Theory of non-Markovian activated rate processes for an arbitrarily shaped potential barrier

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The Mel'nikov-Meshkov (MM) turnover theory [J. Chem. Phys. **85**, 1018 (1986)] for the escape rate of a particle from a metastable state is extended to a non-Markovian activated rate process in a potential with an arbitrary barrier shape. The key points of the extension are a generalized expression for the Kramers-Grote-Hynes transmission coefficient and a properly defined energy loss of the particle per oscillation. The former is derived by approximately solving the respective Fokker-Planck equation, while the latter is obtained from the deterministic particle dynamics. The resulting overall rate expression interpolates the correct limiting behavior for both weak and strong friction. Its validity is tested by comparing with exact numerical rates in potentials with parabolic, cusped, and quartic barriers. In all these cases we obtain excellent agreement between the theory and estimates of the rates from numerical calculations. [S1063-651X(98)04509-7]

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I. INTRODUCTION

The thermally activated escape of a system from a metastable state by crossing a barrier represents a decisive step in the dynamics of various realistic processes. Ever since the pioneering contribution of Arrhenius, the evaluation of the escape rate has become one of the most fundamental problems in physics and chemistry (for reviews of the field, see Refs. [1] and [2]). The modern theory of activated rate processes is essentially due to Kramers [3], who realized the role of the interaction of the system with a surrounding heat bath and fully took it into account for a simple model. The Kramers model consists of a single mechanical particle moving on a metastable potential and interacting with a heat bath. The heat bath causes a velocity proportional friction force and a random force, the former extracting and the latter supplying energy. The correlation time of the random force is supposed to be vanishingly small such that a Markovian process results for the considered system. Kramers showed that depending on the coupling strength (friction coefficient) γ, there are two qualitatively different mechanisms determining the escape process. In the weak friction limit the energy of the particle is an almost conserved quantity undergoing a slow diffusion process, so that the rate is determined by the exchange of energy between the particle and the bath (the so-called energy diffusion regime). On the other hand, for moderate to large friction the heat bath couples sufficiently strongly to maintain a thermal equilibrium within the well. The nonequilibrium effects associated with the escape dynamics are then restricted to the immediate vicinity of the barrier top. Consequently, the passage over the barrier is the rate determining step (the spatial diffusion regime). In the former limit the rate increases with the friction coefficient while in the latter case it decreases with increasing γ. Kramers derived explicit expressions for the escape rate in these two regimes and noted the existence of a turnover region.

The turnover problem was actively studied in the 1980s. Many different formulas were suggested to bridge the two limiting Kramers results [1]. The particular advance in this area can largely be attributed to Mel'nikov and Meshkov (MM) [4]. These authors developed a beautiful approach for the weak damping regime. The basic steps of the approach are reducing the problem to an integral equation in energy variables and solving this equation by the Wiener-Hopf method. An expression for the rate that holds at arbitrary damping was obtained by using an *ad hoc* multiplicative factor to assure the changeover from the weak damping to a strong one [4].

Since the Markovian assumption is not always met in physical applications, generalized Langevin equations proposed by Zwanzig [5] have been introduced to cover more general environments that cause random forces with finite correlation times [6]. A systematic solution of the non-Markovian turnover problem was given by Pollak, Grabert, and Hänggi (PGH) [7], who rederived the MM turnover formula *without* any *ad hoc* bridging. For achieving this, PGH elaborated a theory that combines the normal mode technique, as well as the approach by Mel'nikov and Meshkov. Recently, both turnover theories have found various generalizations to cases with state-dependent friction [8] and multidimensional systems [9].

All the investigations mentioned above make extensive use of a parabolic approximation for the barrier, $U(x) = -\frac{1}{2}\omega^2 x^2$, though parabolic barriers are not the generic case in real activated rate processes. For example, the barrier of charge transfer reactions is often of a cusp-shaped form [10]. Kramers [3] also considered the case of a symmetric cusped barrier, $U(x) = -a|x|$. However, the rate expression he derived in this case is valid only in the strong friction (Smoluchowski) limit. Various rate expressions have been derived that agree in the limiting case of strong friction with the Kramers result for a cusped potential and, in the limit of weak friction with the rate obtained from the transition state theory (TST) [11–15]. An analogous interpolating formula is known for a quartic barrier, $U(x) = -\frac{1}{4}ax^4$ [1]. Only very recently, Berezhkovskii *et al.* [16] have extended this formula to an arbitrarily shaped barrier, $U(x) = -(a/\alpha)|x|^\alpha$. Their generalization agrees with the known rate expressions for nonparabolic potentials, but fails to reproduce the exact Kramers result for a parabolic barrier. Yet another disadvan-

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tage of the above-mentioned formulas is that these are all valid for the particular case of Ohmic (Markovian) dissipation and only in the spatial diffusion regime.

The aim of this paper is to present a rate expression for a barrier of arbitrary shape, which is valid for any dissipation and approaches the correct limiting behavior for both weak and strong friction. The problem is outlined in Sec. II, together with the PGH rate expression. Two approaches for its generalization are discussed in Sec. III. In Sec. IV the theoretical predictions are compared with exact numerical rate constants in different types of cusped and smooth potentials. Section V ends the paper with final remarks.

II. PGH TURNOVER THEORY

As a preliminary we outline the problem and briefly review the central result of the PGH turnover theory. This theory deals with the generalized Langevin equation (GLE) for a particle with mass weighted coordinate x moving on a potential $V(x)$ under the influence of a time dependent friction $\gamma(t)$. In the simplest one-dimensional case, the GLE reads [5]

$$\ddot{x}=-V'(x)-\int_0^t ds\,\gamma(t-s)\dot{x}(s)+f(t), \tag{2.1}$$

where the Gaussian zero mean random force $f(t)$ is related to the friction kernel through the second fluctuation dissipation theorem

$$\langle f(t)f(s)\rangle=\beta^{-1}\gamma(t-s). \tag{2.2}$$

In the above, the dot and prime denote the derivatives with respect to time and position, respectively, and β is the inverse energy available from the thermal bath. The potential is assumed to have a well with minimum at $x_w<0$, separated from the continuum by a barrier at $x=0$ of height $E=-V(x_w)$. Hereby we set for convenience $V(0)=0$. Finally, the static friction coefficient γ is defined by

$$\gamma=\int_0^\infty dt\,\gamma(t). \tag{2.3}$$

The quantity of interest is the escape rate Γ of the particle from the well. It can always be written in the form

$$\Gamma=\mu\Gamma_{\mathrm{TST}}, \tag{2.4}$$

where Γ_{TST} is the TST result

$$\Gamma_{\mathrm{TST}}=\left\{\sqrt{2\pi\beta}\int_{-\infty}^0 dx\,e^{-\beta V(x)}\right\}^{-1}, \tag{2.5}$$

and μ is a transmission coefficient describing the deviation of the rate from Γ_{TST}. In this paper we restrict our consideration to the limit of high barriers (low temperatures), $\beta E \gg 1$, in which case the TST rate becomes

$$\Gamma_{\mathrm{TST}}(\beta E\gg 1)=(\omega_w/2\pi)e^{-\beta E}, \tag{2.6}$$

where ω_w is the frequency at the bottom of the well, $\omega_w^2=V''(x_w)$.

