Self-similar renormalization approach to barrier crossing processes

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(Received 23 March 1999)

An algebraic self-similar renormalization method developed recently for summation of divergent field-theoretical series is applied to the thermally activated escape of a Brownian particle over an arbitrarily shaped barrier. Based on the Mel'nikov–Meshkov result for the underdamped Brownian motion and the inverse friction expansion of the underlying Fokker-Planck equation for strong friction, an overall rate formula is constructed. This formula agrees in the weak friction regime with the rate obtained from a diffusion equation in energy variables and, in the limiting case of strong friction with the rate following from a Smoluchowski equation. Its validity is tested for Brownian motion in bistable potentials with parabolic, cusped, and quartic barriers of different heights. The proposed formula is found to give a reasonable description of activated rate processes even though the barrier is quite low. Our comparison also includes results from various different crossover theories. In most of the cases considered the present formula is in considerably better agreement with exact numerical rates than the other interpolation formulas. [S1063-651X(99)13610-9]

PACS number(s): 05.40.−a, 82.20.Db, 82.20.Fd

I. INTRODUCTION

The phenomenon of thermally activated escape of a classical particle from one metastable state to another by crossing a barrier between the two states, as originally proposed by Kramers in his seminal 1940 paper on chemical reaction rates [1], has attracted a great deal of theoretical attention in recent years. For general reviews of the field see Refs. [2–6]. The present state of the art can be found in Ref. [7]. The dynamics of the Kramers model is governed by the Fokker-Planck equation (or its stochastic analog, the Langevin equation) which describes the Brownian motion under the combined influence of an externally applied potential $V(x)$ and a heat bath. The crossing of the particle over the barrier constitutes reaction. The phenomenological rate constants for the reaction are related to the reciprocal of the longest relaxation time of the system. This rate is characterized by the shape of the potential, the energy of thermal motion $\beta^{-1} = k_B T$, and the strength of the coupling γ to the heat bath. The Kramers model though simple exhibits generic features of many complex systems. Apart from chemical reactions, it has found widespread applications in a multitude of other activated rate processes. In particular, it has been adopted to describe a variety of phenomena in condensed-matter physics, ranging from super-ionic conduction [8] and Josephson junction theory [3] to a driven Ge photoconductor [9]. The ring-laser gyroscope [10] and dye laser [11] are examples of the Kramers problem in optical physics. Another interesting variety of its applications is the transport phenomenon in complex systems as it occurs in glasses [12] and proteins [13].

The enormous theoretical literature has evolved Kramers' theory in many directions that include more formal derivations of Kramers' own results [14,15], improvements of the Kramers method in the weak [16–20] and moderate-to-high [14,21,22] friction regimes, extensions to the full damping range [6,17,18,23] and non-Markovian dissipation models [24,25], generalizations to state-dependent friction [26], more complex potentials [27–33], systems with many degrees of freedom [34], and cases without detailed balance [35]. In most of these investigations the barrier height E is assumed to be much larger than the energy of thermal motion $\beta E \gg 1$. Of course, the presence of a relatively high barrier is vital for the notion of metastability and the feasibility of a rate description. For these purposes, however, a barrier height of already a few $k_B T$ will suffice to separate the inter-well decay time being of the order of $\tau_f \exp(\beta E)$ from the fast time scale τ_f on which the intra-well relaxation takes place. In the above-mentioned asymptotic theories $1/(\beta E)$ itself, rather than $\exp(-\beta E)$, enters as a small parameter; accordingly, the theories do not cover the whole range of parameters where a rate description is appropriate. Therefore, various different approaches have been put forward in the literature to include finite-barrier height corrections to the escape rate [18,21–23,36,37]. A common disadvantage of these approaches is that they are all strongly dependent on a *parabolic* approximation for the barrier. This assumption, though, is not always met in experimental situations. For example, the barrier of charge transfer reactions is often of a cusp-shaped form [27,30,38]. In such a case, large deviations of theoretical predictions from exact numerical rates are observed in the weak-to-intermediate friction regime [30,31,33]. The latter holds true even though the barrier is extremely high, $\beta E \to \infty$, to say nothing of low barriers for which the problem of finite-barrier corrections still poses a challenge.

In this paper we present accurate calculations of thermally activated rates for a symmetric double well potential and compare these with known expressions, as well as with a new rate formula constructed in terms of the Mel'nikov–Meshkov theory [17] for the energy diffusion regime ($\gamma \lesssim 1$) and the expansion of the Fokker-Planck equation in reciprocal powers of the friction coefficient γ for strong damping ($\gamma \gg 1$). The calculations are performed for different shapes of the potential barrier and different temperatures

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and coupling strengths. In all the cases considered the best results are attained with the present rate expression. The paper is organized as follows: In the next section, we briefly review the Kramers rate problem. In Sec. III, a unified rate expression valid for any barrier shape is constructed. Its utility is illustrated in Sec. IV by comparing with estimates of the rates from numerical calculations. Section V provides a summary.

II. PRELIMINARIES

In the framework of general rate theory, the escape rate Γ^- can always be expressed by $\Gamma^-_{\rm TST}$ following from classical transition state theory (TST)

$$\Gamma^-_{\rm TST}=\left\{\sqrt{2\pi\beta}\int_{-\infty}^{0}dx\,e^{-\beta V(x)}\right\}^{-1}, \tag{2.1}$$

and a transmission factor μ which is at most unity and describes the deviation of the escape rate from $\Gamma^-_{\rm TST}$

$$\Gamma^-=\mu\Gamma^-_{\rm TST}. \tag{2.2}$$

In the above we have identified the transition state with the location of the maximum of $V(x)$ at $x=0$ and set for convenience $V(x)=0$. An early work which discussed non-TST effects is the famous paper of Kramers [1], who provided a dynamical framework for the original concepts of Arrhenius. Proposing it primarily as a model of chemical reactions, Kramers studied the motion of a Brownian particle with mass weighted coordinate x in a metastable potential $V(x)$. The dynamics of the model is governed by the Fokker–Planck equation for the probability distribution $P(x,v,t)$ of finding the particle at time t at the phase space point x,v

