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Activated rate processes are often described in terms of a generalized Langevin equation. The concept of an optimized planar dividing surface in conjunction with variational transition state theory has been demonstrated to be useful in understanding the effects of nonlinearities on reaction rates. A different approach is based on the Rayleigh quotient method, in which one varies the trial functions. We prove a restricted identity of the two methods. The restrictions are that the variational transition state theory method is limited to planar dividing surfaces. The Rayleigh quotient method is restricted to the class of Kramers functions. These functions are constructed by replacing the true potential with a parabolic barrier and using the known eigenfunction for the parabolic barrier. The parameters of the parabolic barrier are used as variational parameters in the Rayleigh quotient for the true nonlinear potential.

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I. INTRODUCTION

The theory of activated processes has been extensively developed in recent years. The prototypical model is that of a one-dimensional particle with coordinate q trapped in a metastable potential well of a potential function $V(q)$. The dynamics of the particle is described by a Langevin equation. The particle experiences a frictional force characterized by a damping constant γ and an external Gaussian white random force. The particle can escape from the well by crossing a potential barrier. Kramers [1] showed that, when the damping is weak, the escape rate is limited by the rate of transfer of energy to the particle from the bath and so is proportional to the damping. When the damping is moderate or strong, the process is limited by the spatial rate of diffusion of the particle across the barrier.

In this paper we will concentrate on the moderate to strong damping limit, also known as the "spatial diffusion limit" for the dynamics. Kramers, in his paper, estimated the escape rate using the "flux over population" method. He found a nontrivial solution of the Fokker-Planck equation in phase space, which has the property that the flux associated with it is stationary and it obeys the boundary condition which is that deep in the well, the particle is in thermal equilibrium. The famous Kramers expression for the rate was just the flux associated with his distribution function divided by the density of reacting particles.

In the strong damping limit, it is well known [1] that the Fokker-Planck equation may be reduced to a Smoluchowski equation in which the distribution function is dependent only on the coordinate of the particle. The

strong damping causes the momentum to relax infinitely quickly to equilibrium and so it may be ignored. The Smoluchowski equation has the same formal structure as the Schrödinger equation. It was thus natural that in this limit, the Rayleigh quotient method was used to obtain improved estimates for the escape rate [2-6]. The central advantage of the Rayleigh quotient method over the flux over population method is that in the former, a first-order error in the trial (stationary flux) distribution leads to a second-order error in the estimate for the rate which bounds the rate constant from above. In the flux over population method, the sign of the error is unknown and it is of first order.

In recent years, the Rayleigh quotient method has been generalized to include also the moderate friction limit of the dynamics [7,8]. In this case, the Fokker-Planck operator is no longer Hermitian and care must be taken to ensure the correct orthogonality relations of the trial functions [8,9]. The general structure of the theory is the same as in the Smoluchowski limit and in the resulting expression, a first-order error in the distribution function leads to a second-order error for the rate. It is thus very useful as a variational principle. The generalized Rayleigh quotient method has been utilized to obtain an analytic expansion for the rate in terms of the inverse barrier height [9]. There is though a price to be paid. The non-Hermitian character of the operator destroys the bound property. The generalized Rayleigh quotient method gives a variational estimate, not an upper bound.

Kramers's problem may be generalized by introducing memory friction. Instead of the Langevin equation of motion, one may consider a generalized Langevin equation (GLE) in which the friction function is no longer Markovian. The effect of memory friction on activated rate processes has been studied extensively during the past decade [10,11]. Grote and Hynes [12] generalized Kramers's expression for the rate in the spatial diffusion

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limit. They pointed out that the rate for spatial diffusion across a barrier is a function of frequency-dependent friction and is determined by the component of the friction at the barrier frequency rather than the static friction as in Kramers's original theory.

A further refinement of Kramers's theory may be obtained by introducing a space-dependent friction. The equation of motion, as derived by Zwanzig [13] and others [14,15] is substantially more complex looking than the GLE. Although some theoretical developments were made by Carmeli and Nitzan for this problem [16], they were primarily limited to the energy diffusion limited regime.

The generalized Rayleigh quotient method is applicable as long as one has a well defined Fokker-Planck operator. The operator is known for space and exponential time-dependent friction [17]. The space dependence introduces a coordinate dependence into the transport coefficients. Exponential memory friction is handled by introduction of an additional variable such that the Fokker-Planck operator is well defined in the enlarged space. If the time dependence of the friction is described by a sum of exponentials one must introduce an additional variable for each exponential, but the Fokker-Planck operator remains well defined and the Rayleigh quotient method is applicable, although in practice it does become somewhat cumbersome. General memory friction can systematically be approximated by sums of exponentials [18,19]. Hence the Rayleigh quotient method is in principle applicable for any GLE.