One of the key assumptions of the PGH theory is that the potential can be divided into a *parabolic* barrier part

$$U(x)=-\tfrac{1}{2}\omega^2x^2, \tag{2.7}$$

with $\omega^2=-V''(0)$, and an anharmonic correction V_1 defined by

$$V(x)=U(x)+V_1(x). \tag{2.8}$$

If one ignores the nonlinearity V_1, the associated GLE for a parabolic barrier becomes identical to separable motion for a rotated set of oscillators [5,7]. One of these barrier-top normal modes is unstable and termed ρ. Its imaginary frequency λ is determined by the Laplace transform of the time-dependent friction through the Kramers-Grote-Hynes relation [6]

$$\lambda^2+\lambda\hat{\gamma}(\lambda)=\omega^2. \tag{2.9}$$

The frequency λ defines the spatial diffusion limit transmission coefficient for a parabolic barrier

$$\mu_{\mathrm{sd}}^{\mathrm{pb}}=\lambda/\omega. \tag{2.10}$$

For a metastable well, the nonlinearity mixes the unstable normal mode with the remaining degrees of freedom. This coupling causes an exchange of energy between the unstable normal mode and the bath. The latter process plays a decisive role in the energy diffusion (weak friction) regime. In this way PGH showed that the escape dynamics is governed by the unstable normal mode coordinate ρ rather than the particle coordinate x. Then, applying to the dynamics of ρ the approach of Mel'nikov and Meshkov [4], PGH rederived the main result of the MM turnover theory reading

$$\mu=\mu_{\mathrm{sd}}^{\mathrm{pb}}A(\Delta). \tag{2.11}$$

In the last expression $A(\Delta)$ is the MM depopulation factor

$$A(\Delta)=\exp\left(\frac{1}{\pi}\int_0^\infty dx\frac{\ln\{1-\exp[-\Delta(x^2+\frac{1}{4})]\}}{x^2+\frac{1}{4}}\right), \tag{2.12}$$

which provides the changeover from the energy diffusion limit to the TST result, $A(\Delta\gg 1)=1$; while $\mu_{\mathrm{sd}}^{\mathrm{pb}}$ assures that the theory reduces to the correct spatial diffusion limit. The parameter Δ determining the depopulation factor is the dimensionless energy loss of the particle as it traverses the reactant region [4]. According to PGH the energy loss has the form

$$\Delta_{\mathrm{PGH}}=\tfrac{1}{2}\beta\int_{-T}^{T}dt\int_{-T}^{T}ds\,K(t-s)F(t)F(s), \tag{2.13}$$

where the friction kernel $K(t)$ is defined by its Laplace transform

$$\hat{K}(z)=\int_0^\infty dt\,e^{-zt}K(t)=\frac{z}{u_{00}^2[z^2+z\hat{\gamma}(z)-\omega^2]}-\frac{z}{(z^2-\lambda^2)}, \tag{2.14}$$

while the time dependent force $F(t)$

$$F(t)=-u_{00}V_1'(u_{00}\rho) \tag{2.15}$$

is determined from the zero-order equation of motion for the unstable mode:

$$\ddot{\rho}-\lambda^2\rho=F(t). \tag{2.16}$$

The asymptotic trajectory $\rho(t)$ starts at the barrier in the infinite past with energy close to zero, traverses the metastable well once, and returns to the barrier top at time $T\to\infty$. The factor u_{00} involved in Eq. (2.14) is given by

$$\frac{1}{u_{00}^2}=1+\frac{2}{\pi}\int_0^\infty d\nu\frac{\nu J(\nu)}{(\nu^2+\lambda^2)^2}, \tag{2.17}$$

where $J(\nu)$ is the spectral density defined as

$$J(\nu)=\nu\int_0^\infty dt\,\gamma(t)\cos(\nu t). \tag{2.18}$$

It is seen that both factors of Eq. (2.11) are strongly dependent on the parabolic approximation for the barrier. This makes the PGH rate expression inapplicable to various different nonparabolic potentials that have been introduced in the literature to allow a more flexible description of activated rate processes. In an effort to construct a theory for an arbitrarily shaped potential, Pollak and co-workers [14,15,17] have recently proposed to use the above parabolic barrier solution and treat the barrier frequency as a variational parameter. In the case of Ohmic friction

$$\gamma(t)=2\gamma\delta(t), \tag{2.19}$$

the authors have managed to derive in this way a spatial diffusion limit analog of the Kramers transmission coefficient μ_{sd}^{cusp} for a cusped barrier [14,15]. However, they failed to provide an analogous extension of the theory to the energy diffusion regime. Thus, a satisfactory solution of the non-Markovian turnover problem for arbitrarily shaped barriers is *effectively* still lacking.

III. INTERPOLATING FORMULA

The basic idea underlying our approach is the same as in the turnover theory of Mel'nikov and Meshkov [4]. Following these authors we assume that the overall transmission coefficient for an arbitrarily shaped barrier can be written as the product of the MM depopulation factor and μ_{sd} [cf. Eq. (2.11)]

$$\mu=\mu_{sd}A(\Delta). \tag{3.1}$$

It may be noted that the ansatz of writing a uniform formula for the turnover as a product of a spatial diffusion expression and the MM depopulation factor has been used for space dependent friction [8]. Its utility has been justified by comparing with exact numerical rates. It is our aim here to show that the same ansatz is also applicable to potentials with nonparabolic barriers. The latter is not so obvious as one might think. Specifically, the MM derivation of the depopulation factor, Eq. (2.12), is based on the assumption that the escape dynamics can be described by a probabilistic integral equation in energy-action variables, whose Green function corresponds to the barrier (asymptotic) trajectory. For a smooth potential the trajectory that leaves the barrier with the entire energy close to zero returns to it after time $T\to\infty$ [see Eq. (3.5)]. This infinite time, however, is no longer true for a cusped barrier where the time is of the order of the period of particle oscillation in the well. Thus the interesting issue we shall address in our numerical applications is as follows: Does the finite period of the barrier trajectory spoil the applicability of Eq. (3.1).

With the ansatz (3.1) the construction of a unified rate expression reduces to two separate problems, namely, the derivation of the spatial diffusion limit transmission coefficient μ_{sd} and the determination of the energy loss Δ of the particle per oscillation. The former is derived in Sec. III B by approximately solving the respective Fokker-Planck equation. While the latter is determined in Sec. III C in terms of the deterministic particle dynamics. However, before presenting these results we outline in Sec. III A a heuristic approach to the above-posed problems.

A. Naive approach

The approach consists in using two naive approximations, one for μ_{sd} and another for Δ. The spatial diffusion limit transmission coefficient μ_{sd} can be evaluated by approximating the actual potential barrier $U(x)$ with a parabolic barrier $\frac{1}{2}\beta\omega^2x^2$ and using the standard Kramers-Grote-Hynes transmission coefficient, Eq. (2.10). The effective frequency ω is a free parameter in this case. It is easily determined from the requirement that the integrals over all x of the exponents $\exp[\beta U(x)]$ and $\exp(-\frac{1}{2}\beta\omega^2x^2)$ are equal to each other, which gives

$$\omega=\sqrt{\frac{2\pi}{\beta}}\left[\int_{-\infty}^{\infty}dx e^{\beta U(x)}\right]^{-1}. \tag{3.2}$$

For a bistable potential with minima at $x_\pm$, Eq. (3.2) can be rewritten as

$$\omega=\sqrt{\frac{2\pi}{\beta}}\left[\int_{x_-}^{x_+}dx e^{\beta V(x)}\right]^{-1}. \tag{3.3}$$

The heuristic approximation outlined above is identical to that of Calef and Wolynes [12].

