$. On the other hand, q diverges exactly at the crossover temperature T_0. This divergence can be regularized by a more detailed analysis[8,9] which also takes into account the deviation of the barrier top from the parabolic form. However, the improved result is only needed in the vicinity of T_0.

The leading-order quantum corrections to Γ can be given in closed form. The product (15) may be written as an exponential of a sum of logarithms. Expanding each logarithm in terms of $1/\nu$ we obtain[14]

$$q=\exp[\tfrac{1}{6}\pi^2(\omega_0^2+\omega_b^2)\nu^{-2}+O(\nu^{-4})]. \tag{16}$$

Hence, well above T_0 the rate takes the form

$$\Gamma=\frac{\omega_0}{2\pi}\frac{\omega_R}{\omega_b}\exp\left(\frac{-V_b}{k_BT}+\frac{C}{(k_BT)^2}\right), \tag{17}$$

where $C=(\hbar^2/24)\,(\omega_0^2+\omega_b^2)$ is *independent* of the dissipative mechanism, that is, of the form of the damping kernel $\gamma(t)$. The term $\exp[(\hbar^2/24)(\omega_b/k_BT)^2]$ in (17) is just the exponential appearing in the well-known tunneling calculation by Wigner[15] and Bell[16] for a parabolic barrier in the absence of dissipation, while the exponential $\exp[(\hbar^2/24)(\omega_0/k_BT)^2]$ originates from the well dynamics. Figure 3 shows that for moderately damped systems with comparatively short memory correlation times the approximation (16) describes the enhancement of the rate by quantum effects very accurately down to temperatures where the rate Γ deviates from the classical result already by an order of magnitude. However, the approximation (16) becomes even more accurate for weaker damping and/or longer memory correlation times. Hence, an experimental determination of the coefficient C which contains valuable information about the form of the potential should not present major difficulties, in particular for weakly damped systems with non-Ohmic damping.

A "poor man's" theory for the temperature dependence of the rate Γ frequently employed in solid state

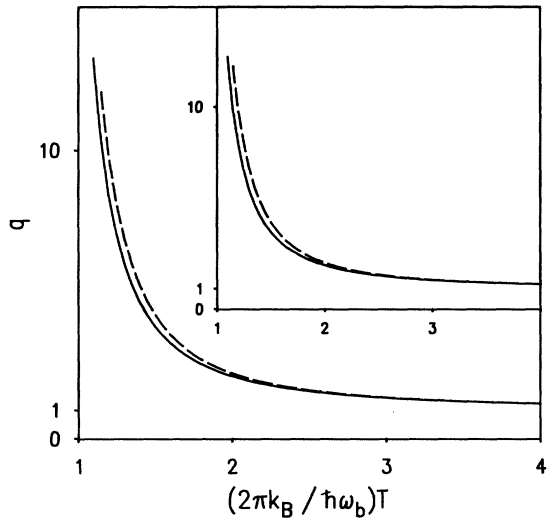

FIG. 3. The approximation (16) for the quantum correction factor q (dashed line) compared with the exact result (solid line) for model A, with parameters $\omega_b = \omega_0$, $\kappa = 0.5$, and $r = 0.25$. The inset shows the same quantities for model B, with parameters $\omega_b = \omega_0$, $\kappa = 0.5$, and $\omega_b \tau_c = 0.5$.

physics[1,4] and chemical kinetics[16] is obtained by adding the classical hopping rate and the zero-temperature WKB rate, i.e., $\Gamma = \Gamma_{cl} + \Gamma_{WKB}$. Such an approach entirely disregards the interplay between thermal and quantum fluctuations. We have shown that a more detailed analysis of the temperature dependence of Γ can yield substantial information about the metastable potential and the dissipative mechanism. This is particularly important for many problems of molecular tunneling in chemical and biological systems where little *a priori* information about the potential shape and the environmental coupling is available. The theory should be useful, e.g., for the analysis of low-temperature migration rates of ligands in biomolecules (see Ref. 2 and Beece *et al.*[11] and Doster[11]), hydrogen transfer rates in polar solvents,[17] and other reaction rates affected by memory and quantum tunneling. The theory has already successfully been applied to the analysis of decay rates of the zero-voltage state in current-biased Josephson junctions.[18] Because of their great generality and simplicity the results (2) and (17) are believed to be particularly helpful for the experimentalists.

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