# Activated rate processes: Finite-barrier expansion for the rate in the spatial-diffusion limit

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A dynamically corrected variational transition-state theory is formulated for the thermally activated escape of a particle trapped in a potential well separated from a different well or continuum by a barrier and coupled to a heat bath. The theory is based on the Hamiltonian-equivalent formulation of the generalized Langevin equation. The dynamical corrections are obtained by utilizing the reactive-flux method in which the choice of dividing surface is guided by minimization of the transition-state flux. Analytic correction formulas, valid for memory friction, are obtained for the Kramers-Grote-Hynes estimate of the rate in the range from moderate friction to the large-friction limit. The analytic expansion is in terms of the inverse barrier height $(1/\beta V^{\ddagger})$. For the special case of an extended Smoluchowski equation containing finite damping corrections, the exact expansion is also obtained using the mean-first-passage-time formulation. The dynamically corrected variational transition-state-theory expansion is shown to be identical to the mean-first-passage-time result.

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## I. INTRODUCTION

Determining the decay rate of a metastable state of a classical particle which interacts with a heat bath is a problem that has intrigued the physics and chemistry communities for quite some time. A very popular formulation of the problem was given by Kramers [1]. He considered a particle whose dynamics is governed by a Langevin equation. In Kramers's picture, the particle moves under the influence of a potential as well as a bath which exerts on it a velocity-dependent frictional force and a fluctuating Markovian Gaussian random force. A more general version of the problem is obtained by introducing the generalized Langevin equation (GLE) which allows for memory effects.

In one dimension, it is assumed that the motion of the particle may be described in terms of the GLE,

$$m\ddot{q} = -\frac{dw(q)}{dq} - m\int_0^t d\tau\,\gamma(t-\tau)\dot{q}(\tau) + \xi(t)\ , \quad (1.1)$$

where $m$ is an effective mass, $q$ is the particle coordinate, and $\gamma(t)$ is the time-dependent friction kernel. The Gaussian random force $\xi(t)$ has zero mean and its correlation function is given in terms of the time dependent friction as $\langle \xi(t)\xi(\tau)\rangle = mk_BT\gamma(t-\tau)$. Apart from the thermodynamic equilibrium effects incorporated in the potential of mean force $w(q)$, the particle "feels" a dynamic time-dependent-friction and random force induced by the medium in the condensed phase. Kramers's work was limited to "Ohmic" friction [$\gamma(t)=2\gamma\delta(t)$ where $\delta(t)$ is the Dirac $\delta$ function].

Kramers derived three major results in his paper. In the weak-damping regime, he showed that the escape rate is dominated by an energy-diffusion process. The energy-diffusion rate is proportional to the friction coefficient $\gamma$. In the intermediate-damping regime, the rate is given in terms of a one-dimensional transition-state-theory (TST) expression and reaches its maximal value. At high friction, the rate is dominated by a spatial-diffusion process and in the limit of very high friction is inversely proportional to the friction coefficient. All these three regimes are also observed in the presence of memory friction. The energy-diffusion regime was considered by Carmeli and Nitzan [2], and the spatial-diffusion limit by Grote and Hynes [3] and Hänggi and Mojtabai [4]. A uniform theory which accounts for all limits was recently given in Ref. [5] and will be referred to as Pollak-Grabert-Hänggi (PGH) theory. A detailed history of these developments may be found in the recent review of Hänggi, Talkner, and Borkovec [6].

The present paper will deal with the rate in the intermediate to strong damping regimes, where one can assume that energy randomization is fast and the reactant particle is in thermal equilibrium with the bath. In this limit, Kramers's result as well as its generalization to include memory friction is really just the steepest-descent estimate to the rate. The "small parameter" of the problem is the inverse of the reduced barrier height $V^{\ddagger}/k_BT$. The steepest-descent solution is identical to considering a problem in which the dynamics is governed purely by a parabolic barrier.

Kramers and his successors realized this limitation. One finds a series of papers following Kramers which attempt to derive expansions for the rate expression in terms of the small parameter $1/\beta V^{\ddagger}$ where $\beta \equiv 1/k_BT$. When the dynamics is Markovian and in the strong-damping limit, the two-dimensional Fokker-Planck equation for the distribution function of the particle position and velocity may be reduced to the Smoluchowski equation. In this limit, the formal result for the mean first-passage time is well known [6] and the saddle-point expansion for the rate in terms of $1/\beta V^{\ddagger}$ is well understood [7–11].

For Ohmic friction, various expressions have been derived beyond the Smoluchowski limit. Ryter [12] uses a boundary layer method to derive an expression for the

 

whole range of friction in the spatial-diffusion limit. His result does not reduce though to the known expansion in the Smoluchowski limit (cf. Sec. V). Talkner [13] has used a generalized Ritz method which leads to an expression that agrees with the known expansion in the Smoluchowski limit (for symmetric potentials) and reduces to the one-dimensional TST expression in the weak-damping limit. Dekker [14] has used a Rayleigh quotient method to derive a result that goes to the correct Smoluchowski limit and is proportional to the square root of the damping constant in the weak-damping limit. All three expressions differ from each other and the "correct" one has not yet been established. In addition, all this work is limited to Ohmic friction. An extension to exponential memory friction, based on a mean-first-passage-time approach, has been applied to a specific example in Ref. [15]. However, this method has not been generalized to arbitrary memory friction.

A different approach which is applicable to memory friction and is not limited to exponential memory is based on variational transition-state theory (VTST) [16–23]. Here, one considers the dynamics for the Hamiltonian equivalent of the GLE. It is well known that the dynamics of the GLE are the continuum limit of the dynamics of the system bilinearly coupled to a harmonic bath [24,25]. Instead of dealing with the dynamics of a stochastic differential equation one may consider the Hamiltonian dynamics and then go to the continuum limit.

By identifying optimal dividing surfaces and considering the equilibrium flux through the surface in the direction from reactants to products one can derive meaningful upper bounds for the rate. These upper bounds depend on the finite reduced barrier height and so can be used as a basis for a $1/\beta V^{\ddagger}$ expansion. Most recently, Berezhkovskii, Pollak, and Zitserman [23] used this approach to determine the optimal planar dividing surface for a given GLE at a fixed temperature. This was then used to derive $1/\beta V^{\ddagger}$ expansions for the VTST rate. However, as stressed by Berezhkovskii, Pollak, and Zitserman, this procedure only gives an upper bound to the rate and especially when the potential is not symmetric does not lead to the exact expansion for the rate constant in terms of $1/\beta V^{\ddagger}$.

The main purpose of the present paper is to provide the leading term in a $1/\beta V^{\ddagger}$ expansion for the rate which is valid for arbitrary time-dependent friction in the spatial-diffusion limit. The method we use is based on a synthesis of the VTST approach and the perturbation theory introduced by PGH [5] when solving the Kramers turnover problem. In the parabolic barrier limit, the dynamics of the equivalent Hamiltonian are separable. The Hamiltonian may be diagonalized using a normal-mode transformation [16,26]. The barrier crossing problem is reduced to the one-dimensional dynamics along the unstable mode $\rho$. Any trajectory initiated at the top of the barrier of the unstable mode with positive velocity along the $\rho$ mode is by definition reactive. Because of the separability there is no restoring force. As a result the VTST approach is identical to the steepest-descent estimate of the rate as derived by Kramers and Grote and Hynes. For a finite barrier, the nonlinearity of the potential can still induce a recrossing of the barrier. However, the nonlinearity may be thought of as the small parameter of the problem and the exact equations of motion may be solved perturbatively in terms of the nonlinearity to obtain a precise estimate for the recrossing.