A naive approach to the energy loss Δ is based on the remark that when friction is weak, the escape process is almost identical to the underdamped deterministic motion. Consequently, the energy loss can be estimated from the dynamics of x rather than the much more complicated dynamics of ρ [4,7]. This results in a weak damping approximation of the form

$$\Delta(\gamma\to0)=\beta\int_{-T}^{T}dt\int_{-T}^{t}ds\,\dot{x}(t)\gamma(t-s)\dot{x}(s), \tag{3.4}$$

where the asymptotic (barrier) trajectory $x(t)$ is determined from the underdamped deterministic equation of motion

$$\ddot{x}=-V'(x), \tag{3.5}$$

with $x(-T)=\dot{x}(-T)=0$. It is a matter of some algebra to show that the explicit expression for the energy loss defined by Eqs. (3.4) and (3.5) reads

$$\Delta=\beta\int_{x_p}^{0}dx\int_{x_p}^{0}dy\{\gamma[|t(x)-t(y)|]-\gamma[t(x)+t(y)]\},$$

$$t(x)=\int_{x_p}^{x}dy[-2V(y)]^{-1/2}, \tag{3.6}$$

where x_p is the turning point of the barrier trajectory, $V(x_p)=0$. For Ohmic friction, the above approximation reduces to the MM energy loss [4]

$$\Delta_{\mathrm{MM}}=2\gamma\beta\int_{x_p}^{0}dx\sqrt{-2V(x)}, \tag{3.7}$$

being thus its straightforward generalization to the case of time-dependent friction. The advantages of Eq. (3.6) are that it allows for an arbitrary potential and is much more simple to implement than the PGH expression, Eqs. (2.13)–(2.16). The disadvantage of this approximation is that it is robust only for those rate processes that do not lead to an energy diffusion controlled regime in the strong damping limit. Otherwise it may fail grossly. We will refer to Eqs. (3.2) and (3.6) as the *naive* approach.

B. Generalized transmission coefficient for the spatial diffusion regime

Now we outline alternatives to the naive approximations for μ_{sd} and Δ. To begin with we consider the spatial diffusion regime. Our purpose is to derive an approximate transmission coefficient μ_{sd} that would allow one to recover different rate expressions that are already obtained in the literature for parabolic, cusped, and quartic barriers. A straightforward way of dealing with a non-Markovian process is to add a sufficient number of supplementary variables such that the resulting process is Markovian in the enlarged phase space [18,19]. To this end, we assume that the Laplace transform $\hat{\gamma}(z)$ has a continued fraction expansion, which can be approximated by its first m terms, as

$$\hat{\gamma}(z)=\frac{\eta_1}{z+\gamma_1+}\,\frac{\eta_2}{z+\gamma_2+}\cdots\frac{\eta_m}{z+\gamma_m}. \tag{3.8}$$

Here the parameters satisfy $\eta_i>0,\gamma_i\geqslant 0$. Then, introducing m auxiliary variables $\mathbf{y}=(y_1,\ldots,y_m)$, the one-dimensional non-Markovian process (2.1) is approximated by a $(m+2)$-dimensional Markov process reading [19]

$$\begin{aligned}\dot{x}&=v,\\ \dot{v}&=-V'(x)+y_1,\\ \dot{y}_1&=-\eta_1 v-\gamma_1 y_1+y_2+F_1(t),\\ \dot{y}_2&=-\eta_2 y_1-\gamma_2 y_2+y_3+F_2(t),\\ &\cdots\\ \dot{y}_m&=-\eta_m y_{m-1}-\gamma_m y_m+F_m(t).\end{aligned} \tag{3.9}$$

The random forces $F_1,\ldots,F_n$ appearing in Eq. (3.9) are uncorrelated zero mean Gaussian white noises

$$\langle F_i(t)F_j(0)\rangle=2\beta^{-1}\delta_{ij}\gamma_i\pi_i\delta(t), \tag{3.10}$$

with

$$\pi_i=\prod_{j=1}^{i}\eta_j. \tag{3.11}$$

The Fokker-Planck equation related to Eqs. (3.9) and (3.10) is

$$\partial_t P(x,v,\mathbf{y},t)=LP(x,v,\mathbf{y},t), \tag{3.12}$$

where

$$\begin{aligned}L=&-v\frac{\partial}{\partial x}+\frac{\partial}{\partial v}[V'(x)-y_1]\\ &+\frac{\partial}{\partial y_1}\left(\eta_1 v+\gamma_1 y_1-y_2+\beta^{-1}\gamma_1\pi_1\frac{\partial}{\partial y_1}\right)\\ &+\frac{\partial}{\partial y_2}\left(\eta_2 y_1+\gamma_2 y_2-y_3+\beta^{-1}\gamma_2\pi_2\frac{\partial}{\partial y_2}\right)+\cdots\\ &+\frac{\partial}{\partial y_m}\left(\eta_m y_{m-1}+\gamma_m y_m+\beta^{-1}\gamma_m\pi_m\frac{\partial}{\partial y_m}\right)\end{aligned} \tag{3.13}$$

denotes the Fokker-Planck operator. Since the noise in the GLE (2.1) obeys the fluctuation dissipation theorem, Eq. (2.2), the above Fokker-Planck equation possesses a Boltzmann-like equilibrium distribution,

$$P_{\mathrm{eq}}(x,v,\mathbf{y})=\exp[-\beta\varphi(x,v,\mathbf{y})],$$

$$\varphi(x,v,\mathbf{y})=V(x)+\tfrac{1}{2}v^2+\tfrac{1}{2}(\pi_1)^{-1}y_1^2+\cdots+\tfrac{1}{2}(\pi_m)^{-1}y_m^2. \tag{3.14}$$

The latter reduces, after integration over the additional variables y_i, to the standard Maxwell-Boltzmann form. In accordance with the problem under consideration, the generalized potential $\varphi(x,v,\mathbf{y})$ has a saddle point at the origin and a metastable minimum at $(x_w,0,\ldots,0)$.