$$\partial_t P(x,v,t)=[-v\partial_x+V'(x)\partial_v+\gamma\partial_v(v+\beta^{-1}\partial_v)]P(x,v,t), \tag{2.3}$$

where the prime denotes the derivative with respect to x. Kramers solved the rate problem outlined above in terms of his flux over population method [1]. 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. He showed that depending on the coupling strength (friction coefficient) γ, there are two qualitatively different mechanisms determining the escape dynamics. For vanishingly small γ, both the energy

$$\varepsilon=\tfrac{1}{2}v^2+V(x), \tag{2.4}$$

and the action

$$I(\varepsilon)=\oint dx\,v, \tag{2.5}$$

are almost conserved quantities undergoing slow diffusion motion. The rate limiting step is thus the excitation of the particle to energies greater than the barrier energy (energy diffusion regime). In that case Kramers transformed the Fokker-Planck equation (2.3) to a diffusion equation for the probability density of the action

$$\partial_t P(I,t)=\gamma\partial_I I\left[1+\frac{2\pi}{\beta\omega(I)}\partial_I\right]P(I,t), \tag{2.6}$$

with $\omega(I)$ being the angular frequency at the action I

$$\omega(I)=2\pi\partial_I\varepsilon(I), \tag{2.7}$$

and found a quasistationary probability flux of particles in *action space* through $I^-=I(0)$

$$I^-=2\int_{x_p}^{0}dx\sqrt{-2V(x)},\quad V(x_p)=0. \tag{2.8}$$

This results in a linear dependence of the rate on γ for vanishingly weak coupling ($\gamma\to 0$)

$$\mu^{\rm Kr}_{\rm wc}=\gamma\beta I^-, \tag{2.9}$$

which is valid if $\beta E\gg 1$, and $\mu^{\rm Kr}_{\rm wc}\ll 1$. It may be noted here that the right-hand side of Eq. (2.9) is nothing but a weak damping approximation for the dimensionless energy loss of the particle as it transverses the reactant region [17].

On the other hand, for moderate-to-large friction γ local equilibrium is established in energy, and the escape dynamics is dominated by collisions with the heat bath when the particle is near the top of the barrier. In this regime, the rate is limited by spatial diffusion across the barrier top (spatial diffusion regime). Accordingly, when constructing a quasistationary flux of particles out of the well, Kramers approximated the full potential $V(x)$ entering Eq. (2.3) by its *parabolic* barrier part

$$V(x)=-\frac{1}{2}\omega^2x^2+O(x^3),\quad \omega^2=-V''(0), \tag{2.10}$$

and fully neglected the anharmonic corrections $V(x)+\omega^2x^2/2=O(x^3)$. This yields for the spatial diffusion limit transmission factor

$$\mu_{\rm pb}=\sqrt{1+\frac{\gamma^2}{4\omega^2}}-\frac{\gamma}{2\omega}. \tag{2.11}$$

The above formula is valid for $\beta E\gg 1$ and $\gamma<\gamma_-=\omega_-/(2\pi\beta E)$ with ω_- being the frequency at the bottom of the well, i.e., $\omega_-^2=V''(x_-)$. Consequently, it becomes asymptotically exact in the extreme high barrier (low temperature) limit, $\beta E\to\infty$, in which case one will ultimately almost always be in the spatial diffusion regime. Kramers derived the explicit expressions for the escape rate in these two regimes, and noted the existence of a crossover region.

The ''crossover problem'' was tackled by a great number of investigators, most notably Büttiker, Harris, and Landauer (BHL) [16], Mel'nikov and Meshkov (MM) [17], and Pollak, Grabert, and Hänggi (PGH) [25] (see also a collection of references in [5]). In particular, BHL [16] extended the asymptotic Kramers solution of Eq. (2.9) to the region of weak-to-moderate friction γ. Their generalization for the energy diffusion limit transmission factor reads

$$\mu^{\rm BHL}_{\rm ed}=\mu^{\rm Kr}_{\rm wc}\frac{\sqrt{1+4/\mu^{\rm Kr}_{\rm wc}}-1}{\sqrt{1+4/\mu^{\rm Kr}_{\rm wc}}+1}. \tag{2.12}$$

The overall transmission factor for the full damping range can then be obtained by using an *ad hoc* multiplicative factor $\mu_{\rm pb}$ [5]

$$\mu_{\rm pb}^{\rm BHL}=\mu_{\rm ed}^{\rm BHL}\mu_{\rm pb}, \tag{2.13}$$

which assures that the bridging expression reduces to the correct spatial diffusion limit. An alternative asymptotic solution for the energy diffusion regime and, accordingly, an interpolating formula were given by Mel'nikov *et al.* [6,17]. These read

$$\mu_{\rm ed}^{\rm MM}=A(\mu_{\rm wc}^{\rm Kr}), \tag{2.14}$$

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

and

$$\mu_{\rm pb}^{\rm MM}=\mu_{\rm ed}^{\rm MM}\mu_{\rm pb}. \tag{2.15}$$

The last equation also contains the correct limiting behaviors at weak and strong damping, but more accurately captures the crossover behavior than $\mu_{\rm pb}^{\rm BHL}$ does. A generalization of Eqs. (2.13) and (2.15) to a parabolic double well is straightforward [5,17]. More recently, PGH [25] generalized the theory to an arbitrary time-dependent friction. They showed that the MM crossover formula can be obtained without any *ad hoc* bridging and gave a different approximation for the energy loss. The PGH theory rate constant has been compared directly to reactive flux simulations [39], and found to provide a good description of the rate in the Kramers turnover regime in many cases [25]. However, subsequent studies have revealed some general situations for which PGH theory will fail to correctly predict the escape rate [40]. Therefore, new rate theories that account for these situations have been set forth [19,41,42].

Note that all the mentioned theories make extensive use of the parabolic barrier approximation. Only very recently, a generalization of the flux over population method to an arbitrarily shaped barrier was put forward by one of the present authors [32]. In this way an interpolating formula was constructed that approaches the correct limiting behavior at weak and strong damping. Its validity was tested for Brownian motion in bistable potentials with parabolic, cusped, and quartic barriers. We found that the proposed expression agrees roughly to within 20% with exact numerical rates for $\beta E=10$ regardless of the particular barrier shape. However, subsequent studies have revealed that with decreasing βE, the accuracy of this formula deteriorates very rapidly so that already for $\beta E=5$ it deviates from the exact result up to 40%. The latter holds true even though the barrier is parabolic. A possible reason for this is the failure of the generalized flux over population method to correctly predict the transmission factor in the crossover region. Yet another source of errors may be finite-barrier corrections fully neglected in all the above-mentioned crossover formulas. A simple way to resolve both problems is presented in the next section.