This approach will be referred to as "dynamical VTST" because of the synthesis of an optimized dividing surface with a dynamical correction term. Dynamical VTST leads to tractable expressions for the exact leading correction term to the rate in terms of $1/\beta V^{\ddagger}$. The resulting term will be expressed purely in terms of the system potential parameters and Laplace transforms of the time-dependent friction such that the continuum limit becomes obvious. For an Ohmic bath in the large-friction limit it reduces to the known results based on the Smoluchowski equation. We will find that for symmetric potentials VTST gives the exact leading term, but for asymmetric potentials it is necessary to solve explicitly for the dynamics to obtain the correct rate.

The reactive-flux method for determining the rate [6,27,28] is reviewed and developed in Sec. II. The Hamiltonian equivalent for the GLE and the normal modes are introduced within the context of the reactive-flux method, leading to an exact expression for the rate which is based on the exact solution of the equations of motion. In Sec. III the equations of motion are solved perturbatively. This solution is then used to obtain the leading-order correction to the steepest-descent estimate. The theory is then applied in Sec. IV to the prototypical cubic and quartic potentials. In Sec. V we compare our results in detail with the somewhat differing expansions derived by previous authors. The dynamical VTST differs from the previous expansions. To verify that dynamical VTST is in fact correct, we present in Sec. V the mean-first-passage-time expression for the rate derived from the Skinner and Wolynes extension [29] of the Smoluchowski equation. We find that this mean-first-passage-time result agrees with dynamical VTST for an Ohmic bath. The Skinner-Wolynes approach is limited, however, to Ohmic friction. The paper ends with a discussion, pointing out the strengths and limitations of dynamical VTST, as well as possible extensions.

## II. THE EXACT RATE EXPRESSION

### A. The Hamiltonian equivalent in normal modes

As already mentioned in the Introduction, the dynamics of the GLE [Eq. (1.1)] is equivalent to the dynamics of the Hamiltonian [24,25],

$$H=\frac{p_q^2}{2}+w(q)+\sum_j \tfrac{1}{2}\left[p_{x_j}^2+\left[\omega_j x_j-\frac{c_j q}{\omega_j}\right]^2\right]. \tag{2.1}$$

The system coordinate $q$ is coupled bilinearly to a bath of harmonic oscillators with frequencies $\omega_j$. The summation is over an infinite set of bath oscillators which tends towards a continuum. In practice, one must consider only a finite discrete sum ($j=1,\ldots,N$) of both oscillators. The continuum limit will become self-evident as all final results will include the bath only through Laplace

transforms of the time-dependent friction. Mass weighted coordinates are used throughout this paper, such that the coordinate $q$ is really $\sqrt{m}\,q$ and similarly for the bath coordinates $x_j$. The system potential $w(q)$ is assumed to have a well at $q=q_a$ and a barrier at $q=0$. The barrier height is $V^{\ddagger}\equiv w(0)-w(q_a)$.

The GLE [Eq. (1.1)] may be rederived from the Hamiltonian by noting that Newton's equation of motion for each bath mode is identical to that of a forced oscillator where the forcing function is determined by the system coordinate (or velocity). Since the formal solution for the forced oscillator is well known, it may be used for each of the bath coordinates and inserted into Newton's equation for the system coordinate $q$. At this point, the equation of motion for $q$ reduces to the GLE with the identification that

$$\gamma(t)=\sum_{j=1}^{N}\frac{c_j^2}{\omega_j^2}\cos(\omega_j t)\ . \tag{2.2}$$

The Laplace transform of the time-dependent friction, denoted as $\hat{\gamma}(s)\equiv\int_0^\infty dt\, e^{-st}\gamma(t)$, is given in terms of the parameters of the Hamiltonian as

$$\hat{\gamma}(s)=\sum_{j=1}^{N}\frac{c_j^2}{\omega_j^2}\frac{s}{\omega_j^2+s^2}\ . \tag{2.3}$$

The spectral density of the bath modes $J(\omega)$ is defined as

$$J(\omega)=\frac{\pi}{2}\sum_{j=1}^{N}\frac{c_j^2}{\omega_j}[\delta(\omega-\omega_j)-\delta(\omega+\omega_j)] \tag{2.4}$$

and is related to the time-dependent friction by

$$J(\omega)=\omega\int_0^\infty dt\,\gamma(t)\cos(\omega t)\ , \tag{2.5}$$

where $\delta(x)$ is the Dirac $\delta$ function.

Without loss of generality, the system potential may be divided into a parabolic part and a nonlinear part,

$$w(q)\equiv w(0)-\tfrac{1}{2}\omega^{\ddagger 2}q^2+w_1(q)\ . \tag{2.6}$$

The nonlinearity $w_1$ will be further subdivided into a combination of symmetric and antisymmetric terms,

$$w_{1s}(q)\equiv\tfrac{1}{2}[w_1(q)+w_1(-q)]\ , \tag{2.7}$$

$$w_{1as}\equiv\tfrac{1}{2}[w_1(q)-w_1(-q)]\ . \tag{2.8}$$

When one ignores the nonlinearity, the Hamiltonian [Eq. (2.1)] is bilinear in the momenta and coordinates and so may be diagonalized using the standard normal-mode transformation. The new normal modes will be denoted $\rho,y_j$; $j=1,N$, where the unstable mode $\rho$ is associated with the unique negative eigenvalue of the normal-mode transformation ($-\lambda^{\ddagger 2}$), while the $y_j$'s denote the stable modes associated with the positive eigenvalues ($\lambda_j^2$). The barrier frequency $\lambda^{\ddagger}$ is just the standard Kramers-Grote-Hynes frequency,

$$\lambda^{\ddagger 2}=\frac{\omega^{\ddagger 2}}{1+\sum_{j=1}^{N}[c_j^2/\omega_j^2(\omega_j^2+\lambda^{\ddagger 2})]}=\frac{\omega^{\ddagger 2}}{1+[\hat{\gamma}(\lambda^{\ddagger})/\lambda^{\ddagger}]}\ , \tag{2.9}$$

where the second expression on the right-hand side is obtained by using the results for the Laplace transform of the time-dependent friction [Eq. (2.3)].

The elements of the normal-mode transformation matrix $\mathbf{U}$ are such that

$$q=u_{00}\rho+\sum_{j=1}^{N}u_{j0}y_j\ . \tag{2.10}$$

The matrix element $u_{00}^2$ may be expressed in terms of the Laplace transform of the time-dependent friction as

$$u_{00}^2=\left[1+\sum_{j=1}^{N}\frac{c_j^2}{(\omega_j^2+\lambda^{\ddagger 2})^2}\right]^{-1}=\left[1+\frac{1}{2}\left[\frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}}+\frac{\partial\hat{\gamma}(s)}{\partial s}\bigg|_{s=\lambda^{\ddagger}}\right]\right]^{-1}\ . \tag{2.11}$$

A detailed solution for the normal-mode transformation may be found in Ref. [26].

