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Quantum decay rates for driven barrier potentials in the strong friction limit

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Quantum decay rates for barrier potentials driven by external stochastic and periodic forces in the strong damping regime are studied. Based on the quantum Smoluchowski equation derived recently by Ankerhold, Pechukas, and Grabert [Phys. Rev. Lett. **87**, 086802 (2001)] explicit analytical and numerical results are presented for the case of the resonant activation phenomenon in a bistable potential and the escape from a metastable well with oscillating barrier, respectively. The significant impact of quantum fluctuations is revealed.

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INTRODUCTION

Escape over a high potential barrier driven by thermal noise is of fundamental interest in physics and chemistry [1]. And it is meanwhile well understood: after a transient period of time the decay is governed by a rate constant, which in the simplest classical case is of Arrhenius type provided the decaying system stays in thermal equilibrium far from the barrier. What happens if due to additional external forces the system is far from thermal equilibrium? This question has recently gained much attention for classical barrier transport in the strong damping limit (Smoluchowski limit). Important examples are stochastic resonance [2], resonant activation in biochemical reactions and tunnel diodes [3], or directed motion in ratchet systems [4]. While even the classical physics of such phenomena is in many cases not yet completely explored, much less is known about corresponding quantum systems.

Namely, in contrast to the classical range, tractable equations of motions of quantum dissipative systems also for strong damping and low temperatures do not exist [5]. The path integral representation provides an exact expression for the time dependent density matrix, but even a numerical evaluation is, in general, prohibitive. Particular progress has been made with the development of master equations [6] and the quasiadiabtic propagator approach [7]. This way, extensive studies exist for bistable systems driven by external periodic forces [8]. However, these and related techniques require—either to be valid or to be practicable—that energy level broadening due to friction remains sufficiently small (depending on the approach) so that for the relevant dynamics the Hilbert space of the bare system can be reduced to a few lowest lying eigenstates. Of course, this condition fails in the domain of very strong friction. Recently we showed [9] that exactly in this range crucial simplifications arise. As in the classical Smoluchowski limit, momentum equilibrates on time scales much faster than any other time scales; accordingly, an equation of motion—the so-called quantum Smoluchowski equation—can be derived for the position probability distribution from the exact path integral result. The influence of quantum fluctuations turns out to be substantial. Hence, for the first time we are now in a position to explore driven barrier escape for arbitrary overdamped quantum systems [10].

Here, we focus on two paradigmatic examples, namely, a bistable potential with a barrier fluctuating randomly in time and a metastable well driven by a periodic monochromatic force. Classically, for the first case the phenomenon of resonant activation is characteristic, while for the second one a substantial rate enhancement by driving is observed. We elucidate the significant impact of quantum fluctuations on both processes.

QUANTUM SMOLUCHOWSKI

For a system coupled to a heat bath environment the reduced density matrix follows from $\rho(t)=\mathrm{Tr}_b[W(t)]$ where $\mathrm{Tr}_b[\cdot]$ denotes the trace over bath degrees of freedom and $W(t)$ is the time dependent density matrix of the system and bath compound. Within the path integral approach a formally exact expression for the position representation $\rho(q,q',t)$ can be given [5]. Now, in Ref. [9] it was shown that within the quantum Smoluchowski range (QSR), i.e.,

$$\gamma/\omega_0^2 \gg \hbar\beta, 1/\gamma \quad \text{and} \quad \hbar\gamma \gg k_B T, \tag{1}$$

the position distribution $P(q,t)=\rho(q,q,t)$ is well determined by a simple time evolution equation coined quantum Smoluchowski equation (QSE). Here γ denotes the friction constant, ω_0 the ground state frequency in a potential $V(q)$, and $\beta=1/k_BT$ inverse temperature. This limit is opposite to the classical Smoluchowski range where $\omega_0\hbar\beta \ll 1$ and $k_BT \gg \hbar\gamma$. The QSE reads $\dot{P}=(1/M\gamma)\partial_q \hat{L}_{\mathrm{qm}} P$ where

