Possibility of quantum effects reducing the rate of escape from a metastable well

Ulrike Griff
Institut für Mathematik, Universität Augsburg, Memminger Strasse 6, D-8900 Augsberg, Federal Republic of Germany

Hermann Grabert
Fachbereich Physik, Universität Essen, D-4300 Essen, Federal Republic of Germany

Peter Hänggi
Institut für Mathematik, Universität Augsburg, Memminger Strasse 6, D-8900 Augsberg, Federal Republic of Germany

Peter S. Riseborough
Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York, 11201
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The quantum corrections to the Kramers rate of escape from a metastable well are considered. Quantum fluctuations inside the well and quantum transmission and reflection in the barrier region are treated in the limit of weak friction. Contrary to common knowledge, the authors find a region where quantum effects suppress the full rate below the corresponding classical escape rate.

Dynamic processes hindered by a potential barrier are ubiquitous in physical and chemical sciences. Presently, we can almost celebrate the fiftieth birthday of Kramers' seminal paper[1] on the rate Γ_{cl} for thermally activated barrier crossings in the presence of frictional forces. This classical theory predicts a vanishing rate as the temperature T approaches absolute zero. Now, quantum mechanics allows for tunneling through the barrier and leads to a finite rate Γ_{qm} at zero temperature. A crude but useful formula for the temperature-dependent rate Γ frequently employed[2] is obtained by adding the classical rate and the zero-temperature tunneling rate, i.e.,

$$\Gamma = \Gamma_{cl} + \Gamma_{qm} . \qquad (1)$$

The basic philosophy behind this formula is that quantum effects open a new channel for barrier crossings thus enhancing the rate above the classical rate Γ_{cl}. For systems with moderate-to-large friction a detailed theory for the temperature-dependent rate describing the crossover from thermally activated to tunneling processes is available.[3] While this theory has made us aware of a more subtle interplay between quantum mechanical and thermal fluctuations than described by (1), the rate Γ is always larger than the classical rate Γ_{cl}. In fact, the theoretical predictions for the quantum enhancement of thermally activated barrier crossings[3] could recently be verified in experiments on Josephson systems.[4]

In this paper we shall show that contrary to common knowledge quantum effects may in fact suppress the full rate below the classical rate. The case of interest here are very weakly damped systems where thermally activated barrier crossing is governed by the energy diffusion mechanism.[1] Specifically, we shall discuss the escape from a metastable potential $U(q)$ with a minimum located at $q = q_0$ and a barrier at $q = q_b$ with the barrier energy being denoted by E_b. We shall address only the quantum corrections to the classical Kramers rate at weak damping.[5] Thus, we consider only temperatures $T > T_0$ at which thermal activation dominates over tunneling-induced escape, i.e., $T > T_0 = \hbar\omega_b / 2\pi k$ where (with a unit mass) $\omega_b = |U''(q_b)|^{1/2}$ denotes the angular frequency at the barrier top, and k is the Boltzmann constant. The generalization of Kramers' low damping result to include quantum effects was the subject of previous papers.[6–8] These authors took into account the quantum transmission $T(E)$ of the potential barrier. However, a thorough investigation of quantum corrections to the classical theory must also consider the quantum reflection $R(E) = 1 - T(E)$ and the quantum fluctuations within the well. We here consistently take all corrections into account and we find a region of parameters where the headline must be answered in the affirmative.

We assume that a particle of unit mass moves in the metastable potential $U(q)$ and obeys the classical, deterministic equation of motion with memory damping $\gamma(t)$, i.e.,

$$\ddot{q} + \frac{\partial U}{\partial q} + \int_0^t ds\, \gamma(t-s)\dot{q}(s) = \xi(t) , \qquad (2)$$

where the thermal noise $\xi(t)$ obeys the Einstein relation

$$\langle \xi(t)\xi(s) \rangle = \beta^{-1}\gamma(|t-s|) \qquad (3)$$

and $\beta = 1/kT$ denotes the inverse temperature. The classical energy diffusion equation [here we measure energy from the well bottom, i.e., $U(q_b) = E_b$] reads[9]

$$\dot{P}_t(E) = \frac{\partial}{\partial E}\Lambda(E)\left[1 + \beta^{-1}\frac{\partial}{\partial E}\right]\frac{\omega(E)}{2\pi}P_t(E) . \qquad (4)$$