It is useful to define also a spectral density of the normal modes [30] as

$$I(\lambda)\equiv\frac{\pi}{2}\sum_{j=1}^{N}\frac{(u_{j0}^2/u_{00}^2)}{\lambda_j}[\delta(\lambda-\lambda_j)-\delta(\lambda+\lambda_j)]\ . \tag{2.12}$$

The spectral density of the normal modes is related to the spectral density $J(\omega)$ and the time-dependent friction [30],

$$u_{00}^2 I(\lambda)=\frac{J(\lambda)}{(\omega^{\ddagger 2}+\lambda^2-\mathrm{Re}[i\lambda\hat{\gamma}(i\lambda)])^2+J(\lambda)^2}\ . \tag{2.13}$$

It is also useful to define a correlation function (cf. the Appendix),

$$H(t)\equiv\Omega^2\frac{1}{u_1^2}\sum_{j=1}^{N}\frac{u_{j0}^2}{\lambda_j^2}\cos(\lambda_j t)\ , \tag{2.14}$$

where the frequency $\Omega$ is defined such that

$$H(0)=1 \tag{2.15}$$

and

$$u_1^2\equiv 1-u_{00}^2\ . \tag{2.16}$$

This correlation function is well defined in the continuum limit since it can be expressed in terms of the spectral density of the normal modes,

$$H(t)=\frac{2}{\pi}\frac{u_{00}^2}{u_1^2}\Omega^2\int_0^\infty d\lambda\frac{I(\lambda)}{\lambda}\cos(\lambda t)\ . \tag{2.17}$$

From Eqs. (2.16) and (2.17) one notes that the collective-mode frequency $\Omega$ may be expressed as

$$\frac{u_1^2\omega^{\ddagger 2}}{\Omega^2}=\omega^{\ddagger 2}\sum_{j=1}^{N}\frac{u_{j0}^2}{\lambda_j^2}=\frac{u_{00}^2\omega^{\ddagger 2}}{\lambda^{\ddagger 2}}-1\equiv\frac{1}{\chi}\ , \tag{2.18}$$

where the second equality on the right-hand side is a property of the normal-mode transformation [5]. The parameter $\chi$ defined in this equation has been termed the nonlinearity parameter in Ref. [23]. Finally, we define a collective bath mode $\sigma$,

$$\sigma \equiv \frac{1}{u_1} \sum_{j=1}^{N} u_{j0} y_j \ . \tag{2.19}$$

The Hamiltonian equivalent for the GLE can now be recast in terms of the normal modes,

$$H = w(0) + \tfrac{1}{2}[p_\rho^2 - \lambda^{\ddagger 2}\rho^2 + \sum_{j=1}^{N} (p_{y_j}^2 + \lambda_j^2 y_j^2)] + w_1(u_{00}\rho + u_1\sigma) \ . \tag{2.20}$$

The *exact* equation of motion for the unstable mode is

$$\ddot{\rho} - \lambda^{\ddagger 2}\rho = -u_{00} w_1'(u_{00}\rho + u_1\sigma) \ , \tag{2.21}$$

where the notation $f'(x) \equiv df/dx$ denotes the derivative with respect to the argument. Similarly the exact equation of motion for each of the stable modes is

$$\ddot{y}_j + \lambda_j^2 y_j = -u_{j0} w_1'(u_{00}\rho + u_1\sigma) \ . \tag{2.22}$$

### B. The reactive-flux expression for the rate

The central purpose of this paper is to find an expression for the rate of reaction. The system potential $w(q)$ is assumed to be such that it defines a domain which may be considered as reactants and a second domain which may be thought of as products. Each domain is presumably well defined in the full phase space of the full Hamiltonian (2.1) of the system and the bath. A dividing surface $f=0$ in the full phase space is defined by having the property that any trajectory that goes from the reactant to the product domain (or vice versa) crosses this surface. Putting it differently, the dividing surface divides the phase space into two disjoint domains—reactants and products. Without loss of generality, $f$ is taken as positive in the reactants domain and negative in the products domain. The characteristic function [27,31] of reactants $\Theta_a = \Theta(f)$, where $\Theta(x)$ is the unit step function, is defined as unity for any point in phase space lying in the reactants domain and zero otherwise. The reactants population can then be described as an average of $\Theta_a$ over some distribution. Similar definitions may be made also for products.

Following the standard derivations [6,27,28], the rate constant is proportional to the plateau value of the reactive flux,

$$\Gamma_a(t) = \frac{\langle \delta(f)[\nabla f \cdot \mathbf{p}]\Theta(f(t)) \rangle}{\langle \Theta(f) \rangle} \ . \tag{2.23}$$

Here $\nabla f$ is the gradient in the full phase space and $\mathbf{p}$ is the generalized velocity vector in phase space with components $\dot{p}_q, \dot{q}, \dot{p}_{x_j}, \dot{x}_j$; $j=1,\ldots,N$. The plateau value is obtained on a time scale which is fast in comparison to the reaction time, i.e., $\Gamma_a t \ll 1$. The time dependence of the surface function $f$ is determined by the Hamiltonian time evolution of each phase-space point at time $t$ that evolved from the initial ($t=0$) phase-space point. The brackets denote an averaging over the initial distribution of phase-space points, which is assumed to be the equilibrium distribution $e^{-\beta H}$.

The VTST expression for the rate is just $\Gamma_a(0^+)$. At very short positive times ($0^+$), only trajectories with velocities perpendicular to the dividing surface in the direction of reactants will enter the reactants domain. One may therefore substitute $\Theta(f(0^+))$ with the unit step function $\Theta(\nabla f \cdot \mathbf{p})$, thus regaining the standard form for the VTST expression for the rate [31,32].

At this point we will specify the dividing surface choosing it to be perpendicular to the unstable normal mode,

$$f = -\rho \ . \tag{2.24}$$

This implies that $\nabla f \cdot \mathbf{p} = -p_\rho$ and the reactants domain is defined by $\Theta_a = \Theta(-\rho)$. In summary, our working expression for the rate is

$$\Gamma_a(t) = -\frac{\langle \delta(\rho) p_\rho \Theta(-\rho(t)) \rangle}{\langle \Theta(-\rho) \rangle} \ . \tag{2.25}$$

The exact rate is obtained if one can determine which trajectories initiated on the dividing surface at time $t=0$ will find themselves at long times still in the reactants domain. For a purely parabolic barrier, motion along the unstable mode is frictionless, therefore the answer is determined by the sign of the momentum $p_\rho$ and is thus identical to the VTST rate. In other words, for parabolic barriers, as is well known, VTST is exact. In the presence of nonlinearities, the nonlinearity can induce a recrossing of the dividing surface and the exact rate demands in principle the full time evolution of the trajectory. However, for "weak" nonlinearity, this evolution can be determined perturbatively, leading to an expansion of the rate in terms of the nonlinearity. This program is implemented in the next section.

## III. DYNAMICAL VTST

The exact rate can be obtained by solving for the exact time dependence of the unstable normal mode. In general, this can only be done numerically and even then at some expense. However, as already noted, for a purely parabolic barrier the solution is trivial. The parabolic barrier estimate for the rate is the leading term in a steepest-descent asymptotic expansion (in the spatial-diffusion limit) in which the small parameter is $1/\beta V^{\ddagger}$. The barrier height $V^{\ddagger}$ is finite only as a result of the nonlinear part of the potential $w_1$. Thus an expansion in $1/\beta V^{\ddagger}$ is really identical to an expansion in the nonlinearity $w_1$. Dynamical VTST is the lowest-order correction to the parabolic barrier dynamics.