$$\hat{L}_{\mathrm{qm}} = V' + \lambda V'''/2 + k_B T \partial_q (1+\lambda\beta V'') \tag{2}$$

with $V'=dV(q)/dq$. Further,

$$\lambda = (\hbar/\pi M\gamma)\ln(\hbar\beta\gamma/2\pi) \tag{3}$$

accounts for the dominating impact of quantum fluctuations. Equivalently, the dynamics of an overdamped quantum systems can be seen as a classical Smoluchowski dynamics with an effective potential $V_{\mathrm{eff}}=V+\lambda V''/2$ and an effective diffusion term $D_{\mathrm{eff}}=k_BT(1+\lambda\beta V'')$. Note that quantum fluctuations in Eq. (2) are of order $\ln(\gamma)/\gamma$ and thus, are much larger than classical finite friction corrections that are of order $1/\gamma^2$.

STATIC BARRIERS

We first recall results for the decay rate in static barrier potentials. There, adjacent to the barrier at $q=q_b$ we assume a well region around a minimum at $q=q_0$ such that the barrier height V_b obeys $V_b \gg k_B T, \hbar\omega_0$. Moreover, we take smooth potentials for granted. Then, in Ref. [9] it was shown that the escape rate out of the well is given within the QSR as

$$\Gamma_{\rm QSR} = \frac{\sqrt{V''(q_0)|V''(q_b)|}}{M\gamma}\, e^{-\beta V_b} \times \exp\{\lambda\beta[V''(q_0)+|V''(q_b)|]\}. \tag{4}$$

The substantial rate increase due to quantum fluctuations well agrees with the exact result [9] (in the limit $\beta V_b \gg 1$). Let us now turn to barrier potentials driven by external forces.

FLUCTUATING BARRIERS

Thermally activated diffusion over a potential barrier that fluctuates randomly in time has evoked much interest recently. In the classical Smoluchowski limit it was shown that the interplay between relaxation, by thermally activated barrier passage, and fluctuation, by correlated external noise, leads to a strongly enhanced reaction rate in the resonant activation regime [3]. Here, we present the first study to this phenomena for corresponding quantum systems. We look at the process of dichotomous barrier fluctuations with a rate η in a symmetric double well and search for the ultimate decay rate $k(\eta)$ of relaxation to equilibrium. Since for this problem an analytical classical theory was derived [11], we can adapt the general technique. In particular, in the case of high barriers considered here, it was shown that rates from the analytical theory are in excellent agreement with numerically exact results [11].

If the potential flips randomly between two surfaces V_+ and V_- at a rate η, we need two probability densities $P_+(q,t)$ and $P_-(q,t)$ with $P_+[P_-]$ being the density to find a particle at time t at position q and the potential in state $V_+[V_-]$. Accordingly, the two-dimensional QSE reads $\partial_t\vec{\rho} = S_\eta\vec{\rho}$ with $\vec{\rho}=(P_+,P_-)$ and

$$S_\eta = \begin{pmatrix} \hat{L}_+ - \eta & \eta \\ \eta & \hat{L}_- - \eta \end{pmatrix}. \tag{5}$$

Here, $\hat{L}_\pm = (1/M\gamma)\partial_q \hat{L}_{\rm qm}^{(\pm)}$ with potentials $V_\pm = U \pm g$. The function g describes the barrier modulations and is assumed to have the following properties: it is symmetric around the barrier top at $q=q_b$ and monotone decreasing away from it; outside some finite range around the top it is zero. In particular, $V_+ = V_-$ around the well minima located at $q=\pm q_0$. Further, its maximum $g(q_b)$ is small compared to the barrier height U_b but not necessarily small compared to $k_B T$. The ultimate decay rate $k(\eta)$ is now defined as the least negative eigenvalue to the operator S_η.