The objective is to find the transmission coefficient, the probability that a particle injected into a well will stick. A simple way for achieving this goal is to employ the flux over population method developed by Kramers [3]. Within its scope, the escape rate is defined as the ratio of a stationary diffusion current at the top of the barrier to the population of the well. Accordingly, we have to look for a current carrying stationary probability density $P(x,v,\mathbf{y})$, which smoothly matches the equilibrium distribution $P_{\mathrm{eq}}(x,v,\mathbf{y})$ in the well and vanishes beyond the barrier. The two stationary densities are related by a form function $\xi(x,v,\mathbf{y})$,

$$P(x,v,\mathbf{y})=\xi(x,v,\mathbf{y})P_{\mathrm{eq}}(x,v,\mathbf{y}). \tag{3.15}$$

Since both $P(x,v,\mathbf{y})$ and $P_{\mathrm{eq}}(x,v,\mathbf{y})$ are stationary solutions of the Fokker-Planck equation, the form function is determined from

$$\Big\{ -v\frac{\partial}{\partial x}+[V'(x)-y_1]\frac{\partial}{\partial v}+(\eta_1 v-\gamma_1 y_1-y_2)\frac{\partial}{\partial y_1}+\beta^{-1}\gamma_1\pi_1\frac{\partial^2}{\partial y_1^2}+(\eta_2 y_1-\gamma_2 y_2-y_3)\frac{\partial}{\partial y_2}+\beta^{-1}\gamma_2\pi_2\frac{\partial^2}{\partial y_2^2}+\cdots$$
$$+(\eta_m y_{m-1}-\gamma_m y_m)\frac{\partial}{\partial y_m}+\beta^{-1}\gamma_m\pi_m\frac{\partial^2}{\partial y_m^2}\Big\}\,\xi(x,v,\mathbf{y})=0. \tag{3.16}$$

Once the form function is known, the reactive flux formula yields for the transmission coefficient

$$\mu=\left[(2\pi/\beta)^m\prod_{i=1}^{m}\pi_i\right]^{-1/2}\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dy_1\cdots\int_{-\infty}^{\infty}dy_m P_{\rm eq}(0,v,\mathbf{y})\frac{\partial\xi(0,v,\mathbf{y})}{\partial v}. \tag{3.17}$$

The chain of approximations that will be made for solving Eq. (3.16) is analogous to that of the standard saddle point approximation [3,20]. First, we assume that the height of the potential barrier E is sufficiently large compared to the energy of thermal motion, $\beta E \gg 1$, so that the immediate region close to the barrier top dominates the dynamics. In such a case, the potential $V(x)$ entering Eq. (3.16) can be approximated by its barrier part $U(x)$. The latter is not *necessarily* parabolic, it may be a sum of arbitrary (parabolic and nonparabolic) terms,

$$U(x)=-\tfrac{1}{2}\omega^2x^2-\frac{a}{\alpha}|x|^{\alpha}-\cdots. \tag{3.18}$$

Next we assume that $\xi(x,v,\mathbf{y})$ is a function of some linear combination of the variables

$$\xi(x,v,\mathbf{y})=\xi(r),\quad r=R_x x+R_v v+R_1 y_1+\cdots+R_m y_m. \tag{3.19}$$

Then, it is not difficult to check by direct substitution that in leading order in r and $(\beta E)^{-1}$ the respective approximate solution to Eq. (3.16) reads

$$\xi(x,v,\mathbf{y})=Z\int_{\nu r}^{\infty}dq\,e^{\beta U(q)}, \tag{3.20}$$

where

$$\nu=(R_x^2-\omega^2R_v^2-\omega^2\vartheta)^{-1/2}, \tag{3.21}$$

with

$$\vartheta=\sum_{i=1}^{m}\pi_i R_i^2, \tag{3.22}$$

and where Z is a normalization constant defined by the requirement that the form function $\xi(x,v,\mathbf{y})$ approaches unity in the initial well and zero in the product side

$$Z^{-1}=\int_{-\infty}^{\infty}dx\,e^{\beta U(x)}. \tag{3.23}$$

The rest of the parameters involved in Eq. (3.19), $(R_x,R_v,R_1,\ldots,R_m)$, constitute an eigenvector of the matrix

$$\begin{pmatrix} 0 & -\omega^2 & 0 & 0 & \ldots & 0 & 0\\ -1 & 0 & \eta_1 & 0 & \ldots & 0 & 0\\ 0 & -1 & -\gamma_1 & \eta_2 & \ldots & 0 & 0\\ 0 & 0 & -1 & -\gamma_2 & \ldots & 0 & 0\\ . & . & . & . & & . & .\\ . & . & . & . & & . & .\\ . & . & . & . & & . & .\\ & & & & & & \eta_m\\ 0 & 0 & 0 & 0 & \ldots & -1 & -\gamma_m \end{pmatrix}, \tag{3.24}$$

corresponding to a single positive eigenvalue λ. The eigenvalues of this matrix admit a continued fraction expansion [19]

$$\lambda=\frac{\omega^2}{\lambda+}\,\frac{\eta_1}{\lambda+\gamma_1+}\,\frac{\eta_2}{\lambda+\gamma_2+}\cdots\frac{\eta_m}{\lambda+\gamma_m}, \tag{3.25}$$

from which it immediately follows that λ is the positive solution of the implicit Kramers-Grote-Hynes relation, Eq. (2.9). As to the associated eigenvector, its first components have the form

$$R_x=1,\quad R_v=-\lambda/\omega^2,\quad R_1=(1-\lambda^2/\omega^2)/\pi_1,$$
$$R_2=[(\lambda+\gamma_1)(1-\lambda^2/\omega^2)-\lambda/\omega^2]/\pi_2, \tag{3.26}$$

while the rest of $R_i (i>2)$ are determined by the recurrence relation

$$R_{i+1}=[(\lambda+\gamma_i)R_i+R_{i-1}]/\eta_{i+1}. \tag{3.27}$$

Inserting Eq. (3.20) into Eq. (3.17), one obtains in a straightforward way (for more details, see the Appendix) the following expression for the transmission coefficient:

$$\mu_{\rm sd}=Z(1+\vartheta\omega^4/\lambda^2)^{-1/2}\int_{-\infty}^{\infty}dx \times\exp\left[\beta U(x)-\tfrac{1}{2}\beta\omega^2x^2\left(\frac{\omega^2}{\lambda^2+\vartheta\omega^4}-1\right)\right]. \tag{3.28}$$

The last equation agrees in the strong damping limit with the transmission coefficient following from the corresponding Smoluchowski equation [21]

$$\mu_{\rm sd}(\gamma\to\infty)=\left\{\gamma\sqrt{\frac{\beta}{2\pi}}\int_{-\infty}^{\infty}dx e^{\beta U(x)}\right\}^{-1}, \quad (3.29)$$

and reduces to unity at zero damping. It may also be noted that for a parabolic barrier, Eq. (3.28) reproduces the exact Kramers-Grote-Hynes result, Eq. (2.10), while for a purely nonparabolic barrier ($\omega=0$) it gives

$$\mu_{\rm sd}(\omega=0)=Z(1+\vartheta\gamma^2)^{-1/2}\int_{-\infty}^{\infty}dx \times\exp\left[\beta U(x)-\frac{\beta\gamma^2x^2}{2(1+\vartheta\gamma^2)}\right]. \quad (3.30)$$

The non-Markovian dynamics of the system only enters Eq. (3.30) through the factor ϑ. The latter is defined by Eq. (3.22), where the components R_i of the eigenvector take for $\omega=0$ the form

$$R_1=1/\pi_1, \quad R_2=(\gamma_1+1/\gamma)/\pi_2, \qquad R_{i+1}(i\geqslant 2)=(\gamma_i R_i+R_{i-1})/\eta_{i+1}. \quad (3.31)$$

In the case of Ohmic dissipation, Eq. (3.30) reproduces the result of Berezhkovskii *et al.* [16]

$$\mu_{\rm sd}^{\rm Ohmic}(\omega=0)=Z\int_{-\infty}^{\infty}dx\,\exp\{\beta[U(x)-\tfrac{1}{2}\gamma^2x^2]\}, \quad (3.32)$$

which is a straightforward generalization of various different transmission coefficients available in the literature for nonparabolic barriers.