Inspection of the exact equations of motion (2.21) and (2.22) shows that the lowest-order correction to the dynamics of the $\rho$ mode in terms of the nonlinearity $w_1$ is obtained from insertion of the zeroth-order solution for the collective mode $\sigma$ in the $\rho$ mode equation of motion. Specifically, from Eqs. (2.19) and (2.22) one finds

$$u_1\sigma_0(t) = \sum_{j=1}^{N} u_{j0} \left[ y_j \cos(\lambda_j t) + \frac{p_{y_j}}{\lambda_j} \sin(\lambda_j t) \right] \ , \tag{3.1}$$

where the subscript denotes the zeroth-order solution. Similarly,

$$\rho_0(t)=\rho\cosh(\lambda^\ddagger t)+\frac{p_\rho}{\lambda^\ddagger}\sinh(\lambda^\ddagger t)\ . \tag{3.2}$$

The first-order correction to the unstable mode equation of motion is identical to the equation of motion of a forced parabolic barrier,

$$\ddot{\rho}_1-\lambda^{\ddagger 2}\rho_1=-u_{00}w_1'(u_{00}\rho_0(t)+u_1\sigma_0(t))\ . \tag{3.3}$$

The solution for this forced barrier is well known,

$$\rho_1(t)=\rho_0(t)-\int_0^t d\tau\frac{\sinh[\lambda^\ddagger(t-\tau)]}{\lambda^\ddagger}u_{00}\times w_1'(u_{00}\rho_0(\tau)+u_1\sigma_0(\tau))\ . \tag{3.4}$$

The rate constant is determined by the long-time evolution of trajectories which are initiated at the barrier $\rho=0$. The collective mode $\sigma_0(t)$ is a bounded function whose long-time correlations die out with the rate $\lambda^\ddagger$ (cf. the Appendix). This assures that its Laplace transform does not diverge. In addition, as also detailed in the Appendix, the time evolution of $\rho_0(t)$ when inserted in $w_1'$ induces a correction which is of second order with respect to the nonlinearity $w_1$ and so may be ignored. This means that for long times,

$$\rho_1(t)\simeq\frac{e^{\lambda^\ddagger t}}{2\lambda^\ddagger}\left[p_\rho-u_{00}\int_0^t d\tau\, e^{-\lambda^\ddagger\tau}w_1'(u_1\sigma_0(\tau))\right]\ . \tag{3.5}$$

The condition implicit in Eq. (2.25) that $\rho(t)$ be negative at long times is then identical to the condition that the initial momentum obeys the central inequality,

$$p_\rho\le u_{00}\int_0^t d\tau\, e^{-\lambda^\ddagger\tau}w_1'(u_1\sigma_0(\tau))\ . \tag{3.6}$$

This result may be further simplified by noting that the stationarity of $\sigma_0(t)$ assures that for long times one can replace the upper limit of the integration by $\infty$,

$$p_\rho\le u_{00}\hat{w}_1'(u_1\sigma_0(\lambda^\ddagger))\ , \tag{3.7}$$

where the "hat" notation implies the Laplace transform.

The dynamical TST expression for the rate is now obtained by inserting this condition into the reactive-flux rate expression [Eq. (2.25)]. The integration over $\rho,p_\rho$ is straightforward and one finds the deceptively simple result,

$$\Gamma_a=\frac{e^{-\beta w(0)}}{\beta}\frac{\int\prod_{j=1}^N dp_{y_j}dy_j\exp\left[-\frac{\beta}{2}\sum_{j=1}^N(p_{y_j}^2+\lambda_j^2y_j^2)\right]\exp\left[-\beta w_1\left[\sum_{j=1}^N u_{j0}y_j\right]\right]e^{-(\beta/2)u_{00}^2[\hat{w}_1'(u_1\sigma_0(\lambda^\ddagger))]^2}}{\int dp_q dq\prod_j dp_{x_j}dx_j e^{-\beta H}\theta(-\rho)}\ . \tag{3.8}$$

In the numerator of this expression one finds two terms that serve to modify the rate relative to the parabolic barrier result. The term $e^{-\beta w_1}$ appears in the VTST expression for the rate when one chooses the dividing surface to be $\rho=0$. The second exponent is the dynamical contribution and one notes that it will always reduce the rate relative to the VTST prediction which is an upper bound.

At this point it is important to note that the derivation of the dynamical VTST expression hinges upon the assumption that the fate of a given trajectory is determined mainly by the dynamics in the immediate vicinity of the parabolic barrier. As long as the rate of energy diffusion in the well is faster than the spatial-diffusion rate, this is a valid assumption. The fast energy-diffusion process in the well assures that a trajectory which "feels" the nonlinearity of the well strongly is randomized almost immediately, and is thus trapped in the well region. In other words, the dynamical VTST presented in this paper is only valid provided that the decay rate is dominated by the spatial-diffusion process. As shown by Kramers [1] and Mel'nikov and Meshkov [33] for Ohmic friction, and by PGH [5] for memory friction, the approach to the spatial-diffusion limit is exponential and occurs when the damping is actually quite weak. Dynamical VTST is thus expected to be valid for a rather large range of friction parameters.

The denominator in Eq. (3.8) is just the partition function of reactants. It is readily evaluated by noting that substitution of the step function $\Theta(-\rho)$ with the step function $\Theta(-q)$ will only cause exponentially small changes. Using the form for the Hamiltonian given in Eq. (2.1) one can perform the integration over all momenta and all bath coordinates; this gives the result $(2\pi/\beta)^{1/2}\int_{-\infty}^0 dq\, e^{-\beta w(q)}\prod_{j=1}^N(2\pi/\beta\omega_j)$.

If one ignores the nonlinearity of the potential then the integration over all momenta and coordinates in the numerator gives $\prod_{j=1}^N(2\pi/\beta\lambda_j)$. The resulting parabolic barrier estimate for the rate is

$$\Gamma_a^{\rm pb}=\prod_{j=1}^N\frac{\omega_j}{\lambda_j}\Gamma_a^{\rm 1D}=\frac{\lambda^\ddagger}{\omega^\ddagger}\Gamma_a^{\rm 1D}\ , \tag{3.9}$$

where $\Gamma_a^{\rm 1D}\equiv e^{-\beta w(0)}/[(2\pi\beta)^{1/2}\int_{-\infty}^0 dq\, e^{-\beta w(q)}]$ is the one-dimensional TST rate constant found when using the simple dividing surface $f=-q$ and the second equality is a known property of the normal-mode transformation (cf. Ref. [16]). Equation (3.9) is just the Kramers-Grote-Hynes estimate for the rate. One may now rewrite the rate expression as

$$\Gamma_a=\Gamma_a^{\rm pb}\left\langle\exp\left[-\beta w_1\left[\sum_{j=1}^N u_{j0}y_j\right]\right]\times\exp\left\{-\frac{\beta}{2}u_{00}^2[\hat{w}_1'(u_1\sigma_0(\lambda^\ddagger))]^2\right\}\right\rangle_0\ , \tag{3.10}$$

where the brackets with a zero subscript denote the

phase-space average over the normalized harmonic distribution $\prod_{j=1}^{N}(2\pi/\beta\lambda_j)^{-1}\exp[-(\beta/2)(p_{y_j}^2+\lambda_j^2 y_j^2)]$.

Our purpose is to obtain the leading corrections to the parabolic barrier rate which are due to the nonlinearity. One must thus expand the exponents involving $w_1$ to the lowest contributing order. Using the division of the nonlinearity into symmetric and antisymmetric components as in Eqs. (2.7) and (2.8) the necessary expansion is

$$\left\langle \exp\left[-\beta w_1\left[\sum_{j=1}^{N} u_{j0}y_j\right]\right]\exp\left\{-\frac{\beta}{2}u_{00}^2[\hat{w}_1'(u_1\sigma_0(\lambda^\ddagger))]^2\right\}\right\rangle_0 \simeq 1-\beta\langle w_{1s}\rangle_0+\frac{\beta^2}{2}\left[\langle w_{1as}^2\rangle_0-\frac{u_{00}^2}{\beta}\langle \hat{w}_{1as}'^2\rangle_0\right] . \tag{3.11}$$

The term linear in $w_{1as}$ and in general any term that has an odd power of $w_{1as}$ will vanish upon averaging over the momenta and coordinates and so is ignored. We have also used the fact that generally the terms $w_{1s}$ and $w_{1as}^2$ will contribute to the same order in the expansion. This has already been demonstrated explicitly in Ref. [23] and will also be evident in the next section where specific examples will be dealt with in some detail. This fact implies though that to leading order in the expansion, the symmetric part of the nonlinearity does not contribute to any recrossing of the dividing surface.