In the adiabatic range of small η, qualitatively, there is not much change to the classical result. After each flip the system has enough time to relax to equilibrium inside the well regions of the instantaneous potentials. Consequently, the rate follows as the least negative eigenvalue of S_η when replacing the operators $\hat{L}_{\rm qm}^{(\pm)}$ by the static quantum rates $-\Gamma_\pm$ for the individual potentials, see Eq. (4). Hence, similarly to the classical rate we obtain

$$k(\eta) = (\Gamma_+ + \Gamma_-)/2 + \eta - [\eta^2 + (\Gamma_+ - \Gamma_-)^2/4]^{1/2}. \tag{6}$$

As expected $k(0)=\Gamma_+$ and $k(\eta)\to k_{\rm res} \equiv (\Gamma_+ + \Gamma_-)/2$ for $\eta\to\infty$.

More interesting is the region of moderate to fast barrier flippings, i.e., $\eta \gg k(\eta)$. There, the procedure is to solve $S_\eta\vec{\rho}\approx 0$ with the boundary condition $\vec{\rho}(q_b)=0$ so that due to symmetry $\vec{\rho}(q) = -\vec{\rho}(-q)$. This way, we solve the equation for the equilibrium eigenfunction, i.e., with zero eigenvalue, but under boundary conditions corresponding to the relaxation eigenfunction with the least negative eigenvalue. As long as $k(\eta)$ is the smallest frequency in the system this approximation is justified. Now, in the limit of a high barrier we employ a semiclassical type of ansatz $\vec{\rho} = \vec{z}\exp(-\phi/k_B T)$ with an effective potential ϕ and a prefactor accounting for terms of higher order in $k_B T$. To obtain the dominant exponential contribution we do the following: The two coupled second order differential equations corresponding to Eq. (5) are transformed to four coupled equations of first order. This linear system is solved by diagonalizing the coefficient matrix. The relevant eigenvalue turns out to be $-\phi'$ and is determined by the solution to the cubic equation

$$2k_B T\eta(1-\lambda\beta U'')(\tilde{U}'-\phi') = \phi'(\tilde{V}'_+ - \phi')(\tilde{V}'_- - \phi') \tag{7}$$

obeying $0 \leq \phi'\tilde{U}' \leq (\tilde{U}')^2$. Here, we introduced effective potentials that are related to the bare potentials by $\tilde{Y} = Y + (3\lambda/2)Y'' - (\lambda\beta/2)(Y')^2$ for $Y=U$, V_+, and V_-. Of course, by formally putting $\lambda=0$ in Eq. (7) one regains the known classical result [11]. For the prefactor we solve perturbatively the differential equations $S_\eta\vec{\rho}=0$. Since this scheme works similarly as in the classical case we refer to the literature for further details [11].

For the rate one first derives from $S_\eta\vec{\rho} = -k\vec{\rho}$ that $k(\eta) \approx [P'_+(q_b) + P'_-(q_b)]/[M\gamma\beta\int_{-\infty}^{q_b}(P_+ + P_-)]$. Then, inserting the results for $P_\pm$ we gain

$$k(\eta) = [\Omega(\eta)\omega_0/\gamma]e^{-\beta\phi(q_b)} \times \exp\{\lambda\beta[U''(q_0) - |\phi''(q_b)|/2]\} \tag{8}$$

with $\omega_0^2 = U''(q_0)/M$. The frequency $\Omega(\eta)$ coincides with the classical result [11] and thus, its lengthy expression is omitted here. However, quantum fluctuations strongly affect the dominant exponential factor. In the limits of very slow and very fast barrier fluctuations λ-dependent terms lead basically to a renormalization of temperature. For small η we derive from Eqs. (8) and (5) that $k(\eta)\to\Gamma_+$. In the region of motional narrowing $\eta\to\infty$ it is $k(\eta)\to\Gamma_U$ where Γ_U is given by Eq. (4) with V replaced by the average potential U.