III. IMPROVED INTERPOLATION FORMULA

During the past two decades one could broadly identify two approaches of calculating the rate of thermally activated escape of a particle over a barrier out of a well. One is to recognize the difficulty of obtaining exact rate expressions excepting some special cases, such as a parabolic barrier, and proceed to find the numerically exact rate. A number of efficient methods for numerically integrating Brownian motion on a grid have been devised during the past decade which help to reveal and clarify some interesting phenomena in the transition region between the two extreme limits of weak and strong friction [3,39,40,42–45]. A second approach was to replace rigor with reasonable approximations. The advantage of having accurate analytical formulas as compared to numerical results of numerical methods is in the simplicity of analyzing such formulas with respect to the variation of parameters. A strategy that has gained much popularity in recent years is entirely based on the underlying Fokker-Planck equation and involves various different techniques, such as the Kramers flux over population method, the mean first passage time formalism, the generalized moment expansion technique, and the eigenmode expansion method [1–3,5,22,23,28,31,32,34–37,45]. Another major class of approximation methods rests on the transformation of the original stochastic and dissipative dynamics by an infinite dimensional Hamiltonian system [46,47]. The rate is then calculated by means of the reactive flux [48] through an optimized planar dividing surface [25,29,30,40,49]. Both approaches are rather efficient when treating bistable potentials with *high parabolic* barriers. However, complications arise if the barrier is not parabolic.

In this paper we choose a different starting point. It is based on the observation that exact solutions of the barrier crossing problem are available only in the limiting cases of underdamped and overdamped Brownian motion. Before proceeding two remarks are in order. First, by ''exact solution'' we mean a closed form expression for the escape rate derived *without* using high-barrier approximations. The derivation is straightforward in both limits of weak and strong friction where the dynamics is governed by one-dimensional diffusion equations [Eqs. (2.6) and (3.5), respectively]. In the whole friction range such an expression cannot be obtained with present mathematical techniques. Thus numerical methods must be used. The latter are, in principle, approximate. However, since the error of a general numerical calculation is controllable and can be made as small as one wants, we will refer to such a solution as the *numerically exact* result. Second, we note that it is generally impossible to derive a phenomenological rate description from the underlying dissipative dynamics. As a consequence, there is no unique identification (precise definition) of the escape rate with dynamical characteristics of Eq. (2.3). Thus various different determinations of this phenomenological quantity have resulted. In the above we have already mentioned four rather general approaches to this problem. The calculation of the ratio of a stationary current at the top of the barrier to the population of the well, as originally proposed by Kramers [1], is the method most frequently used in the past [2,3,5,22,31–34]. Alternative derivations are based on the mean first passage time formalism [2,3,5,22] and the gener-

alized moment expansion method [37]. The former identifies the escape rate with the inverse of the mean time after which a stochastic trajectory starting within the well passes the stochastic separatrix for the first time. While the latter determines the rate as the inverse of the mean relaxation time given by the first moment of the equilibrium time correlation function [48]. Finally, a more precise definition of the kinetic rate is adopted in the eigenmode expansion method, which recognizes the smallest nonzero eigenvalue of the Fokker-Planck operator as the sum of forward and backward rates [3,21,22,28,36,45]. All the above-mentioned methods though different give almost indistinguishable results in the high-barrier limit. With decreasing barrier height the difference between the various estimations for the escape rate becomes noticeable even though no approximations have been made to derive these estimations. It is of order $\exp(-\beta E)$ and comes from the different determinations of the rate constant. One may note, however, that this difference is usually much smaller than the error involved in asymptotic rate theories due to neglecting finite-barrier corrections, which are of the order of $1/(\beta E)$.

Turning back to the problem of interest we first consider the weak damping limit, $\gamma \to 0$, where Eq. (2.3) can be approximated by a diffusion equation for the action, Eq. (2.6). This equation is readily solved exactly by the flux over population method to yield for the transmission factor in a potential with only one metastable well [5]

$$\mu(\gamma \to 0) \equiv \mu_{\rm wc}^{-} = \gamma \left\{ \beta \Gamma_{\rm TST}^{-} \int_0^{I^-} dI \exp[-\beta \varepsilon(I)] \times \int_I^{I^-} dI' \frac{\omega(I')}{2\pi I'} \exp[\beta \varepsilon(I')] \right\}^{-1}. \quad (3.1)$$

The generalization to a bistable potential with minima at $x_{\pm}$ is straightforward reading

$$\mu(\gamma \to 0) = \frac{\mu_{\rm wc}^{-} \mu_{\rm wc}^{+}}{\mu_{\rm wc}^{-} + \mu_{\rm wc}^{+}}, \quad (3.2)$$

where $\mu_{\rm wc}^{+}$ is given by Eq. (3.1) with the transcription $- \to +$ and

$$\Gamma_{\rm TST}^{+} = \left\{ \sqrt{2\pi\beta} \int_0^{\infty} dx\, e^{-\beta V(x)} \right\}^{-1}. \quad (3.3)$$

In the opposite limiting case ($\gamma \to \infty$) the reaction coordinate is a slowly varying quantity undergoing diffusive motion. In this regime, the velocity may be eliminated adiabatically from Eq. (2.3) leading us to a Smoluchowski equation for the reduced probability

$$P(x,t) = \int_{-\infty}^{\infty} dv P(x,v,t). \quad (3.4)$$

The equation is [50,3]

$$\partial_t P(x,t) = \partial_x D(x) [\beta^{-1} \partial_x + V'(x)] P(x,t), \quad (3.5)$$

where

$$D(x) = \gamma^{-1} + \gamma^{-3} V''(x) + O(\gamma^{-5}). \quad (3.6)$$

The exact transmission factor is then easily obtained in terms of the mean first passage time formalism to give

$$\mu(\gamma \to \infty) = \sqrt{\frac{2\pi}{\beta}} \left[\int_{-\infty}^{\infty} dx\, e^{\beta V(x)} / D(x) \right]^{-1}. \quad (3.7)$$