To conclude this section we note that for a bistable system with a high potential barrier and minima at $x_\pm$ the barrier part $U(x)$ can be replaced by the bare potential $V(x)$ itself. Then, the integration in the above equations has to be performed with the lower and upper limits at x_- and x_+, respectively. The same can also be done for a metastable potential, in which case the integration has to be restricted to the barrier region with a lower limit at, say, x_w and the upper limit at a value beyond the barrier from where the recrossing probability of a particle with zero initial velocity can safely be neglected. Moreover, the present rate formula, Eq. (3.28), can be improved if one employs instead of the flux over population expression, Eq. (3.17), a Rayleigh quotient [20,22] with the same approximate form function as test function. The barrier frequency ω entering Eqs. (3.20)–(3.27) may then be left and treated as a variational parameter even if the barrier is purely nonparabolic [17]. Finally, the approximate form function itself can systematically be improved by means of a perturbation theory using Eq. (3.20) as an unperturbed solution [22].

C. Energy loss

Next we outline an alternative to the naive approximation for the energy loss, Eq. (3.6). Recall that this approximation has been obtained in terms of the underdamped particle dynamics, Eq. (3.5), and therefore may fail considerably in the limit of intermediate and strong damping. The validity of the last statement becomes apparent from the following example. Let us consider for a moment the motion of a particle in a metastable well with an exponentially decaying friction kernel of the form

$$\gamma(t)=(\gamma/\tau)e^{-t/\tau}, \quad (3.33)$$

where the correlation time τ of the noise is assumed to be independent of the static friction γ. With Eq. (3.33) it is not difficult to see that when $\gamma\to\infty$ the naive approximation for the energy loss also goes to infinity, regardless of the barrier height. By definition, however, the energy loss cannot be larger than the barrier height.

An obvious way to correct the naive approximation is to take into account the dissipative and fluctuating terms fully neglected in Eq. (3.5). This can be achieved by introducing the mechanical energy ε

$$\varepsilon=\tfrac{1}{2}\dot{x}^2+V(x) \quad (3.34)$$

and averaging the difference

$$\varepsilon(0)-\varepsilon(t)=\int_0^t du\int_0^u ds\dot{x}(u)\gamma(u-s)\dot{x}(s)-\int_0^t du\dot{x}(u)f(u) \quad (3.35)$$

over trajectories $x(t)$ that start at the top of the barrier with $x(0)=\dot{x}(0)=0$ and traverse the metastable region once. It is clear that the stochastic energy loss so determined will be valid in the whole friction range, though realization of the above strategy is far from straightforward.

Instead, we suggest an effective way to reach the same goal without extraordinary computational effort. The key idea of our approach is the observation that for large potential barriers, $\beta E\gg 1$, the stochastic dynamics governed by Eqs. (2.1) and (2.2) can be well approximated by the deterministic equation of motion. The latter becomes more evident, if one rescales the variables of the GLE by the barrier height as

$$t\to t\sqrt{\beta E}, \quad x\to x\sqrt{\beta}, \quad \gamma(t)\to\gamma(t)/(\beta E), \qquad V(x)\to V(x)/(\beta E).$$

This rescaling renders the deterministic contribution independent of the barrier height and the noise term proportional to the inverse square root of the barrier height,

$$\ddot{x}=-V'(x)-\int_0^t ds\,\gamma(t-s)\dot{x}(s)+(\beta E)^{-1/2}f(t), \qquad \langle f(t)f(0)\rangle=\gamma(t). \quad (3.36)$$

Hence one may split the equations of motion into a leading contribution, describing the deterministic dynamics

$$\ddot{x}=-V'(x)-\int_0^t ds\,\gamma(t-s)\dot{x}(s), \quad (3.37)$$

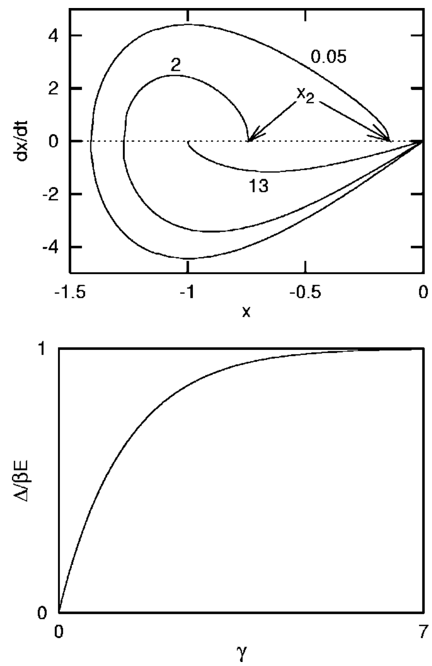

FIG. 1. Asymptotic deterministic trajectories (for $\gamma = 0.05$, 2, and 13) and energy loss, Eq. (3.39), for a Markov rate process in a symmetric double well potential, Eq. (4.1) with $a=2$, $b=4$, and $\beta E = 10$.

and the fluctuating correction $(\beta E)^{-1/2} f(t)$ and construct a perturbation expansion in powers of the inverse barrier height $1/(\beta E)$.

For high potential barriers, $\beta E \gg 1$, a good approximation for the energy loss is already attained in zero order in the perturbation. In this case, the energy loss is determined from the unperturbed equation of motion, Eq. (3.37), for the asymptotic trajectory that starts at the barrier with energy close to zero and period $T \to \infty$. Since no explicit solutions of Eq. (3.37) are known, it must be solved numerically with initial conditions

$$x(0)=0, \quad \dot{x}^2(0) \ll 1. \tag{3.38}$$

The numerical solution of Eq. (3.37) does not present a more difficult problem than that of the zero-order equation of motion for the unstable mode ρ, Eq. (2.16). High efficiency is achieved by making use of a fourth-order symplectic integrator developed in a previous paper [23]. The energy loss is determined as

$$\Delta = -\beta V(x_2), \tag{3.39}$$

where x_2 is the point at which $\dot{x}(t)$ crosses zero for the second time. Typical asymptotic trajectories and energy losses are shown in Fig. 1 for a Markov double well process. The utility of the present approach was already tested for Brownian motion in different types of parabolic barrier potentials [23,24]. We found that its implementation is as simple as that of the naive approximation, Eq. (3.6), and still results in an accurate estimate for the energy loss valid in the full friction range. In Sec. IV we shall show that our method works quite accurately for cusped and quartic potentials as well. It may also be noted that for low barriers, a further improvement of the method can be obtained by taking into account the noise term $f(t)$. A simple way of doing so is to employ the systematic expansion around the deterministic path proposed by van Kampen [25]. The approach based on Eqs. (3.28) and (3.37)–(3.39) will be referred to as the *deterministic* approximation.