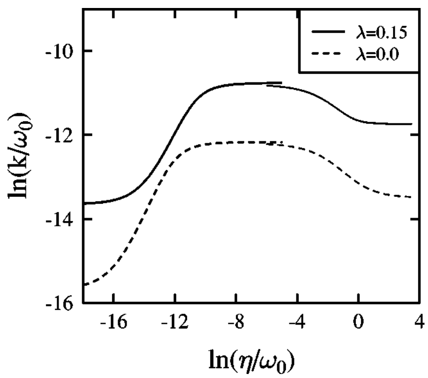

FIG. 1. Quantum (solid) and classical (dashed) decay rate vs the barrier fluctuation rate in a double well potential with height $U_b/\hbar\omega_0 = 4$ and $\omega_0\hbar\beta = 3$. Shown are the adiabatic approximation Eq. (6) (thick) and the effective potential approach Eq. (8) (thin).

To study the ultimate quantum decay rate for all values of η we evaluated Eq. (6) and Eq. (8) with Eq. (7) numerically. Results are displayed in Figs. 1 and 2. Besides an obvious rate increase, the major effects of quantum fluctuations are to *substantially decrease* the relative height as well as the width of the resonant activation maximum. The shrinking relative height $k_{\rm res}/\Gamma_+ = (\Gamma_+ + \Gamma_-)/2\Gamma_+$ is a consequence of effectively reduced barrier modulations $g(q_b) \to g(q_b)[1 - \lambda|g''(q_b)|]$. The decreasing width of the plateau range is ascribed for sufficiently large η to the fact that then quantum fluctuations on the left hand side in Eq. (7) lead to an effectively enhanced flipping rate $\eta \to \eta[1 + \lambda\beta|U''(q_b)|]$ near the barrier top. For intermediate fluctuation rates the cubic Eq. (7) gives rise to a nonlinear dependence on λ leading to an intimate relation between external barrier fluctuations and intrinsic quantum fluctuations.

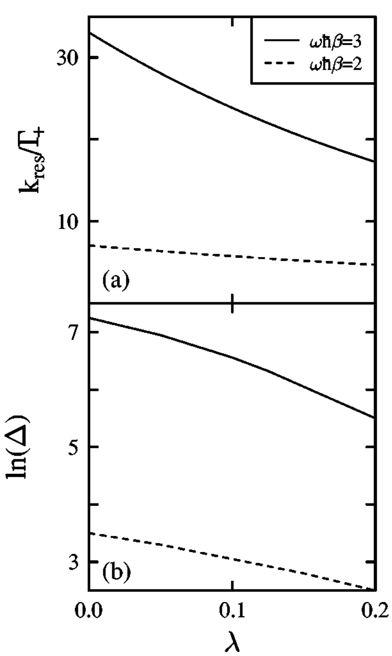

FIG. 2. (a) Ratio of the resonant activation rate $k_{\rm res}$ to $k(0) = \Gamma_+$ and (b) width of the resonant activation maximum vs λ for two different temperatures. Other parameters as in Fig. 1.

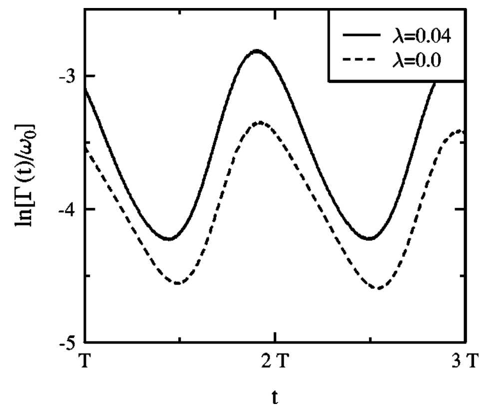

FIG. 3. Time dependent quantum (solid) and classical (dashed) rate $\Gamma(t)$ for $\Omega/\omega_b = 2\pi$, $A = a/\sqrt{\hbar M\omega_b^3} = 0.5$, $\omega_b\hbar\beta = 3$, and $V_b/\hbar\omega_b = 4/3$.