In the limit of a high parabolic barrier this approach leads to a perturbative approximation of the form [50]

$$\mu_{\rm pb}(\gamma \gg 1) = \omega/\gamma - (\omega/\gamma)^3 + 2(\omega/\gamma)^5 + O(\gamma^{-7}), \quad (3.8)$$

whose terms coincide, of course, with the corresponding terms in the series expansion of Eq. (2.11), in powers of γ^{-1}. For a bistable potential with an arbitrary barrier height explicit expressions are available only for the first two terms of the inverse friction expansion. These are

$$\mu(\gamma \to \infty) = \omega_e/\gamma - \vartheta/\gamma^3 + O(\gamma^{-5}),$$
$$\omega_e = \sqrt{2\pi/\beta} \left[\int_{x_-}^{x_+} dx\, e^{\beta V(x)} \right]^{-1}, \quad (3.9)$$
$$\vartheta = \frac{\omega_e^2 \beta^{3/2}}{\sqrt{2\pi}} \int_{x_-}^{x_+} dx\, V'^2(x) e^{\beta V(x)}.$$

Finally, we note that exact results for the full friction range are available only in the extreme high-barrier (low temperature) limit, $\beta E \to \infty$, and only for a potential with a parabolic barrier, Eq. (2.15).

A. Unified rate expression

Now let us see how this asymptotic information can be used when constructing an accurate rate expression. On account of Eq. (2.15) one may assume that the overall transmission factor μ for an arbitrary bistable potential has a multiplicative form (MF) reading

$$\mu_{\rm MF} = \mu_{\rm ed} \mu_{\rm sd}. \quad (3.10)$$

Here $\mu_{\rm ed}$, respectively, $\mu_{\rm sd}$ are transmission factors for the energy, respectively, the spatial diffusion limit. These factors must be determined so that they approach the TST value in the two opposing limits

$$\mu_{\rm ed}(\gamma \to \infty) = \mu_{\rm sd}(\gamma \to 0) = 1. \quad (3.11)$$

It may be noted that the ansatz of writing a uniform formula in the multiplicative form is extensively used in the literature on activated rate processes (see, e.g., Refs. [5,6,17,18,23,26,28,32,33,44]). A reason for this seems to be the belief that it yields much better results than nonmultiplicative overall rate expressions. In the following we shall see that this assumption is not actually necessary for accuracy.

B. Weak and intermediate damping

With Eq. (3.10) the construction of a unified rate formula reduces to two separate problems, namely, the derivation of $\mu_{\rm ed}$ and $\mu_{\rm sd}$. A straightforward approach to the energy dif-

fusion limit transmission coefficient $\mu_{\rm ed}$ is based on two remarks. First, when deriving their weak-to-moderate friction result, Eq. (2.14), Mel'nikov *et al.* [6,17] did not make any assumption on the shape of the potential barrier. Second, in the limit of vanishing friction a correct rate formula should reduce to Eq. (3.2) which is exact. For a bistable potential this immediately yields the following rate expression:

$$\mu_{\rm ed}=\frac{A(\mu_{\rm wc}^{-})A(\mu_{\rm wc}^{+})}{A(\mu_{\rm wc}^{-}+\mu_{\rm wc}^{+})}, \tag{3.12}$$

where $A(y)$ is the MM depopulation factor defined by Eq. (2.14). As we shall see in Sec. IV, such the simple transformation of the MM rate formula reduces the error in the weak damping regime by factors and even by orders of magnitude. Mel'nikov and co-workers [44] also have attained a similar reduction of errors in this regime but with much more involved mathematics [18].

C. Spatial diffusion regime

The construction of a spatial diffusion limit transmission factor is a bit more complicated. In this case, the interpolation problem consists in answering the following question: What can be said about the behavior of $\mu_{\rm sd}$ in the full damping range $[0,\infty)$ being based on the asymptotic information in Eqs. (3.9) and (3.11)? Clearly, not much, because the asymptotic expressions (3.9) and (3.11) have nothing in common with each other. In addition, the inverse friction expansion results in a divergent series. Of course, it is possible to invoke some summation techniques, such as Padé approximation and Borel summation, in order to ascribe an effective sum to a divergent series [51,52]. However, to be accurate, all these summation techniques usually require the knowledge of tens of terms in an asymptotic series. It is evident that such luxurious information is not available in principle for the problem we are interested in here, where only the first two terms are generally known. How could we proceed in such a difficult case in order to find an accurate formula connecting Eqs. (3.9) and (3.11)?

An obvious way to resolve the above-mentioned problem is to employ instead of summation techniques an efficient interpolation method which is capable of treating crossover phenomena where just a few asymptotic terms are available. Only very recently has such a method been developed for summation of divergent field-theoretical series [53]. The method is based on an algebraic self-similar renormalization (SSR) of asymptotic series, with control functions defined by crossover conditions. To make this paper self-contained we briefly outline the main ideas of the SSR approach. Assume that a physical characteristic we are looking for is presented by a function $f(y)$ in the interval $[0,\infty)$ and has a power series expansion of the form

$$f(y)=\sum_{m=0} a_m y^m, \tag{3.13}$$

where the expansion coefficients a_m are derivable by a kind of perturbation theory. Being truncated at different m this series forms a divergent sequence of approximants $\{f_k(x)\}$ defined by

$$f_k(y)=\sum_{m=0}^{k} a_m y^m \quad (y\to 0). \tag{3.14}$$

Assume further that an asymptotic behavior of $f(y)$ at large y is also known

$$f_{as}(y)=\lim_{y\to\infty} f(y). \tag{3.15}$$

Two important points of the SSR approach are the following. First, we have to rearrange the sequence in such a way as to improve its convergence properties. The latter is achieved with the help of a simple algebraic transformation [53]

$$F_k(y,s_k)=\sum_{m=0}^{k} a_m y^{m+s_k}, \tag{3.16}$$

whose powers play the role of control functions. This transform increases the approximation order from k to $k+s_k$ thus changing the convergence properties of the renormalized series. The objective is to find a self-similar transformation from $F_{k-1}(y,s_{k-1})$ to $F_k(y,s_k)$ such that having only a few initial terms we would be able to extrapolate them to higher orders of k defining finally an effective limit f^* of the original sequence. A straightforward application of this strategy results in a sequence of nested roots reading [53]

$$f_k^*=(\{\cdots[(f_0^{1/n_1}+B_1 y)^{n_1/n_2}+B_2 y^2]^{n_2/n_3}\cdots\}^{n_{k-1}/n_k} + B_k y^k)^{n_k} \tag{3.17}$$

with $f_0=a_0$. The parameters n_k and B_k appearing in Eq. (3.17) are two sets of control functions which govern the convergence of the sequence $\{f_k^*(y,n_k,B_k)\}$.