The first two averages may be carried out by introducing an additional integration over the Fourier expansion of a $\delta$ function

$$(1/2\pi)\int d\sigma\, d\kappa \exp\left\{i\kappa\left[\sigma-(1/u_1)\sum_{j=1}^{N}u_{j0}y_j\right]\right\}$$

into the average. This reduces all the integrations over the harmonic bath variables to simple Gaussians and the result is

$$\left\langle g\left[\sum_{j=1}^{N}u_{j0}y_j\right]\right\rangle_0 = \left[\frac{\beta\Omega^2}{2\pi}\right]^{1/2}\int_{-\infty}^{\infty}d\sigma\, e^{-(\beta/2)\Omega^2\sigma^2}g(u_1\sigma) , \tag{3.12}$$

where specifically $g=w_{1s},w_{1as}^2$. The frequency $\Omega$ has been defined in Sec. II [Eqs. (2.14) and (2.15)] and its continuum limit is given by Eq. (2.17), setting $t=0$.

The final average over the Laplace transform of $w_{1as}^2$ can be performed analogously, but by introducing two $\delta$ functions, one for $\sigma(t)$ and one for $\sigma(\tau)$. Some straightforward but lengthy algebra gives the result

$$\langle \hat{w}_{1as}'^2\rangle_0=\frac{\beta}{2\pi}\int_{-\infty}^{\infty}ds\, d\bar{s}\, e^{-(\beta/2)(s^2+\bar{s}^2)}\int_0^{\infty}dt\, d\tau\, e^{-\lambda^\ddagger(t+\tau)}w_{1as}'(u_1\sigma_+(s,\bar{s},\tau-t))w_{1as}'(u_1\sigma_-(s,\bar{s},\tau-t)) , \tag{3.13}$$

where the time-dependent variables $\sigma_+,\sigma_-$ are

$$\sigma_\pm(s,\bar{s},t)=\frac{1}{\Omega\sqrt{2}}\{[1+H(t)]^{1/2}s\pm[1-H(t)]^{1/2}\bar{s}\} . \tag{3.14}$$

The correlation function $H(t)$ has been defined in Sec. II [cf. Eqs. (2.14) and (2.17)]. Equation (3.10)–(3.14) are the central result of this paper. They give the leading-order correction to the Kramers-Grote-Hynes rate expression in terms of the nonlinear part of the potential. The results are well defined in the continuum limit for arbitrary memory friction. In the next section we will demonstrate their application to some specific cases.

## IV. EXPANSION FOR THE CUBIC AND QUARTIC POTENTIALS

### A. The cubic potential

The cubic potential has the form

$$w(q)=-\tfrac{1}{2}\omega^{\ddagger 2}q^2\left[1+\frac{q}{q_0}\right] . \tag{4.1}$$

The barrier height for the cubic potential is $V^\ddagger=\frac{2}{27}\omega^{\ddagger 2}q_0^2$. The nonlinearity in this case is purely antisymmetric.

From Eq. (3.11) one easily finds that

$$\langle w_{1as}^2\rangle_0=\frac{1}{\beta^2}\frac{5}{18}\frac{1}{\beta V^\ddagger}\frac{1}{\chi^3} , \tag{4.2}$$

where we have used the notation defined in Eq. (2.18). Using the continuum limit expression for the correlation function (Eq. 2.17) it is possible to perform both the Gaussian integration and the Laplace transforms to obtain

$$\langle \hat{w}_{1as}'^2\rangle_0=\frac{1}{\beta}\frac{1}{6\beta V^\ddagger}\left[\frac{1}{\chi^2}\frac{\omega^{\ddagger 2}}{\lambda^{\ddagger 2}}+\frac{2u_{00}^4\omega^{\ddagger 6}}{\pi^2}\int_{-\infty}^{\infty}d\lambda\, d\lambda'\frac{I(\lambda)}{\lambda}\frac{I(\lambda')}{\lambda'}\frac{1}{\lambda^{\ddagger 2}+(\lambda+\lambda')^2}\right] . \tag{4.3}$$

Combining Eqs. (4.2) and (4.3) and inserting them into Eqs. (3.9) and (3.10) gives the expansion up to order $(1/\beta V^{\ddagger})$ for the decay rate of the cubic oscillator in the presence of arbitrary memory friction,

$$\frac{\Gamma_a}{\Gamma_a^{\rm pb}}=1+\frac{1}{\beta V^{\ddagger}}\frac{1}{36\chi^3}\left[2-3\chi-\frac{6(\chi+1)^3\lambda^{\ddagger 6}}{\pi^2}\int_{-\infty}^{\infty}d\lambda\, d\lambda'\frac{I(\lambda)}{\lambda}\frac{I(\lambda')}{\lambda'}\frac{1}{\lambda^{\ddagger 2}+(\lambda+\lambda')^2}\right]. \tag{4.4}$$

To complete this example and to provide a basis for comparison with other theories developed for Ohmic friction, we describe in detail the application of Eq. (4.4) for an Ohmic bath. In this case the friction function is

$$\gamma(t)=2\gamma\delta(t) \tag{4.5}$$

and it is useful to define a reduced friction parameter,

$$\alpha\equiv\frac{\gamma}{2\omega^{\ddagger}}\ . \tag{4.6}$$

The Kramers-Grote-Hynes equation is quadratic with two roots. The positive root is the barrier frequency

$$\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}=(1+\alpha^2)^{1/2}-\alpha\ . \tag{4.7}$$

The absolute value of the negative root is denoted as $\lambda_2$ so that $\lambda_2>\lambda^{\ddagger}$,

$$\frac{\lambda_2}{\omega^{\ddagger}}=(1+\alpha^2)^{1/2}+\alpha\ . \tag{4.8}$$

The transformation matrix element $u_{00}$ [cf. Eq. (2.11)] is now found to be

$$u_{00}^2=1-\frac{\alpha}{(1+\alpha^2)^{1/2}} \tag{4.9}$$

and the nonlinearity parameter defined in Eq. (2.18) is

$$\chi=\frac{(1+\alpha^2)^{1/2}}{\alpha}\ . \tag{4.10}$$

Note that in the large damping limit, the nonlinearity parameter tends to unity.

The spectral density $J(\omega)$ of the bath modes is seen from Eq. (2.5) to be $J(\omega)=\gamma\omega$. Using Eq. (2.13) one finds that the normal-mode spectral density is [30],

$$\frac{I(\lambda)}{\lambda}=\frac{1}{2\lambda^{\ddagger}}\left[\frac{1}{\lambda^{\ddagger 2}+\lambda^2}-\frac{1}{\lambda_2^2+\lambda^2}\right]. \tag{4.11}$$

It is now only a matter of some lengthy but standard integration to find that the rate for the cubic oscillator with Ohmic friction is

$$\frac{\Gamma_a}{\Gamma_a^{\rm pb}}=1+\frac{1}{\beta V^{\ddagger}}\frac{1}{36\chi^3}\left[2-3\chi-\tfrac{1}{2}(\chi+1)^3+\frac{3}{2}\frac{(\chi-1)^2(\chi+1)(3\chi^2+12\chi+1)}{9\chi^2-1}\right]. \tag{4.12}$$

In the Smoluchowski limit ($\alpha\gg 1$) the parameter $\chi=1$ and one finds that the correction term in this limit is $-\frac{5}{36}(1/\beta V^{\ddagger})$, it is identical to the derivation based on the mean first-passage time. In the weak-damping limit ($\alpha\ll 1$) the parameter $\chi$ becomes infinite such that for $\alpha=0$ the correction term vanishes as it should. Further comparisons will be provided in Sec. V.