IV. APPLICATIONS

The aim of this section is twofold. First, we want to present exact numerical rate constants in potentials of different shapes that would allow one to test various analytical predictions. One might, at first, believe that this matter should have been settled long ago, mainly because of its continuous importance in many problems of chemical physics. To the best of our knowledge, however, there are no numerical solutions of such a type, other than those obtained in Refs. [15] and [16] under the assumption that the potential consists only of a barrier part. This assumption results in a *monotonic* dependence of the transmission coefficient on the static friction γ; the coefficient increases with decreasing γ and reaches its maximal value at zero damping, when there is no coupling between the system and the bath. It is clear that the data so obtained are not suited for testing analytical predictions for the rate in the most problematic intermediate and weak damping regions. Second, we wish to test the accuracy of the various approaches discussed above by comparing them with exact numerical rates.

A. Exact numerical results

To achieve the above goals, we consider four specific examples. The examples include a non-Markovian model with a piecewise harmonic potential and Markovian activated rate processes in a symmetric double well of the form

$$V(x) = \frac{E}{b-a}\left[a\left(\frac{x}{x_w}\right)^b - b\left|\frac{x}{x_w}\right|^a \right], \quad 0<a<b, \tag{4.1}$$

whose barrier part

$$U(x) = -\frac{bE}{b-a}\left|\frac{x}{x_w}\right|^a \tag{4.2}$$

varies with the parameter a from cusped $(0<a\leq 1)$ to smooth $(1<a<2)$, parabolic $(a=2)$, and higher order $(a>2)$ barriers, see Fig. 2. In the former case we shall compare with the numerical simulation data of Straub, Borkovec, and Berne (SBB) [26]. While for the Markov processes comparison will be made with numerical rate constants obtained by the present author. It may be noted that the problem of evaluation of the escape rate in a double well is equivalent to finding the least nonvanishing eigenvalue of the Fokker-Planck equation. For a symmetric potential, this eigenvalue is given by twice the rate, Eq. (2.4), where the transmission coefficient can be written as [4]

$$\mu = \mu_{sd} A^2(\Delta)/A(2\Delta). \tag{4.3}$$

The method used to numerically solve the Fokker-Planck equation is described in a previous paper [27]. The calculations were performed in the potential (4.1) with $\beta E = 10$ and

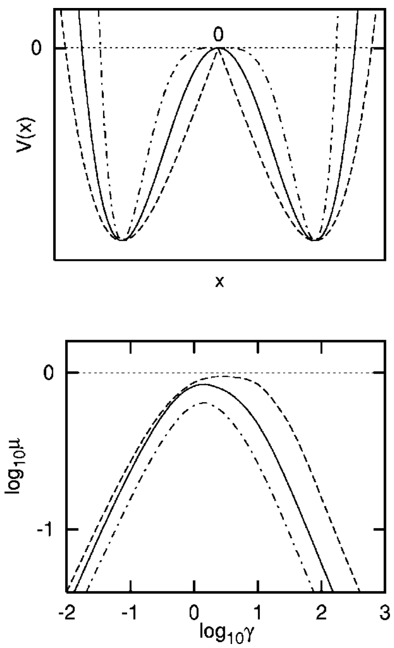

FIG. 2. Different shapes of the potential $V(x)$, Eq. (4.1), and numerically exact transmission coefficients for a cusped ($a=1$, $b=4$, dashed line), parabolic ($a=2$, $b=4$, solid line), and quartic ($a=4$, $b=6$, dot-dashed line) barrier. The numerical data are also presented by lines for an eye guide convenience only.

$x_w=1$ for a parabolic ($a=2$, $b=4$), cusped ($a=1$, $b=4$), and quartic ($a=4$, $b=6$) barrier. The exact numerical estimates of the least nonvanishing eigenvalue for a large interval of γ are presented in Table I and exhibited in Fig. 2, together with the potential shapes. These results provide the necessary foundation for testing various rate expressions in all regimes of physical interest, from the extremely underdamped Brownian motion to the strong friction (Smoluchowski) limit. As evidenced by the figure, the transmission coefficient for the cusped potential is larger than those for the two other potentials. Moreover, in contrast to the latter it has a well pronounced plateau ($\mu\approx 1$) in the intermediate damping region. This is explained by the fact that with decreasing damping the spatial diffusion transmission coefficient $\mu_{\rm sd}$ in the cusped potential reduces to unity faster than in the smooth potentials.

TABLE I. First nonzero eigenvalue in a symmetric double well potential, Eq. (4.1), with $\beta E=10$ and $x_w=1$, for different values of γ and for different barrier shapes. Exponential notation $[k]$ means that the number preceding is to be multiplied by 10^{-k}.

γ	$a=1$, $b=4$ cusped	$a=2$, $b=4$ parabolic	$a=4$, $b=6$ quartic
0.01	0.365[5]	0.399[5]	0.485[5]
0.05	0.144[4]	0.171[4]	0.195[4]
0.1	0.247[4]	0.304[4]	0.350[4]
0.25	0.456[4]	0.593[4]	0.705[4]
0.5	0.640[4]	0.868[4]	0.107[3]
0.75	0.735[4]	0.100[3]	0.128[3]
1	0.791[4]	0.106[3]	0.138[3]
1.5	0.840[4]	0.109[3]	0.143[3]
2	0.856[4]	0.106[3]	0.138[3]
3	0.862[4]	0.997[4]	0.122[3]
4	0.858[4]	0.925[4]	0.107[3]
6	0.838[4]	0.797[4]	0.853[4]
8	0.806[4]	0.692[4]	0.700[4]
10	0.770[4]	0.607[4]	0.590[4]
20	0.564[4]	0.361[4]	0.323[4]
30	0.439[4]	0.251[4]	0.220[4]
100	0.145[4]	0.780[5]	0.674[5]
1000	0.147[5] [a]	0.783[6] [a]	0.675[6] [a]

[a]Exact estimate of the eigenvalue calculated from the respective Smoluchowski equation.

B. Comparison of the theoretical approaches with numerical results

It should be pointed out here that the three approaches to the turnover problem, outlined in Secs. II and III, differ from each other even though the barrier is parabolic. The difference arises due to the different approximations for the energy loss. Therefore it would be instructive to begin our comparison with the parabolic barrier model used by PGH [7] for testing their turnover theory. The dynamics of the model is that of a particle moving in the piecewise continuous harmonic potential

$$U(x)=\begin{cases} -E+\frac{1}{2}\omega_w^2(x+x_w)^2, & x<-x^* \\ -\frac{1}{2}\omega^2x^2, & x\geqslant -x^*, \end{cases} \tag{4.4}$$

with

$$x_w=(1+\omega^2/\omega_w^2)x^*, \quad E=\tfrac{1}{2}\omega^2x^*x_w, \tag{4.5}$$

and experiencing an exponential friction kernel of the form

$$\gamma(t)=\alpha^{-1}\exp(-t/\alpha\gamma). \tag{4.6}$$

The above model was studied numerically by SBB [26], who computed the escape rate for a large range of parameters.