A very different theoretical treatment is based on the variational transition state theory (VTST) approach to activated rate processes in the spatial diffusion limit [20,22]. Instead of dealing with a stochastic differential equation, one may recast the GLE in terms of a Hamiltonian in which the system is coupled to a harmonic bath [13,23]. The stochastic dynamics may be represented as the continuum limit of the Hamiltonian dynamics.

Transition state theory [24–26], which is applicable to Hamiltonian systems, provides an upper bound [27] to the decay rate by considering the unidirectional flux across a dividing surface between "reactants" and "products". TST is exact if the particle does not recross the dividing surface. Otherwise, it gives an upper bound to the rate, since any recrossing is counted as a reactive event. By varying the dividing surface one may find a minimal upper bound, hence the name variational transition state theory.

In general, especially for a system as complicated as the Hamiltonian equivalent of the GLE, one might expect that the variational procedure is rather cumbersome and difficult. Substantial progress may be achieved by optimizing a planar dividing surface in the full configuration space of the system and the bath [28,29]. For high barriers, such an optimization reduces to the Kramers-Grote-Hynes expression. In the presence of nonlinearity, optimized planar dividing surfaces account correctly for the effects of memory [30] and space-dependent friction [31] and anisotropic friction [32].

The connection between the Hamiltonian dynamics and the Fokker-Planck equation has been recently studied for the parabolic barrier potential [33]. One may show that a solution for the dynamics in the Hamiltonian system may be used to construct eigenfunctions of the Fokker-Planck operator. Kramers's stationary flux distribution was shown to be identical to the projection of the characteristic function of reactive phase points onto the physical phase space of the reacting particle [33]. Tannor and Kohen have recently derived this same property directly from the Fokker-Planck equation [34].

At this point though, there is no clear connection between the generalized Rayleigh quotient method and the VTST method for estimating the rate. Both are variational in character: in the Rayleigh quotient method one is varying parameters of a trial distribution function, in VTST one is varying the dividing surface. The purpose of this paper is to demonstrate that there is a close connection between the two methods. If one restricts the VTST method to planar dividing surfaces and the trial functions for the generalized Rayleigh quotient method to belong to a restricted class of parabolic barrier trial functions, one will find that the two methods are identical. The VTST method leads to an upper bound to the rate, so through the identity we prove that for the restricted class of functions the generalized Rayleigh quotient method also gives an upper bound to the rate.

In Sec. II we review the optimized planar dividing surface VTST. We note that it is identical to a VTST in which one uses the normal mode parabolic barrier frequency as in the Kramers-Grote-Hynes theory, but treats the parabolic barrier frequency and location as variational parameters. In this way, optimized planar dividing surface VTST may be mapped to an equivalent optimized parabolic barrier fitting for the nonlinear potential acting upon the particle. In Sec. III we review the generalized Rayleigh quotient method for the Fokker-Planck equation. The identity of the optimized planar dividing surface VTST method and the generalized Rayleigh quotient method is demonstrated explicitly for exponential memory friction in Sec. IV. This implies also identity for the (white noise) Langevin equation, which is just a special case of exponential memory friction. We end with a discussion of the relative merits of the two approaches and further generalizations.

II. OPTIMIZED PLANAR DIVIDING SURFACE VTST

The GLE for a one-dimensional system is of the form

$$\ddot{q} + \frac{dV(q)}{dq} + \int^t dt'\gamma(t-t')\dot{q}(t') = \xi(t). \qquad (2.1)$$

Here q is the (mass weighted) system coordinate and $V(q)$ is the system potential. The Gaussian random force $\xi(t)$ is related to the friction kernel $\gamma(t)$ through the second fluctuation dissipation theorem $\langle \xi(t)\xi(0) \rangle = \frac{1}{\beta}\gamma(t)$ and $\beta \equiv \frac{1}{k_B T}$ throughout this paper.

The dynamics of the GLE (2.1) is equivalent to the dynamics of the system bath Hamiltonian [13,23]

$$H = \frac{p_q^2}{2} + V(q) + \sum_j \frac{1}{2}\left[p_{x_j}^2 + \left(\omega_j x_j - \frac{c_j q}{\omega_j}\right)^2\right] , \quad (2.2)$$

where the system coordinate q is coupled bilinearly to a bath of harmonic oscillators with frequencies ω_j. The summation is in principle over an infinite set of bath oscillators which tends towards a continuum. The bath coordinates x_j are mass weighted. By explicit solution for the time dependence of each of the bath coordinates, one can show that Hamilton's equation of motion for the system coordinate q reduces to the GLE (2.1), with the identification that

$$\gamma(t) = \sum_j \frac{c_j^2}{\omega_j^2} \cos(\omega_j t). \quad (2.3)$$

Transition state theory uses the flux over population expression for the rate. The flux is the equilibrium unidirectional flux through the dividing surface, the population is the equilibrium population of reactants [24–26]:

$$\Gamma = \frac{\int dp_q dq \prod_j dp_{x_j} dx_j \delta(f)(\mathbf{p} \cdot \nabla f)\theta(\mathbf{p}\cdot\nabla f)e^{-\beta H}}{\int dp_q dq \prod_j dp_{x_j} dx_j \theta(-f)e^{-\beta H}}. \quad (2.4)$$