Since we are interested here in treating crossover phenomena, yet another important point of the SSR procedure is to self-similarly connect the left and right asymptotic expansions of a function on a given interval. The latter is attained with the requirement that the found approximation (3.17) satisfies the asymptotic condition (3.15)

$$f_k^*(y\to\infty)=f_{as}(y). \tag{3.18}$$

This defines the sets of crossover indexes $\{n_k\}$ and crossover amplitudes $\{B_k\}$. *Practical application* of the SSR approach is the following. If we want to construct a kth-order approximation we may at once write down it in the form of nested roots, Eq. (3.17), and directly define n_k and B_k from the condition (3.18).

Clearly, an analogous procedure can be constructed to self-similarly connect an asymptotic expansion at the right boundary of the interval $[0,\infty)$ with a known asymptotic form at the left boundary where $x\to 0$. But we will not do so here. Instead, we cast the problem of interest, Eqs. (3.9) and (3.11), into the standard form considered above by defining $f=(\gamma/\omega_e)\mu_{\rm sd}$ and $y=\gamma^{-2}$. This yields

$$f(y)=\begin{cases} 1-(\vartheta/\omega_e)y, & y\to 0 \\ 1/(\omega_e\sqrt{y}), & y\to\infty. \end{cases} \tag{3.19}$$

When applied to Eq. (3.19), the second-order crossover approximation gives

$$\mu_{\rm sd}=\left[1+\frac{\gamma^4}{\omega_e^4}\left(1+\frac{4\vartheta}{n\omega_e\gamma^2}\right)^n\right]^{-1/4}, \qquad (3.20)$$

where n is any number from the interval $[0,2]$. As prescribed by Gluzman and Yukalov [53], if the condition (3.18) gives several solutions for control functions, one should opt for the solution that leads to the decrease of B_k with increasing k. It is not difficult to see, however, that this prescription does not fit well in the present case. Instead, we suggest to determine the free parameter n from the requirement that for a parabolic barrier Eq. (3.20) reproduces the fifth-order term in the inverse friction expansion (3.8). This gives $n=8/7$. The resulting spatial diffusion limit transmission factor $\mu_{\rm sd}$ reduces to the TST value at zero damping and, in the strong damping limit to Eq. (3.9). Besides, it becomes effectively a third-order approximation for a purely parabolic barrier. The overall rate formula thus obtained [Eqs. (3.10), (3.12), and (3.20) with $n=8/7$] is exact in both limits of underdamped and overdamped Brownian motion. One may thus expect that it will be reasonably accurate in the crossover region as well.

Before closing this section we note that the SSR approach allows one to go beyond the standard MF approximation for the transmission factor μ. For this purpose it is enough to self-similarly connect the strong damping (Smoluchowski) expression (3.9) with the corrected MM formula (3.12) rather than with the TST result. In that event, the SSR approach gives for the overall transmission factor

$$\mu_{\rm SSR}=\left[\mu_{\rm ed}^{-4}+\frac{\gamma^4}{\omega_e^4}\left(1+\frac{7\vartheta}{2\omega_e\gamma^2}\right)^{8/7}\right]^{-1/4}. \qquad (3.21)$$

By construction, it approaches the correct limiting behavior for both regimes of weak and strong friction. Applications to bistable potentials with different barrier shapes show that in these regimes the interpolating formulas $\mu_{\rm SSR}$ agrees well with the MF approximation, Eq. (3.10), and may slightly deviate from the latter in the intermediate friction region $0.1\leqslant\gamma\leqslant 10$.

IV. APPLICATIONS

A. Numerical results

The proposed formulas are tested for Brownian motion in a symmetric double well of the form

$$V(x)=\frac{E}{b-a}(ax^b-b|x|^a), \quad 0<a<b, \qquad (4.1)$$

whose barrier part $-bE|x|^a/(b-a)$ varies with the parameter a from cusped ($0<a\leqslant 1$) to smooth ($1<a<2$), parabolic ($a=2$), and higher order ($a>2$) barriers. Numerically exact results for the least nonvanishing eigenvalue in this potential were calculated in a previous paper [32] for a parabolic ($a=2,b=4$), a cusped ($a=1$, $b=4$), and a quartic ($a=4$, $b=6$) barrier. The calculation was performed for $\beta E=10$ by a path integral method described elsewhere [42,54]. However, since we are interested here not only in high- but also in low-barrier heights, we have carried out similar calculations for smaller values of βE. The results for the least nonvanishing eigenvalue are presented in Table I. In addition, we have recalculated the least nonvanishing eigenvalue in the quartic double well for $\beta E=10$ and $\gamma=0.01$. It is 0.446[-5] rather than 0.485[−5] as was reported in [32]. The reason is that in the weak friction limit, the long time behavior is governed by a set of low lying eigenvalues that are all very small. In such a case, calculations over very long times are required to get a convergent result for the first nonzero eigenvalue, even though this eigenvalue is well separated from the rest of the spectrum of the Fokker-Planck operator. The previously reported result 0.485-5 was extracted from the time evolution of the distribution function in the intermediate time domain where the single exponential decay had not yet been reached.

TABLE I. First nonzero eigenvalue in a symmetric double well potential, Eq. (4.1), calculated for parabolic ($a=2$, $b=4$), cusped ($a=1$, $b=4$), and quartic ($a=4$, $b=6$) barriers of different heights. Exponential notation [−k] means that the number preceding is to be multiplied by 10^{-k}.