### B. The quartic potential

The second example is the symmetric quartic double-well potential,

$$w(q)=-\tfrac{1}{2}\omega^{\ddagger 2}q^2\left[1-\frac{q^2}{2q_0^2}\right]. \tag{4.13}$$

The two wells are located at $\pm q_0$ and the barrier height is $V^{\ddagger}=\frac{1}{4}\omega^{\ddagger 2}q_0^2$. For the quartic potential the nonlinear part of the potential is proportional to $q_0^{-2}$ and so is of the order of $1/\beta V^{\ddagger}$. This should be contrasted with the cubic case where the nonlinearity is of order $q_0^{-1}$ and is thus proportional to $(1/\beta V^{\ddagger})^{1/2}$. As a result, in the cubic case it is necessary to expand up to second order in the nonlinearity while for the quartic potential the leading term is of first order in the nonlinearity. This substantially simplifies the quartic case so that the leading expansion term is identical to the leading VTST expansion term which has already been estimated in Refs. [17] and [23]. The only added contribution in our present treatment is the proof that in fact there are no dynamic corrections to this order. For the sake of completeness and the comparisons of the next section we bring here again the expansion for the quartic double-well potential.

The expansion up to terms of order $(1/\beta V^{\ddagger})^2$ is

$$\frac{\Gamma_a}{\Gamma_a^{\rm pb}}=1-\beta\langle w_{1s}\rangle_0=1-\frac{3}{16\beta V^{\ddagger}\chi^2}\ . \tag{4.14}$$

For Ohmic friction in the strong-damping limit, $\chi\simeq 1$ and one regains the well-known Smoluchowski limit. In the limit that $\alpha=0$ the term of order $1/\beta V^{\ddagger}$ vanishes.

Note that for both the cubic and the quartic potentials for finite reduced barrier height, the correction term can still be large if the nonlinearity parameter $\chi$ can be become substantially smaller than unity. For Ohmic friction we have seen that $1<\chi<\infty$ and so nothing of great interest will occur. However, for memory friction, the nonlinearity parameter can indeed become substantially smaller than 1 [21,23] and in such cases the present ex-

pansion may be used to ascertain whether the steepest-descent estimate for the rate remains valid.

## V. COMPARISON WITH OTHER RESULTS

### A. Corrections to the rate beyond the Smoluchowski limit

The time dependence of the probability density $p(q,t)$ for a particle whose motion is governed by a Langevin equation (1.1) with large ($\alpha \gg 1$) Ohmic friction is given by the following (generalized) Smoluchowski equation:

$$\frac{\partial p(q,t)}{\partial t}=\frac{1}{\beta\gamma}\frac{\partial}{\partial q}\left[1+\frac{\omega''(q)}{\gamma^2}\right]\left[\frac{\partial}{\partial q}+\beta w'(q)\right]p(q,t)\ . \tag{5.1}$$

The leading correction to the infinite friction limit derived by Skinner and Wolynes [29], is included through the term $w''(q)/\gamma^2$. Higher-order corrections have also been derived and may be found in Refs. [11] and [29]. They contribute only terms of the order of $\gamma^{-4}$ and higher and cause deviations from a Smoluchowski-type equation and so will not be considered further.

For the diffusion process described by Eq. (5.1) the reaction rate is just the escape rate of a particle out of the potential well. This rate is determined by the mean inverse time it takes a particle initiated at the bottom of the well ($q_a$) to reach a point ($q_e > q_a$) beyond the barrier where the potential $w(q_e)$ is at least $\beta^{-1}$ lower than the barrier energy. The precise location of either of these two points is of no importance since any variation within the indicated limits will cause changes in the rate which are exponentially small (of order $e^{-\beta V^{\ddagger}}$).

The escape time $t(q)$, which is a function of the initial coordinate $q$, is a solution of the following boundary-value problem [6,11]

$$\left[-\frac{\partial}{\partial q}+\beta w'(q)\right]\left[1+\frac{w''(q)}{\gamma^2}\right]\frac{\partial}{\partial q}t(q)=\beta\gamma\ , \tag{5.2}$$

where the boundary conditions are

$$t'(q_r)=t(q_e)=0\ . \tag{5.3}$$

The reflecting boundary condition $[t'(q_r)=0]$ at $q_r$ has to be chosen on the reactant side, opposite the barrier, sufficiently far away from the bottom of the well ($q_r < q_a$). The solution of Eqs. (5.2) and (5.3) is readily obtained by standard means,

$$t(q_a)=\beta\gamma\int_{q_a}^{q_e}dx\frac{e^{\beta w(x)}}{1+[w''(x)/\gamma^2]}\int_{q_r}^{x}dy\,e^{-\beta w(y)}\ , \tag{5.4}$$

and may be checked by direct insertion into the differential equation (5.2).

The integrals appearing in the solution for the mean time may be estimated by an asymptotic expansion in terms of the "large" parameter $\beta V^{\ddagger}$. Since the main contribution to the first integral on the right-hand side of Eq. (5.3) comes from the barrier region, the upper limit in the second integral can be kept fixed at the barrier top. Hence the second integral is just proportional to the population of the well and is identical to the partition function appearing in the one-dimensional rate constant $\Gamma_a^{1D}$ [cf. Eq. (3.9)]. The modified Smoluchowski equation contains correction terms for finite values of the friction constant only up to order $\gamma^{-2}$. Therefore higher-order terms in Eq. (5.3) should be ignored.

Using the separation [cf. Eqs. (2.6)–(2.8)] of the potential into a parabolic and a nonlinear part, an expansion of the remaining integrand in Eq. (5.3) in powers of the nonlinearity leads to the following expression for the mean escape time:

$$t(q_a)=\Gamma_S^{-1}\left[\left[1+\frac{\omega^{\ddagger 2}}{\gamma^2}\right][1+\beta\langle w_{1s}(q)\rangle_{00}+\tfrac{1}{2}\beta^2\langle w_{1as}^2(q)\rangle_{00}]-\gamma^{-2}[\langle w_{1s}''(q)\rangle_{00}+\beta\langle w_{1as}''(q)w_{1as}(q)\rangle_{00}]\right]\ , \tag{5.5}$$

where the leading-order term $\Gamma_S^{-1}$ is just the well-known Smoluchowski rate [cf. Eq. (3.9)],

$$\Gamma_S=\frac{\omega^{\ddagger}}{\gamma}\Gamma_a^{1D}\ . \tag{5.6}$$

The brackets with subscript 00 denote a Gaussian average with vanishing mean and second moment such that

$$\langle q^2\rangle_{00}=\frac{1}{\beta\omega^{\ddagger 2}}\ . \tag{5.7}$$

For the cubic potential [Eq. (4.1)] we thus find

$$t(q_a)=\Gamma_S^{-1}\left[1+\frac{\omega^{\ddagger 2}}{\gamma^2}+\frac{5}{36\beta V^{\ddagger}}\left[1-\frac{7}{5}\frac{\omega^{\ddagger 2}}{\gamma^2}\right]\right] \tag{5.8}$$

and, consequently, for the rate we find

$$\Gamma_a=\Gamma_S\left[1-\frac{\omega^{\ddagger 2}}{\gamma^2}-\frac{5}{36\beta V^{\ddagger}}\left[1-\frac{17}{5}\frac{\omega^{\ddagger 2}}{\gamma^2}\right]\right]\ . \tag{5.9}$$

For the quartic potential [Eq. (4.12)] Eq. (5.5) yields

$$\Gamma_a=\Gamma_S\left[1-\frac{\omega^{\ddagger 2}}{\gamma^2}-\frac{3}{16\beta V^{\ddagger}}\left[1-5\frac{\omega^{\ddagger 2}}{\gamma^2}\right]\right]\ . \tag{5.10}$$

These rate expressions for the cubic and quartic potentials coincide with the expansion up to the same order in $1/\beta V^{\ddagger}$ and $\omega^{\ddagger 2}/\gamma^2$ obtained from the dynamical VTST results as given in Eqs. (4.11) and (4.13), respectively.