The numerical results for the transmission coefficient obtained from the SBB simulation data are presented in Fig. 3 together with the predictions of the three theoretical approaches discussed above. Also shown are the respective approximations for the energy loss. As anticipated, the three approaches coincide with each other in the weak damping region ($\gamma<0.1$). In the intermediate damping region ($0.1<\gamma<10$) the difference between the various approximations for the energy loss becomes noticeable, though this does not reflect on the transmission coefficient. The reason is that the energy loss is sufficiently large in this region ($\Delta\gtrsim\beta E\gg 1$) to reduce the depopulation factor $A(\Delta)$ to unity. Finally, in the strong damping region ($\gamma>10$) the deterministic approach and the PGH theory are characterized by a similar accuracy, while the naive approach overestimate the rate by one order of magnitude.

The same, however, is not true for a rate process, whose bath correlation time is independent of γ. In such a case, the escape dynamics does not lead to an energy diffusion controlled regime as γ goes to infinity. Instead, it is characterized by large energy loss at large damping such that $A(\Delta)\approx 1$; accordingly, the naive approach provides an accurate

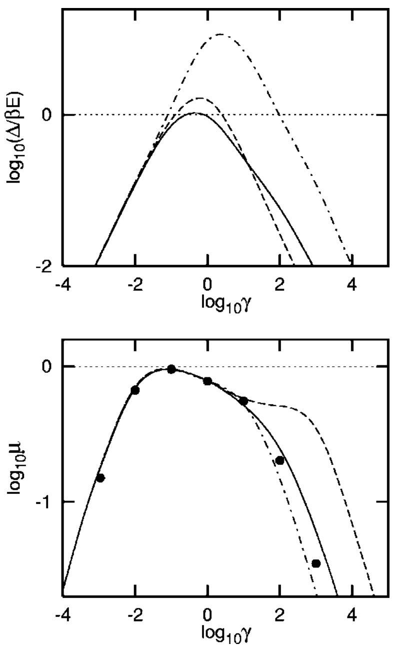

FIG. 3. Energy loss and transmission coefficient for the SBB model, Eqs. (4.4)–(4.6) with $\beta E = 20$, $\omega/\omega_w = 2$, and $\omega^2\alpha = 4/3$. Dot-dashed lines: PGH theory; dashed lines: naive approximation; solid lines: deterministic approach; circles: exact numerical results.

description of the rate in the strong damping limit as well. The latter is seen from Fig. 4, which shows the energy loss and the transmission coefficient in a parabolic barrier potential with Ohmic friction. As evidenced by the figure, the naive approach remains correct in the whole damping range. On the other hand, this approximation is least favorable, it systematically overestimates the rate. The deterministic approach is in better agreement with numerical calculations than the two other approaches for all values of γ excepting $\gamma \sim 1$. For $\gamma \sim 1$ the best agreement is achieved with the PGH theory. It may also be pointed out that in the weak damping limit ($\gamma \ll 1$) all the approaches are relatively inaccurate and overestimate the rate by $\sim 18\%$.

Next we apply the naive and the deterministic approaches to a cusp shaped barrier, Eq. (4.1) with $a = 1$ and $b = 4$. The exact values of the transmission coefficient for the cusped double well potential are presented in Fig. 5, together with the theoretical predictions. The figure shows that the two approximations are characterized by a similar accuracy. The deterministic approach is better in the low damping region, while the naive approach gives better results in the intermediate damping regime. In the strong damping limit both deviate from the exact result by roughly the same amount, the deterministic approach underestimates the rate, while the naive approximation overestimates it. It is remarkable that the errors obtained for the cusped barrier are comparable to those for the parabolic barrier (cf. Figs. 4 and 5). The latter allows us to conclude that the ansatz (3.1) works quite well even though the time T taken by the deterministic particle to go from the barrier and back to it is finite. This result is not surprising because periods of particle oscillation do not enter the integral equation in energy variables used by MM in their derivation of the depopulation factor, Eq. (2.12). The equation depends only on the action along the barrier trajectory, which is always finite regardless of whether or not the corresponding period is infinite.

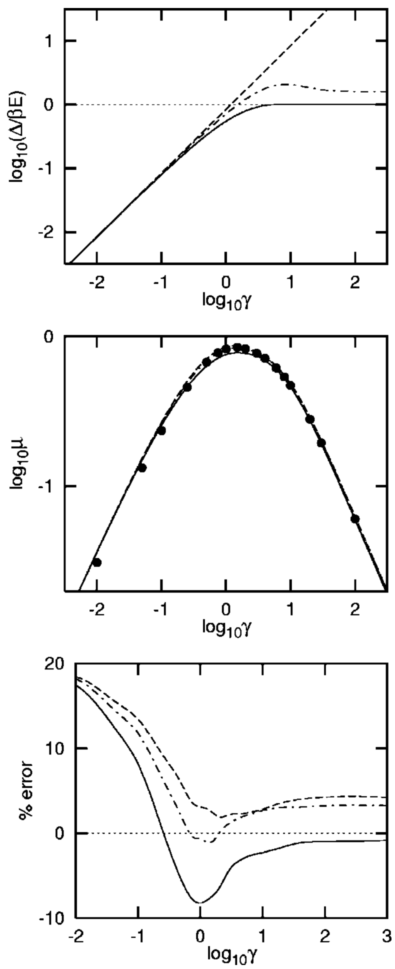

FIG. 4. Energy loss, transmission coefficient, and percentage error [$100\times$ (approximate – exact)/exact] made in μ for a Markov parabolic double well, Eq. (4.1) with $a = 2$, $b = 4$, and $\beta E = 10$. Dot-dashed lines: PGH theory; dashed lines: naive approximation; solid lines: deterministic approach; circles: exact numerical results.

Finally, we consider the rate of escape over a quartic barrier, Eq. (4.1) with $a = 4$ and $b = 6$. The naive and the deterministic predictions for the symmetric quartic double well potential are compared in Fig. 6 with the numerical rates. It is seen that in this case both approximations give an upper bound to the exact result for the rate. The deviation of the deterministic approach from the numerical results varies from $\sim 2\%$ in the strong damping limit, reaches a maximum of $\sim 30\%$ at $\gamma \sim 3$ and decreases to $\sim 14\%$ in the weak damping region. The error made by the naive approximation is larger than that of the deterministic approach everywhere except for the intermediate damping region ($1 < \gamma < 10$).

V. CONCLUDING REMARKS

In this paper, we presented accurate calculations of thermally activated rates in a symmetric double well potential with parabolic, cusped, and quartic barriers. The results were used to analyze the relative validity of two approaches to the

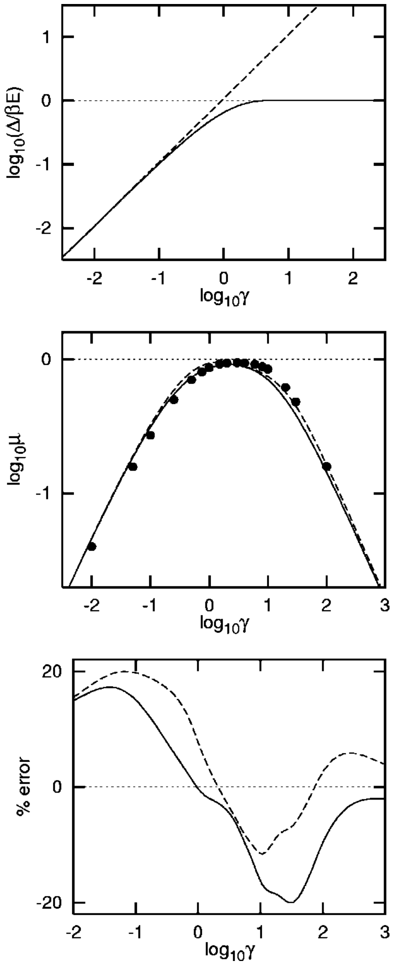

FIG. 5. Same as in Fig. 4 but for a cusped barrier, Eq. (4.1) with $a=1$, $b=4$.