$\Lambda(E)$ denotes the energy-loss coefficient

$$\Lambda(E) = \int_0^\infty ds\, \gamma(s) J(E,s) \qquad (5)$$

and $J(E,s)$ is the delayed action of the undamped trajectory, i.e.,

$$J(E,s)=\int_0^{2\pi/\omega(E)} dt\,\dot q(E,t)\dot q(E,t-s)\,, \tag{6}$$

where $2\pi/\omega(E)=\partial J(E,0)/\partial E$ is the period of the oscillation with energy E. Now, let $f_{cl}(E,t)=[\omega(E)/2\pi]P_t(E)$ denote the (classical) probability density per unit time to find the system in the barrier region near a classical turning point with energy E. Injecting particles into the well, and removing them at the barrier top, i.e., $f_{cl}(E=E_b)=0$, we find from (4) for the steady-state distribution $f_{cl}(E)$

$$\frac{\partial}{\partial E}\Lambda(E)\left[1+\beta^{-1}\frac{\partial}{\partial E}\right]f_{cl}(E)=0\,. \tag{7}$$

With the classical partition function $Z_{cl}=(\hbar\beta\omega_0)^{-1}$ and a normalization which accounts for one particle inside the well, we obtain for $f_{cl}(E)$ the boundary condition

$$f_{cl}(E)=(2\pi\hbar Z_{cl})^{-1}\exp(-\beta E),\ \text{for } E/E_b\ll 1\,. \tag{8}$$

Next we turn to the quantum case. To determine the leading quantum corrections, we may restrict ourselves to the semiclassical approximation with the energy levels being distributed quasicontinuously. Following a method outlined by Larkin and Ovchinnikov,[10] one derives for the steady-state quantum probability $f(E)$ the integral equation

$$f(E)=\int_0^\infty dE'\,P(E/E')R(E')f(E')\,, \tag{9}$$

where $P(E/E')$ is the classical conditional probability that the particle leaves the barrier region with energy E' and returns after a round trip with energy E. Upon an expansion of (9) to second order in $(E-E')$ one finds

$$T(E)f(E)=\frac{\partial}{\partial E}\Lambda(E)\left[1+\beta^{-1}\frac{\partial}{\partial E}\right]R(E)f(E)\,. \tag{10}$$

To derive (10) we made use of the detailed balance symmetry obeyed by $P(E/E')$. As opposed to previous approaches,[6-8] the right-hand side of (10) explicitly contains the quantum reflection $R(E)$. The boundary conditions for $f(E)$ are given as follows: For $E\rightarrow+\infty$, $f(E)$ approaches zero, whereas deep inside the well, $f(E)$ approaches the equilibrium value. Using the harmonic quantum partition function $Z=[2\sinh(\frac{1}{2}\hbar\beta\omega_0)]^{-1}$, $\omega_0^2=U''(q_0)$, we find

$$f(E)=\frac{\sinh(\frac{1}{2}\hbar\beta\omega_0)}{\pi\hbar}\exp(-\beta E),\quad E/E_b\ll 1\,. \tag{11}$$

The full quantum rate of escape Γ is given by the outgoing flux, i.e.,

$$\Gamma=\int_0^\infty dE\,T(E)f(E)\,. \tag{12}$$

Together, Eqs. (10)–(12) yield a solution of our problem for any given quantum transmission $T(E)$.

Here, we want to determine the quantum corrections to the classical Kramers rate formula. In this case $f(E)$ will deviate from a Boltzmann distribution only for energies near the barrier energy. Hence, we may approximate the transmission coefficient $T(E)$ by the parabolic barrier result, i.e., $T(E)=(1+\exp[-2\pi(E-E_b)/\hbar\omega_b])^{-1}$. To simplify the calculations, we now measure energy from the barrier top and use the dimensionless variable $\epsilon=\beta(E-E_b)$. Equation (10) then becomes

$$\beta(\partial/\partial\epsilon)\Lambda(\epsilon)(1+\partial/\partial\epsilon)g(\epsilon)=\exp(2\pi\epsilon/\hbar\beta\omega_b)g(\epsilon)\,, \tag{13}$$