γ	Parabolic $\beta E=1.25$	Parabolic $\beta E=2.5$	Parabolic $\beta E=5$	Cusped $\beta E=5$	Quartic $\beta E=5$
0.01	0.681[-2]	0.204[-2]	0.269[-3]	0.263[-3]	0.299[-3]
0.05	0.300[-1]	0.908[-2]	0.120[-2]	0.120[-2]	0.134[-2]
0.1	0.546[-1]	0.167[-1]	0.219[-2]	0.209[-2]	0.239[-2]
0.25	0.112	0.352[-1]	0.453[-2]	0.410[-2]	0.504[-2]
0.5	0.176	0.565[-1]	0.711[-2]	0.625[-2]	0.817[-2]
0.75	0.215	0.701[-1]	0.866[-2]	0.738[-2]	0.102[-1]
1	0.235	0.783[-1]	0.954[-2]	0.826[-2]	0.114[-1]
1.5	0.241	0.839[-1]	0.101[-1]	0.893[-2]	0.124[-1]
2	0.225	0.823[-1]	0.100[-1]	0.910[-2]	0.123[-1]
3	0.182	0.728[-1]	0.927[-2]	0.904[-2]	0.111[-1]
4	0.148	0.630[-1]	0.838[-2]	0.865[-2]	0.974[-2]
6	0.105	0.481[-1]	0.685[-2]	0.779[-2]	0.757[-2]
8	0.812[-1]	0.382[-1]	0.570[-2]	0.662[-2]	0.611[-2]
10	0.658[-1]	0.315[-1]	0.484[-2]	0.613[-2]	0.509[-2]
20	0.334[-1]	0.165[-1]	0.267[-2]	0.378[-2]	0.272[-2]
30	0.224[-1]	0.111[-1]	0.181[-2]	0.273[-2]	0.184[-2]
100	0.673[-2]	0.335[-2]	0.554[-3]	0.835[-3]	0.558[-3]
1000	0.673[-3] [a]	0.335[-3] [a]	0.555[-4] [a]	0.769[-4] [a]	0.558[-4] [a]

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

B. Comparison of the interpolating formulas with numerical results for the parabolic double well

As closed form expressions for the leading nonvanishing corrections of the Kramers rate in powers of the inverse barrier height are available only for potentials with parabolic barriers, it would be instructive to begin our comparison with a parabolic barrier double well ($a=2$, $b=4$). In this case, a second-order perturbation theory based on a Rayleigh quotient method gives for the spatial diffusion limit transmission factor [22]

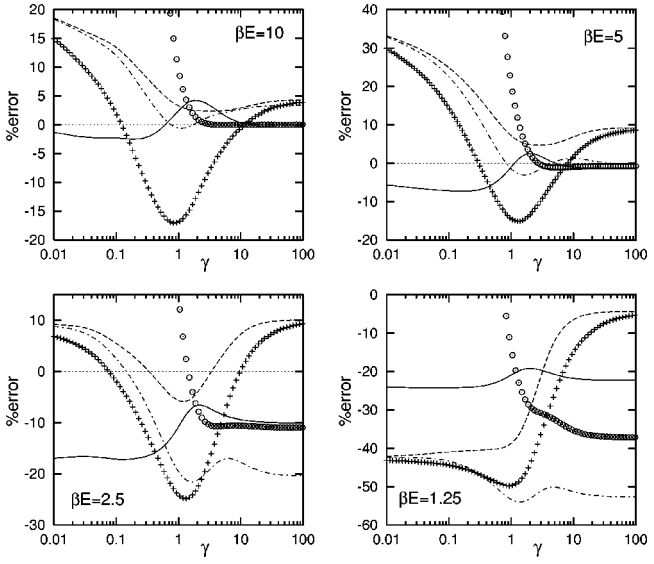

FIG. 1. Percentage errors, $100\times$(approximate−exact)/exact, made in μ for a parabolic double well, Eq. (4.1) with $a=2$, $b=4$, and $\beta E=1.25$, 2.5, 5, and 10. Solid lines, μ_{SSR}, Eq. (3.21); dashed lines, $\mu_{\mathrm{pb}}^{\mathrm{MM}}$, Eq. (2.15); dot-dashed lines, PGH crossover theory [25]; crosses, $\mu_{\mathrm{pb}}^{\mathrm{BHL}}$, Eq. (2.13); open circles, $\mu_{\mathrm{sd}}^{\mathrm{FBC}}$, Eq. (4.2).

$$\mu_{\mathrm{sd}}^{\mathrm{FBC}}=\mu_{\mathrm{pb}}\left\{1-\frac{3}{16\beta E}\left(\frac{1-\nu}{1+\nu}\right)^2+\frac{3}{512\beta^2E^2}\left(\frac{1-\nu}{1+\nu}\right)^4\times\left[35-\frac{16(30\nu^3+103\nu^2+70\nu+12)}{(1-\nu)(3\nu^3+13\nu^2+13\nu+3)}\right]\right\},\quad(4.2)$$

where $\nu=\mu_{\mathrm{pb}}^2$. It contains all contributions to the rate up to $(\beta E)^{-2}$. An alternative approach to this problem, that gives finite-barrier corrections in the whole friction range, has been put forward by Mel'nikov [18]. However, this method appears to be very complicated for practical applications and we will not consider it here.