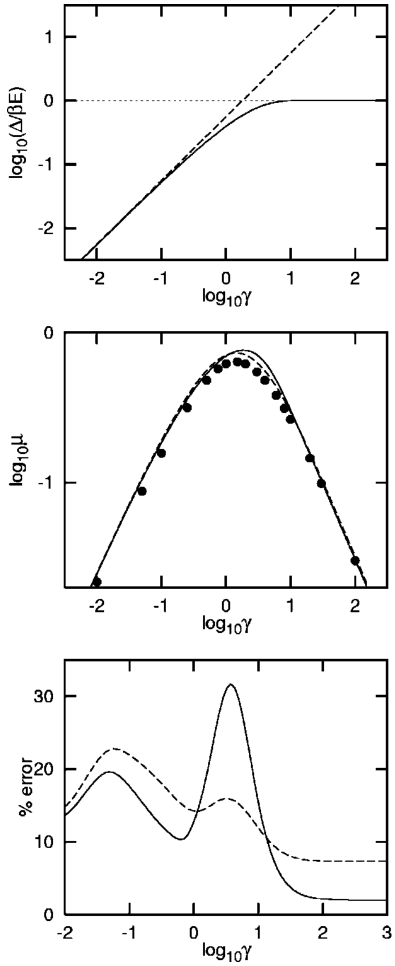

FIG. 6. Same as in Fig. 4 but for a quartic barrier, Eq. (4.1) with $a=4$, $b=6$.

calculation of the escape rate in arbitrarily shaped potentials. The basic idea underlying the approaches is the assumption that the MM ansatz for the transmission coefficient, Eq. (3.1), is correct without regard to the barrier shape. An approximate rate expression was then constructed by using a generalized energy loss of the underdamped deterministic dynamics, Eq. (3.6), and the standard Kramers-Grote-Hynes transmission coefficient with an effective barrier frequency ω given by Eq. (3.2). This naive approximation is generally robust for Markov activated rate processes and may fail considerably for non-Markovian systems, which exhibit an energy diffusion controlled regime in the strong damping limit. An alternative approach free of this drawback consists in using a properly defined energy loss of the deterministic dynamics and a generalized Kramers-Grote-Hynes transmission coefficient obtained by means of the flux over population method. The resulting rate expression approaches the correct limiting behavior for both weak and strong friction. It generalizes in a natural way various different rate formulas that are available in the literature for parabolic and nonparabolic barriers. Numerical applications showed this approach to be superior over the naive approximation for the escape rate. Yet another important finding revealed in our calculations is that the finite period of oscillation along the deterministic barrier trajectory is not an obstacle for the application of the MM ansatz (3.1). The latter, however, is obviously true for Ohmic dissipation and may not be a generic case for non-Markovian processes. If the noise correlation time is longer than the period of the barrier trajectory, then the Mel'nikov derivation is not necessarily correct. Therefore, care must be taken when applying the MM ansatz to non-Markovian activated rate processes in a cusp shaped potential.

For parabolic barriers our comparison also included results from the PGH turnover theory. We found that in the limits of weak and strong damping the PGH theory and the deterministic approach are characterized by a similar accuracy. In the intermediate damping region the PGH theory is in better agreement than the two present approaches. The naive approximation gives the worst approximation to the exact results in both limits of weak and strong damping and works better than the deterministic approach in the intermediate damping domain.

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APPENDIX A

In this appendix we outline the central result of Sec. III B as given in Eq. (3.28). Inserting Eq. (3.20) into Eq. (3.17) and integrating over the Gaussian (environmental) variables y_i yields for the transmission coefficient

$$\mu_{\rm sd} = Z(\det \mathbf{M})^{-1/2}\int_{-\infty}^{\infty} dx \exp\left[\beta U(x) - \frac{\beta\omega^4 x^2}{2\nu^2\lambda^2}\right.$$
$$\left.\times\left(1 - \frac{\omega^4}{\lambda^2}\sum_{i,j=1}^{m} M^{ij} R_i R_j \sqrt{\pi_i\pi_j}\right)\right], \tag{A1}$$

where the matrix M_{ij} reads

$$M_{ij} = \delta_{ij} + (\omega^4/\lambda^2) R_i R_j \sqrt{\pi_i \pi_j}. \tag{A2}$$

By explicitly evaluating the determinant of this matrix and its inverse M^{ij}, it is possible to prove that [20]

$$\det \mathbf{M} = 1 + (\omega^4/\lambda^2)\vartheta \tag{A3}$$

and

$$M^{ij} = \delta_{ij} - \frac{\omega^4 R_i R_j \sqrt{\pi_i\pi_j}}{\lambda^2 + \omega^4\vartheta}, \tag{A4}$$

where ϑ is defined by Eq. (3.22). With these findings it is a simple matter to go from Eq. (A1) to the final result, Eq. (3.28).

Before closing the Appendix we would like to show that Eq. (3.28) agrees in the limiting case of high friction with the transmission coefficient obtained from the corresponding Smoluchowski equation, Eq. (3.28), and in the limit of weak friction with the TST result, $\mu_{\rm TST}=1$. To simplify the proof, we rescale the memory function $\gamma(t)=\gamma\tilde{\gamma}(t)$ and assume that the expansion coefficients $\tilde{\eta}_i$ and $\tilde{\gamma}_i$ of the rescaled Laplace transform $\hat{\tilde{\gamma}}(z)$ remain finite whatever the static friction coefficient γ is. Under this assumption, one finds that for $\gamma\to\infty$ the eigenvalue λ and the components R_i of the eigenvector go to zero as

$$\lambda = \omega^2/\gamma, \quad R_i = c_i/\gamma, \quad \vartheta = c/\gamma,$$

where c_i and c are regular functions of γ. Thus Eq. (3.28) reduces to

$$\mu_{\rm sd}(\gamma\to\infty) = Z(c\gamma)^{-1/2}\int_{-\infty}^{\infty} dx \exp[\beta U(x) - \tfrac{1}{2}\beta(\gamma/c)x^2]. \tag{A5}$$

The integral in the last equation is dominated by its Gaussian contribution and can be evaluated analytically to yield Eq. (3.29), as we set out to prove. On the other hand, for vanishingly weak friction ($\gamma\to 0$) one has

$$\lambda = \omega, \quad R_i = c_i, \quad \vartheta = c\gamma.$$

Consequently,

$$\mu_{\rm sd}(\gamma\to 0) = Z(1 + c\gamma\omega^2)^{-1/2}\int_{-\infty}^{\infty} dx$$
$$\times \exp[\beta U(x) - \tfrac{1}{2}\beta c\gamma\omega^2 x^2], \tag{A6}$$

from which it immediately follows the desired result $\mu_{\rm sd}(\gamma=0)=1$.

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