where $g(\epsilon)=R(E-E_b)f(E-E_b)/\beta$. This equation shows that quantum effects will modify the classical distribution in an energy band of width $\hbar\omega_b$ around the barrier energy. Now, in the classical limit, nonequilibrium effects of $f_{cl}(E)$ only occur for energies of order kT below E_b. Hence, the energy dependence of $\Lambda(\epsilon)$ only matters for energies typically $\hbar\omega_b$ or kT away from E_b. Thus, for systems with high barriers, we may replace $\Lambda(E)$ by an asymptotically constant energy loss

$$\delta\equiv\Lambda(E_b)\,. \tag{14}$$

Setting $g(\epsilon)=h(\epsilon)\exp(-\epsilon/2)$, and using the transformation $z=\exp[\pi\epsilon/\hbar\beta\omega_b]$, (13) transforms into a differential equation for modified Bessel functions. With $\nu\equiv\hbar\beta\omega_b/2\pi$, the physically acceptable solution reads

$$g(\epsilon)=A\exp(-\epsilon/2)K_\nu[\hbar\omega_b(\beta/\delta)^{1/2}\exp(\epsilon/2\nu)/\pi]\,, \tag{15}$$

where A is determined from (11), i.e.,

$$A=\frac{2\sinh(\frac{1}{2}\hbar\beta\omega_0)\exp(-\beta E_b)}{\pi\hbar\beta\Gamma(\nu)}\left[\frac{\nu^2}{\beta\delta}\right]^{\nu/2}. \tag{16}$$

Next, combining (10) and (12), we find that the quantum rate Γ equals the plateau value

$$\Gamma=-\lim_{\epsilon\ll -1}\beta\delta(1+\partial/\partial\epsilon)g(\epsilon)\,, \tag{17}$$

which the right-hand side of (17) approaches below the barrier. Inserting (15), we thus obtain with $\nu_0=\hbar\beta\omega_0/2\pi$ the answer for the quantum rate

$$\Gamma=\frac{\omega_0}{2\pi}\frac{\sinh(\pi\nu_0)}{\pi\nu_0}\frac{\pi\nu}{\sin(\pi\nu)}\left[\frac{\nu^\nu}{\Gamma(1+\nu)}\right]^2\times(\beta\delta)^{1-\nu}\exp(-\beta E_b)\,, \tag{18}$$

which holds uniformly both for $\nu^2\ll 1$ and $\beta\delta\ll 1$. With the appropriate substitution for $\delta=\Lambda(E_b)$, the rate formula (18) holds both for Ohmic friction, $\gamma(t)=2\gamma\delta(t)$, i.e., $\delta=\gamma J(E_b)$, and memory friction. At very high temperatures ($\nu,\nu_0\ll 1$), (18) approaches the Kramers result[5] $\Gamma_{cl}=(\omega_0/2\pi)\beta\delta\exp(-\beta E_b)$.

The leading quantum corrections Q, with $\Gamma\equiv Q\Gamma_{cl}$, are given by

$$Q=\exp\left\{\frac{\hbar\beta\omega_b}{2\pi}\left[2C+\ln\left[\frac{\hbar^2\omega_b^2\beta}{4\pi^2\delta}\right]\right]+\tfrac{1}{24}(\hbar\beta\omega_0)^2\right\}, \tag{19}$$

where $C=0.5772\ldots$ is Euler's constant. Clearly, for $\nu^2<\beta\delta\ll 1$, the logarithmic term in the exponent of (19) gives a negative contribution that may compensate the other positive terms. Hence, well within the range of validity of our formula, there is a region where the correction factor Q is smaller than 1. In this region in parameter space quantum reflection above the barrier dominates over quantum transmission, thus leading to a net *reduction* of the rate below its classical value. We also remark that the leading correction in (19) is proportional to $\hbar$ pointing to nontrivial quantum corrections since the underlying Hamiltonian contains only $\hbar^2$. In conclusion, the answer to the headline is yes. Is the reduction measurable? For Josephson systems where the metastable potential has equal curvature at the barrier top and in the well minimum the reduction is always small and not very likely to be readily observable despite the fact that the weak-damping regime is experimentally accessible.[11] The reduction is more pronounced, however, for systems with very flat barriers as they occur, e.g., in absorption-desorption problems on surfaces.

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