### B. Previous results

In the case of Ohmic friction the Langevin equation is identical to a Fokker-Planck equation for the probability

density $p(q,v,t)$ in the phase space of the system,

$$\frac{\partial p(q,v,t)}{\partial t} = Lp(q,v,t) , \tag{5.11}$$

where $L$ denotes the Fokker-Planck operator

$$L = -\frac{\partial}{\partial q}v + \frac{\partial}{\partial v}[w'(q)+\gamma v] + \frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2} . \tag{5.12}$$

Within the Fokker-Planck description, the rate is the lowest nonzero eigenvalue $l$ of $-L$ where an absorbing boundary condition is imposed in the product well.

The Fokker-Planck operator (5.11) is not self-adjoint. With respect to the scalar product $(f,g)=\int dq\, dv\, f(q,v)g(q,v)$ the adjoint operator coincides with the backward operator,

$$L^\dagger = v\frac{\partial}{\partial q} - [w'(q)+\gamma v]\frac{\partial}{\partial v} + \frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2} . \tag{5.13}$$

When one defines a scalar product weighted by the equilibrium distribution,

$$\langle f|g\rangle = \frac{\int dv\, dq\, f(q,v)g(q,v)e^{-\beta[(v^2/2)+w(q)]}}{\int dv\, dq\, e^{-\beta[(v^2/2)+w(q)]}} , \tag{5.14}$$

the adjoint operator $L^*$ of $L^\dagger$ is related to $L$ by

$$L^* = e^{\beta[(v^2/2)+w(q)]}Le^{-\beta[(v^2/2)+w(q)]} . \tag{5.15}$$

From detailed balance (which holds for Brownian motion [11]) the adjoint operator $L^*$ is just the time-reversed backward operator,

$$L^* = -v\frac{\partial}{\partial q} + [w'(q)-\gamma v]\frac{\partial}{\partial v} + \frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2} . \tag{5.16}$$

Note that $L^\dagger$ and $L^*$ act on the same function space, namely, on phase-space $(v,q)$ functions with finite second equilibrium moments. This is a much more general class of functions than those operated on by the original Fokker-Planck operator $L$ which must be absolutely integrable. It is therefore more convenient to deal with $L^\dagger$ and $L^*$ with the equilibrium weighted scalar product (5.14) rather than with $L$ and $L^\dagger$. It is obvious that the operators $-L$, $-L^\dagger$, and $-L^*$ have the same smallest nonvanishing eigenvalue $l$.

An expression for this eigenvalue that generalizes the Rayleigh Ritz quotient for the ground state of a symmetric operator was proposed by Dekker [14],

$$l_D \equiv -\frac{\langle f|L^*f\rangle}{\langle f|f\rangle} . \tag{5.17}$$

For the exact eigenfunction of $L^*$ corresponding to $l$ this expression yields the exact rate. Since the exact function is unknown, a reasonable trial function chosen by Dekker is the Kramers function which satisfies

$$L^*_{\rm pb} f = 0 \tag{5.18}$$

for the parabolic barrier. This function is

$$f = \left[\frac{\beta\omega^{\ddagger 4}}{2\pi\gamma\lambda^\ddagger}\right]^{1/2} \int_{q-(\lambda^\ddagger/\omega^{\ddagger 2})v}^{\infty} du\, e^{-(\beta\omega^{\ddagger 4})/(2\gamma\lambda^\ddagger)u^2} . \tag{5.19}$$

For the quartic potential (4.13) and large friction, expansion up to all terms which are first order with respect to $1/\beta V^\ddagger$ and $\omega^{\ddagger 2}/\gamma^2$ gives

$$l_D = \Gamma_S\left[1-\frac{\omega^{\ddagger 2}}{\gamma^2}-\frac{3}{16\beta V^\ddagger}\left[1+3\frac{\omega^{\ddagger 2}}{\gamma^2}\right]\right] . \tag{5.20}$$

This result agrees with the dynamical TST (4.14) and the Skinner-Wolynes (5.10) based expansions in the Smoluchowski limit only if one ignores corrections of order $\omega^{\ddagger 2}/\gamma^2$.

A different approach for obtaining the rate for general Markov processes [28] of which the Langevin equation is a specific case which is based on the reactive-flux method has been suggested by Talkner [13]. The working expression for the plateau value also has the form of a Rayleigh Ritz quotient

$$l_\Gamma = -\frac{\langle \tilde{f}|L^*f\rangle}{\langle \tilde{f}|f\rangle} , \tag{5.21}$$

where $\tilde{f}(q,v)=f(q,-v)$ is the function $f$ time reversed. This means that if $f$ is an eigenfunction of $L^*$ then $\tilde{f}$ is an eigenfunction of $L^\dagger$ with the same eigenvalue.

Choosing as a trial function the Kramers parabolic barrier function (5.19) for a quartic barrier one finds that the expansion up to first order in $1/\beta V^\ddagger$ coincides with the dynamic VTST (4.14) expansion. For a cubic potential the same procedure leads to the result obtained from VTST without a dynamic correction, that is,

$$l_\Gamma = \Gamma_a^{\rm pb}\left[1+\frac{5}{36\beta V^\ddagger\chi^3}\right] . \tag{5.22}$$

This result is an upper bound to the rate, but even in the Smoluchowski limit, the term of order $1/\beta V^\ddagger$ has the wrong sign. We believe that the source for the deviation lies in the choice of the Kramers parabolic barrier function as the trial function. For the quartic potential this choice leads to the exact result. This is not surprising since we have seen that for the quartic potential up to first order, VTST is exact and the nonlinearity does not induce any dynamic corrections. In the cubic case, the dynamic corrections are crucial and are missing in the Kramers parabolic barrier trial function. The ensuing Rayleigh Ritz estimate is therefore only identical to the VTST result but is not exact.

Still another expansion was obtained by Ryter [12] which was based on boundary layer methods [34]. His leading-order correction to the Kramers rate is of order $(1/\beta V^\ddagger)(\omega^\ddagger/\gamma)^4$. This means that in the high damping limit his result does not contain even the finite-barrier corrections to the Smoluchowski rate [7–9] and thus must be incorrect.

In summary, we believe that the agreement between the Skinner-Wolynes based estimate for the rate and dynamical VTST provides strong evidence for the correctness of the dynamical VTST method. The deviations of the expressions obtained by Dekker and Talkner from the dynamical VTST result are necessarily related to the choice of trial function. The quartic case shows

though that the formulation based on the reactive-flux method converges more rapidly.

## VI. DISCUSSION

The main result of this paper is an explicit expression for the leading-order correction term in a $1/\beta V^{\ddagger}$ expansion for the rate in the spatial-diffusion limit. In contrast to all previous attempts, the present methodology is applicable to arbitrary memory friction and is not limited to the Smoluchowski limit. Even for the Ohmic-friction case the present results have not been demonstrated before, to our knowledge. By analyzing the Skinner-Wolynes extension of the Smoluchowski equation it was demonstrated that all previous expansions were actually wrong. The present method gives results (when compared to the same order) that are identical to the inverse of the mean first-passage time as obtained from the modified Smoluchowski equation. They, of course, reduce to the correct and known results in the Smoluchowski limit itself.

Our results are obtained by incorporating the following ingredients. Instead of dealing with the reduced stochastic equation of motion for the system coordinate (the GLE) or its counterpart for the position and velocity distribution function (a Fokker-Planck equation) we replace the GLE by its Hamiltonian equivalent. Use is then made of the normal-mode diagonalization of this Hamiltonian about the parabolic barrier to set up an equation of motion for the unstable normal mode. This equation is solved perturbatively. The rate is obtained through the reactive-flux formalism which is adapted here to Hamiltonian systems. In contrast to previous treatments, the reactive flux is estimated using the unstable normal-mode dividing surface instead of the system coordinate. This assures that for the purely parabolic case, the zero time limit of the reactive-flux expression is already exact. This observation then allows for the development of a perturbative expansion of the reactive-flux expression about the parabolic barrier limit. The resulting expressions are easily obtainable in the continuum limit through the introduction of the spectral density of the normal modes [30].