OSCILLATING BARRIERS

A prominent example for a system far from equilibrium is a metastable potential driven periodically by an external force. Recently, in the classical Smoluchowski limit, decay rates were studied for weak and moderate to strong driving as well [12–14]. Here, we explore the corresponding quantum problem by calculating numerically the time dependent decay rate $\Gamma(t)$ from Eq. (2) for long times. The time dependent potential is chosen as $V(q,t;a) = V_0(q) + qa\sin(\Omega t)$ with a static barrier $V_0(q) = -(M\omega_b^2/2)q^2[1 + q/q_0]$. The static barrier top is located at $q = 0$, the well minimum at $q = -2q_0/3$, and the static height is $V_b/M\omega_b^2 = 10q_0^2/27$. For the driven case ($a \neq 0$) the location of the barrier top moves periodically in time with $q_b(t) \approx (a/M\omega_b^2)\sin(\Omega t)$. Consequently, as in the classical case, the rate $\Gamma(t) = -\dot{N}(t)/N$ with $N(t) = \int_{-\infty}^{q_b(t)} P(q,t)$ also oscillates in time. Then, from $\dot{P} = (1/M\gamma)\partial_q \hat{L}_{\rm qm} P$ we derive up to negligible corrections

$$\Gamma(t) = -\frac{k_B T}{M\gamma}\{1 + \lambda\beta V_0''[q_b(t)]\}\frac{\partial_q P[q_b(t),t]}{N(t)}. \qquad (9)$$

Note that for high barriers and times $t \ll 1/\Gamma(t)$ one can put $N(t) \approx 1$ if initially one starts from a normalized distribution $P(q,0)$.

High precision numerical results based on the QSE [Eq. (2)] are shown in Fig. 3 for the time dependent rate $\Gamma(t)$. Apart from a rate enhancement the influence of quantum fluctuation is twofold: first, $\Gamma(t)$ tends to be more symmetric around its minima and maxima and second, both extrema are slightly shifted to the left. In Ref. [13] Lehmann *et al.* developed a nice theory for the pure classical case ($\lambda = 0$) based on an asymptotic expansion for $\beta V_b \gg 1$ (for a related theory see also Ref. [14]). There, one finds a weak dependence of the location of the extrema on temperature. Since locally in position space the λ dependence can be partially incorporated in an effective temperature, we attribute the observed shift in the quantum case to a similar kind of process. However, what is not possible is to mimic the numerical data for finite λ by an effective temperature only.

The averaged rate

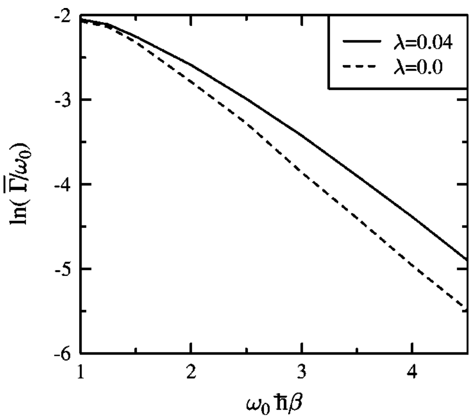

FIG. 4. Arrhenius plot of the time-averaged quantum (solid) and classical (dashed) rate $\overline{\Gamma}$. Other parameters as in Fig. 3.