The relative error made by $\mu_{\mathrm{sd}}^{\mathrm{FBC}}$ in the transmission factor of the parabolic double well is exhibited in Fig. 1, together with those of the other theoretical predictions discussed above. Since the proposed formulas μ_{MF} and μ_{SSR} give in this case results that differ at most by a few percent, we show only those for μ_{SSR}. As anticipated, for a high barrier ($\beta E=10$) the rate expression obtained from the Rayleigh quotient, Eq. (4.2), is most accurate in the spatial diffusion regime. For $\gamma\gtrsim 4$ the relative error made by $\mu_{\mathrm{sd}}^{\mathrm{FBC}}$ is less than 0.03%. With the present expression μ_{SSR} an analogous accuracy is attained for $\gamma\gtrsim 10$. The other three interpolating formulas overestimate the rate by $\sim 4\%$ in this damping region. Away from the spatial diffusion regime, that is, in the crossover region where the rate reaches its maximal value at $\gamma\approx 1.5$ and then falls off with further decreasing γ, the relative error made by $\mu_{\mathrm{sd}}^{\mathrm{FBC}}$ rapidly increases and very soon grows out of the scale of the figure. In this region the best agreement is attained with the PGH crossover theory, which underestimates the rate by 0.3%. While the MM and SSR interpolating formulas give results that are larger than the numerically exact transmission factor by 3% and 5%, respectively. The BHL expression is least accurate in the crossover region, underestimating the rate for $\gamma=1$ by 17%. In the weak damping regime ($\gamma<1$) the present expression is with maximally 2% considerably better than the other three interpolating formulas, which have maximal relative errors of more than 15%. The small deviations, which still exist in the underdamped regime, between μ_2^{CFE} and estimates of the transmission factor from path integral calculations can be fully taken into account by the difference between the flux-over-population rate expression [Eqs. (3.1) and (3.2)] and the least nonvanishing eigenvalue.

For a relatively low barrier ($\beta E=5$) the overall situation remains almost the same. In the strong damping regime ($\gamma\gtrsim 10$) $\mu_{\mathrm{sd}}^{\mathrm{FBC}}$ and μ_{SSR} are characterized by a similar accuracy, underestimating the transmission factor by less than 1%. The PGH theory is with maximally 2% only a bit worse, while $\mu_{\mathrm{pb}}^{\mathrm{BHL}}$ and $\mu_{\mathrm{pb}}^{\mathrm{MM}}$ deviate up to 9%. In the crossover region ($\gamma\sim 1.5$) the SSR and PGH expressions deviate by roughly the same amount, the former overestimates the rate by 2% while the latter underestimates it by 3%. The relative errors of the MM and BHL interpolating formulas in this region are 6% and 15%, respectively. For weak damping ($\gamma<1$) the present expression is again in considerably better agreement with numerical calculations than the other three interpolating formulas. It underestimates the transmission factor by less than 6%, while the other three approaches overestimate it by more than 30%.

With further decreasing barrier height all the theoretical expressions become relatively inaccurate. Even the present formula μ_{SSR}, which is exact for both weak and strong friction, deviates in these limits for $\beta E=2.5$ by 17% and 10%, respectively. For strong friction the deviations are due to the difference between the mean-first passage-time expressions for the rate and the least nonvanishing eigenvalue. This difference becomes noticeably large for $\beta E<5$. The same reasoning holds true for the limit of underdamped motion, in which case μ_{SSR} reduces to the flux-over-population expression, Eq. (3.2). As far as the Rayleigh quotient formula $\mu_{\mathrm{sd}}^{\mathrm{FBC}}$ is concerned, the reason for its failure in the strong damping limit is different. It is caused by the dependence, for $\beta E<5$, of the denominator of the Rayleigh quotient on the detailed shape of the trial function [36,37], the fact fully neglected by Talkner [22] in his derivation of Eq. (4.2). The above observations indicate that the rate description as a whole looses its meaning for too low barriers. In such a case, the equilibrium distribution no longer allows an unambiguous definition of the populations of the different metastable states and, correspondingly, the rate constants, although the long-time dynamics may still be governed by a single least nonvanishing eigenvalue that is well separated from the rest of the finite eigenvalues [36,45]. It is remarkable, however, that the accuracy of the interpolating formula μ_{SSR} deteriorates with decreasing barrier height only slowly. Thus for instance, its maximal relative error for a very low barrier ($\beta E=1.25$) is 24%. It is not so bad, taking into account that the other interpolating formulas deviate in this case by 43% and over.

Summarizing the results of this subsection, the present treatment is characterized by the best predictions for the rate in both regimes of weak and strong friction. As long as the rate description is valid, the relative errors made in these regimes by the proposed formulas μ_{SSR} and μ_{MF} are less by

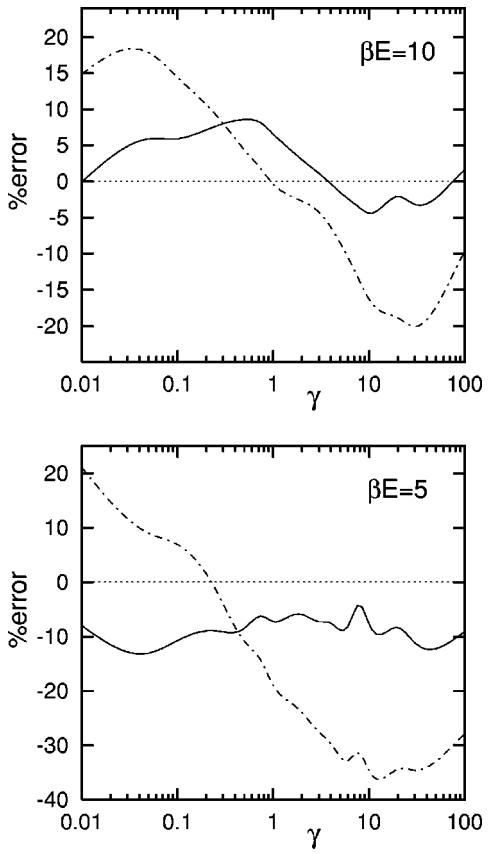

FIG. 2. Percentage errors made in the transmission factor for a cusped double well, Eq. (4.1) with $a=1$, $b=4$, and $\beta E=5$ and 10. Solid lines, μ_{SSR}, Eq. (3.21); dot-dashed lines, deterministic approach [32].