From a practical point of view, the expansion presented in this paper has shown that in the presence of memory friction, one cannot assume that the steepest-descent Kramers-Grote-Hynes (KGH) estimate for the rate is correct as long as $1/\beta V^{\ddagger}$ is small. One must also consider the nonlinearity parameter $\chi$ which when small can lead to serious deviations from the KGH limit.

Perhaps though the more important result of the present paper is conceptual in nature. Instead of following the "old" method, which is to attempt a solution of a Fokker-Planck equation for the distribution function, we find that it is much easier to consider directly the dynamics of the Hamiltonian equivalent of the GLE. It is this approach which has enabled considerable progress in extension of Kramers theory to a much more general class of dissipative systems than considered by Kramers originally. The Hamiltonian approach has led to the solution of the Kramers turnover problem in the presence of memory friction [6,35]. New and instructive upper bounds have been developed for the rate by applying VTST to the Hamiltonian equivalent of the GLE [17–22]. Additional results include a finite-barrier generalization of the Kramers-Grote-Hynes theory [23] and a deeper understanding of multidimensional processes in dissipative systems such as the consideration of anisotropic friction (detailed references for this problem may be found in Ref. [23]).

Viewed in terms of this series of developments, the present paper adds an important step. After using VTST to identify an optimal dividing surface, one may get even better estimates for the reaction rates by incorporating dynamical corrections within the framework of the reactive-flux method. This approach may be generalized to multidimensional systems where the analog of the KGH parabolic barrier limit is the Langer expression [36] for the rate and its generalization to include memory friction [23,37,38]. Having identified the unstable normal mode in the multidimensional case, a straightforward application of the method presented in this paper will lead to the exact leading-order corrections to Langer's expression.

In principle, the same approach should also be useful for deepening our understanding of the rate process in the underdamped limit. In contrast though to the present paper, where the small parameter is the nonlinearity, in the energy-diffusion limit, the small parameter is $u_1^2$ as used in PGH theory. The same perturbation theory as used by PGH when incorporated within the reactive-flux method should be considered as a useful way for developing a different approach for the rate in this limit.

This paper has been limited exclusively to a classical mechanics study of the rate process. However, as demonstrated in a number of previous papers [30,39,40] the Hamiltonian approach coupled with the normal-mode analysis can lead to substantial improvement in our understanding of quantum dissipation. For example, the Wolynes high-temperature quantum expression for the decay rate [41] has been shown to be identical to a parabolic quantum transition-state theory [40]. An extension of the same approach has led to a quantum analog of the PGH turnover theory [30]. It should be possible to use the perturbative approach presented in the present paper to derive finite-barrier corrections to Wolynes' expression.

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## APPENDIX: LONG-TIME LIMITS

The purpose of this appendix is to describe in detail the long-time analysis of the first-order equation of motion for the $\rho$ mode [Eq. (3.4)] which leads to the working result given in Eq. (3.5).

The first step is to put $\rho_0=0$ in Eq. (3.4) and consider only the term that results from the time evolution of the collective mode $\sigma_0(\tau)$,

$$\rho_1(t)=\rho_0(t)-\int_0^t d\tau\frac{1}{2\lambda^\ddagger}[e^{\lambda^\ddagger(t-\tau)}-e^{-\lambda^\ddagger(t-\tau)}] \times u_{00}w_1'(u_1\sigma_0(\tau)) . \quad \text{(A1)}$$

The first term that arises from the sinh function leads to Eq. (3.5). The zeroth-order contribution to the collective mode $\sigma_0$ is a bounded function since it is a combination of sin and cos functions. In the long-time limit, the second term, because of this boundedness, can contribute at most a constant term [i.e.,

$$e^{-\lambda^\ddagger t}\int_0^t d\tau e^{\lambda^\ddagger\tau}\sigma_0(\tau)\le\sigma_0^{\max}/\lambda^\ddagger ,$$

where $\sigma_0^{\max}$ is the maximal value attainable for the collective mode]. It is therefore clear that this term may be neglected at long enough times when compared to the first term that grows without bound at long times as $e^{\lambda^\ddagger t}$. This observation also allows for replacement of the upper limit of integration ($t$) in Eq. (3.6) with $\infty$.

To verify Eq. (3.5), it remains to be shown that inclusion of the (zeroth-order) time dependence of the unstable normal mode will at most lead to a second-order correction to the rate in terms of the nonlinearity. For high enough momentum $-p_\rho$, a trajectory initiated at the top of the barrier $\rho=0$ will immediately be trapped in the reactants region and the nonlinearity cannot cause a recrossing of the barrier. For a purely parabolic barrier, only the set of measure zero trajectories initiated with no momentum at the top of the barrier are not immediately reactive and so VTST is exact. In other words, the nonlinearity, when weak, will affect only those trajectories initiated at the top of the barrier with very small momentum along the unstable mode. The zeroth-order time dependence of the $\rho$ mode for this critical set of trajectories at long times is $(p_\rho(w_1)/2\lambda^\ddagger)e^{\lambda^\ddagger t}$ where the notation $p_\rho(w_1)$ serves to remind us that the maximal value of the initial momentum which must be considered is small and is itself dependent on the nonlinearity $w_1$.

For a perturbation theory which is lowest order in the nonlinearity we may thus use the expansion

$$w_1'[u_{00}\rho_0(\tau)+u_1\sigma_0(\tau)] \simeq w_1'[u_1\sigma_0(\tau)]+u_{00}\rho_0(\tau)w_1''[u_1\sigma_0(\tau)] .$$

The long-time dependence for the unstable mode may now be written explicitly as

$$\rho_1(t)=\frac{e^{\lambda^\ddagger t}}{2\lambda^\ddagger}\left[p_\rho\left[1-\frac{u_{00}^2}{2\lambda^\ddagger}\int_0^t d\tau w_1''(u_1\sigma_0(\tau))\right] -u_{00}\int_0^t d\tau e^{-\lambda^\ddagger\tau}w_1'(u_1\sigma_0(\tau))\right] . \quad \text{(A2)}$$

The condition for trapping is that the right-hand side of Eq. (A2) be negative at long times. Keeping only the lowest-order terms in $w_1$ leads immediately to Eq. (3.6). It now becomes evident that the time dependence of $\rho_0(t)$ when included in the time integral on the right-hand side of Eq. (3.4) will induce only a contribution which is second order with respect to $w_1$ and so may be ignored.

Finally, we note that the correlation function for the zeroth-order component of the collective mode decays at long times with the rate $\lambda^\ddagger$. Adapting the notation of Eq. (3.10) and using the explicit form for the time dependence of $\sigma_0(t)$ [cf. Eq. (3.1)] one finds that the correlation function of the collective mode is just proportional to the function $H$ defined in Eq. (2.14),

$$\langle\sigma_0(t)\sigma_0(\tau)\rangle_0=\frac{1}{\beta u_1^2}\sum_{j=1}^N\frac{u_{j0}^2}{\lambda_j^2}\cos[\lambda_j(t-\tau)] =\frac{1}{\beta\Omega^2}H(t-\tau) . \quad \text{(A3)}$$

From the dependence of $H$ on the spectral density of the normal modes [Eq. (2.17)] it is evident that the long-time behavior will be determined by the lowest positive pole of $I(\lambda)$ [cf. Eq. (2.13)] which is the barrier frequency $\lambda^\ddagger$. An explicit example dealing with Ohmic friction has been given in Eq. (4.11).

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