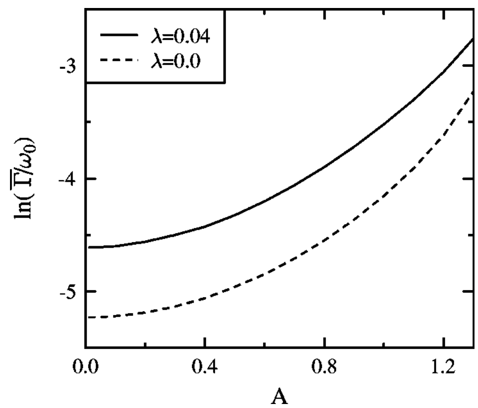

FIG. 5. Time-averaged quantum (solid) and classical (dashed) rate as a function of the driving amplitude $A=a/\sqrt{\hbar M\omega_b^3}$. Other parameters as in Fig. 3.

$$\overline{\Gamma}=\lim_{\omega_b t>1}\frac{1}{T}\int_t^{t+T}dt'\,\Gamma(t') \tag{10}$$

as a function either of inverse temperature or driving amplitude is depicted in Figs. 4 and 5. Again the rate enhancement is significant. Interestingly, while on a logarithmic scale the classical rate shows a simple linear behavior as a function of $\omega_0\hbar\beta$ for sufficiently low temperatures (according to the well-known exponential Arrhenius law), the quantum rate exhibits a weak nonlinearity. Of course, in the high temperature limit quantum corrections become negligible. As a function of the driving amplitude the difference between quantum and classical rate shrinks with increasing amplitude. As for strong driving most of the escape happens to occur when the barrier is low and thus, is much less effective in hindering the transport, the effect of a λ induced rate enhancement due to a smaller barrier height in $V_{\rm eff}=V+\lambda V''/2$ is diminished.

What about an analytical theory? We think that, in principle, the classical theory [13,14] can be generalized to the quantum case, a detailed analysis, however, still needs substantial work. Even then an explicit evaluation in closed analytical form for all realistic potentials seems prohibitive. Our intention here is to give for a highly nontrivial example a first account about the significant role of quantum fluctuations in the QSR.

To summarize we have studied for two important examples quantum transport over driven barrier potentials in the strong friction limit. For the case of a fluctuating bistable potential we explored the impact of quantum fluctuations on the resonant activation phenomenon. In a case of a metastable potential driven externally by a periodic force we found a sensitive behavior of the decay rate on the relevant parameters. These notable findings may stimulate further studies of the quantum Smoluchowski equation in physics and chemistry as well.

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[1] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[2] L. Gammaitoni, P. Hänggi, P. Jung, and F. Marchesoni, Rev. Mod. Phys. **70**, 223 (1998).
[3] C. R. Doering and J. C. Gadoua, Phys. Rev. Lett. **69**, 2318 (1992); P. Pechukas and P. Hänggi, *ibid.* **73**, 2772 (1994); P. Reimann, T. Elston, *ibid.* **77**, 5328 (1996); R. N. Mantegna and B. Spagnolo, *ibid.* **84**, 3025 (2000).
[4] R. D. Astumian, Science **276**, 917 (1997).
[5] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 1999).
[6] W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).
[7] D. E. Makarov and N. Makri, Chem. Phys. Lett. **221**, 482 (1994).
[8] M. Thorwart and P. Jung, Phys. Rev. Lett. **78**, 2503 (1997); M. Grifoni and P. Hänggi, Phys. Rep. **304**, 230 (1998), and references therein; M. Thorwart, M. Grifoni, and P. Hänggi, Phys. Rev. Lett. **85**, 860 (2000).
[9] J. Ankerhold, P. Pechukas, and H. Grabert, Phys. Rev. Lett. **87**, 086802 (2001).
[10] As in the classical Smoluchowski limit steep potentials are excluded from this study.
[11] J. Ankerhold and P. Pechukas, Physica A **261**, 458 (1998); Phys. Rev. E **58**, 6968 (1998).
[12] V. N. Smelyanskiy, M. I. Dykman, and B. Golding, Phys. Rev. Lett. **82**, 3193 (1999).
[13] J. Lehmann, P. Reimann, and P. Hänggi, Phys. Rev. Lett. **84**, 1639 (2000).
[14] R. S. Maier and D. L. Stein, Phys. Rev. Lett. **86**, 3942 (2001).