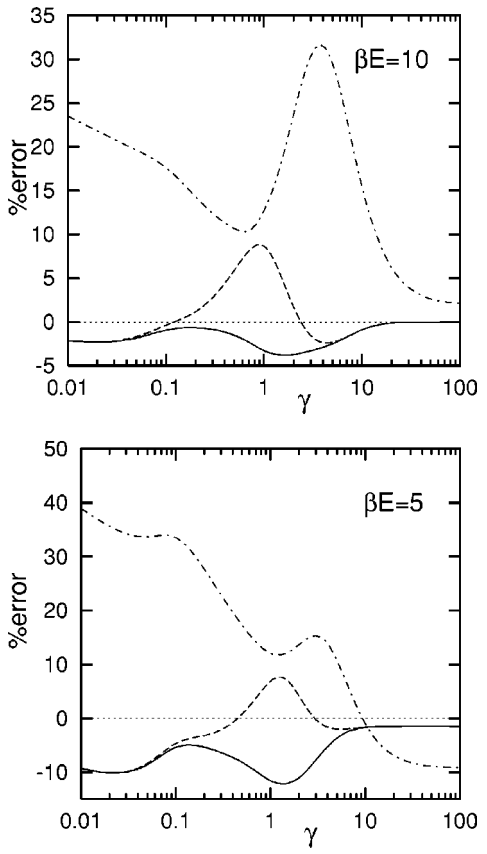

FIG. 3. Same as in Fig. 1 but for a quartic double well, Eq. (4.1) with $a=4$ and $b=6$. Dashed lines are for μ_{MF}, Eq. (3.10).

nearly one order of magnitude than those of the BHL, MM, and PGH expressions. In the crossover region, the accuracy of all methods is a few percent, excepting the BHL method. The latter is least accurate in this regime, underestimating the rate by more than 15%.

C. Cusped and quartic double well potentials

Next we apply the present approach to a cusped and a quartic barrier. Since the standard rate expressions discussed in Sec. II are not applicable in such a case, we will compare to an interpolating formula suggested in a previous paper [32]. Based on the MM weak damping result [Eq. (2.14)] it combines a generalized spatial diffusion limit transmission factor with a properly defined energy loss of the particle per oscillation. The former is derived by approximately solving the Fokker-Planck equation while the latter is obtained from the deterministic particle dynamics. In the following we will refer to this approach as the deterministic method.

Relative errors made by the different interpolating formulas in the transmission factor of a cusped double well potential are shown in Fig. 2. Since theoretical predictions obtained with μ_{MF} and μ_{SSR} are almost indistinguishable in this case, both expressions are presented by one curve in the figure. Moreover, we note that unlike smooth potentials for which an accuracy of 0.01% is easily attained with a mild computational effort, path integral calculations for a cusped potential are much less stable. In fact we were able to generate, in a reasonable amount of time, convergent results only with two to three stable digits. Whereas more accurate results would require an excessive computational effort. That is the reason for slight oscillations of the curves presented in Fig. 2. Turning back to our comparison one sees that the present approach gives the best predictions in the whole friction range regardless of the barrier height. As is the case for the parabolic double well, the accuracy of the method deteriorates with decreasing barrier height slowly. The maximal deviation from the exact numerical rate varies from 8% for $\beta E=10$ to 14% for $\beta E=5$. This in contrast to the deterministic approach, whose maximal relative error are 20% and 37%, respectively.

Finally, we consider the rate of escape over a quartic barrier ($a=4$, $b=6$). The corresponding results are shown in Fig. 3. We find that in this case the interpolating formulas μ_{MF} and μ_{SSR} noticeably differ from each other in the crossover region ($\gamma\approx 1.5$) where the former overestimates the rate while the latter underestimates it. The maximal relative errors for μ_{SSR} are 4% and 12% for $\beta E=10$ and 5, respectively, while μ_{MF} deviates in both cases up to 8%. The deterministic approach is, with maximally 32% and 39%, considerably worse than μ_{SSR} and μ_{MF}.

V. CONCLUSIONS

Based on the exact rate expressions available in the limits of underdamped and overdamped Brownian motion we constructed a formula for the transition rate over a barrier of arbitrary shape by means of the self-similar normalization

method. Moreover, path integral calculations were presented for the least nonvanishing eigenvalue in a double well potential with a parabolic, a cusped, and a quartic barrier. The calculations were performed over a broad range of the friction coefficient γ and for different temperatures (barrier heights) βE. The results for a parabolic barrier were used to analyze the relative validity of existing approaches to the calculation of the overall rate expression. Besides the SSR method, our comparison includes predictions from the BHL, MM, and PGH crossover theories. We found that the present approach is most accurate in the regimes of weak ($\gamma<1$) and strong ($\gamma>3$) damping. In both regimes its maximal relative error is smaller by factors and even by orders of magnitude than those of the other three approaches. In the crossover region ($\gamma\sim1.5$) the SSR, MM, and PGH expressions deviate by a few percent from the exact result, while the BHL formula is the worst, systematically underestimating the rate in this region by over 15%. The above observations hold true as long as the barrier height is high enough, $\beta E\gtrsim5$. Otherwise, all the theoretical expressions become relatively inaccurate. This failure is due to the equilibrium properties of the system that do not allow an unambiguous definition of the populations of the different metastable states for too low barriers. Although the difference between the mean-first passage-time expressions for the rate and the least nonvanishing eigenvalue is ''exponentially small,'' for $\beta E \lesssim3$ it does not much differ in magnitude from the ''leading'' algebraic corrections in powers of the inverse barrier height. Accordingly, the rate description looses its meaning for very low barrier heights. However, even in such a difficult situation the present approach gives a reasonable description of the escape dynamics, underestimating the numerical rate for $\beta E=1.25$ up to 24%. For comparison, the maximal errors of the other three approaches are nearly two times larger in this case. Finally, applications to nonparabolic (cusped and quartic) barriers showed that the SSR method is in considerably better agreement with the numerically exact rates than the deterministic approach to the crossover problem suggested in a previous paper [32].

Summarizing the results of this work, one may conclude that the present method offers a systematic strategy for constructing explicit analytical expressions for the rate valid in the whole parameter space. We note the relative ease with which highly accurate predictions for the escape rate can be obtained using the SSR technique. The accuracy of the method in the crossover region can be further improved when more terms of the asymptotic expansion are available. Although this whole paper was limited to a one-dimensional barrier crossing process with Markovian dissipation, the approach may be generalized to the case of memory friction and systems with many degrees of freedom. Yet another interesting variety of its applications is the crossover phenomenon in systems without detailed balance, the problem that is difficult to treat by other means.

ACKNOWLEDGMENT

Financial support of the Ministry of Education, Science, Sports, and Culture of Japan is greatly appreciated.

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