The Dirac delta function $\delta(f)$ localizes the integration onto the dividing surface $f = 0$. The gradient of the surface (∇f) is in the full phase space, $\mathbf{p}$ is the generalized velocity vector in phase space with components $\dot{q}, \dot{p}_q, (\dot{x}_j, \dot{p}_{x_j}), j = 1, ..., N$, and $\theta(y)$ is the unit step function which chooses the flux in one direction only. The term $(\mathbf{p}\cdot\nabla f)$ is proportional to the velocity perpendicular to the dividing surface. The TST expression is an *upper bound* for the rate. The VTST is obtained by varying the dividing surface f looking for that dividing surface which gives the least upper bound.

The choice for the dividing surface implicit in Kramers's paper is the barrier top $(q = 0)$ of the potential $V(q)$. In this case the dividing surface takes the form $f = q = 0$ and the rate expression (2.4) is just the one-dimensional result

$$\Gamma_{1D} = (2\pi\beta)^{-\frac{1}{2}} \frac{e^{-\beta V(0)}}{\int dq \theta(-q)e^{-\beta V(q)}} \simeq \frac{\omega_a}{2\pi} e^{-\beta V^\ddagger}, \quad (2.5)$$

where ω_a is the frequency at the bottom of the well.

The Kramers-Grote-Hynes expression for the rate may be derived from the TST formulation by noting that for a purely parabolic barrier $[V(q) = V(0) - \frac{1}{2}\omega^{\ddagger^2}q^2]$ the Hamiltonian (2.2) is a bilinear form which may be diagonalized using a normal mode transformation [20]. In the diagonal form, one finds one unstable mode, denoted ρ, with associated barrier frequency, denoted $\lambda_\infty^\ddagger$, and N stable modes. The ∞ subscript will serve to remind us that this is the solution for the purely parabolic barrier or, equivalently, for an infinite reduced barrier height $(\beta V^\ddagger)$. The normal mode barrier frequency $(\lambda_\infty^\ddagger)$ is the solution of the equation

$$\omega^{\ddagger^2} = \lambda_\infty^{\ddagger^2}\left(1 + \frac{\hat{\gamma}(\lambda_\infty^\ddagger)}{\lambda_\infty^\ddagger}\right), \quad (2.6)$$

where $\hat{\gamma}(s)$ denotes the Laplace transform of the friction kernel with frequency s. The rate may now be obtained by choosing the dividing surface $f = \rho = 0$. The resulting expression for the rate is [21]

$$P_0 \equiv \frac{\Gamma}{\Gamma_{1D}} = \frac{\lambda_\infty^\ddagger}{\omega^\ddagger}\left[\frac{\beta\Omega^2}{2\pi}\right]^{\frac{1}{2}} \int_{-\infty}^\infty dq\, e^{-\beta[\Omega^2 q^2/2 + V_1(q)]}, \quad (2.7)$$

where we have used the notation

$$V(q) = -\frac{1}{2}\omega^{\ddagger^2}q^2 + V_1(q) \quad (2.8)$$

and the generalized frequency Ω is given in terms of the barrier frequency

$$\Omega^{-2} = \frac{u_{00}^2}{\lambda^{\ddagger^2}} - \frac{1}{\omega^{\ddagger^2}}. \quad (2.9)$$

Here the matrix element u_{00} is also given in terms of Laplace transforms of the time-dependent friction

$$u_{00}^2 = \left[1 + \frac{1}{2}\left(\frac{\hat{\gamma}(\lambda_\infty^\ddagger)}{\lambda_\infty^\ddagger} + \frac{\partial\hat{\gamma}(s)}{\partial s}\bigg|_{s=\lambda_\infty^\ddagger}\right)\right]^{-1}. \quad (2.10)$$

In the limit of a very high (reduced) barrier height $(\beta V^\ddagger \gg 1)$ Eq. (2.7) reduces to the usual Kramers-Grote-Hynes result [1,12] for the spatial diffusion limit

$$\Gamma_\infty = \frac{\lambda_\infty^\ddagger}{\omega^\ddagger}\Gamma_{1D}. \quad (2.11)$$

The Kramers-Grote-Hynes solution has been obtained by replacing the one-dimensional dividing surface $f = q = 0$ by a dividing surface in the full space of system and bath $f = \rho = u_{00}q + \sum_j u_{0j}x_j = 0$, where the u_{ij}'s are elements of the orthogonal normal mode transformation matrix. To obtain a generalization of this approach, in the presence of a finite reduced barrier height one poses the following question: What is the optimal *planar* dividing surface? The most general planar dividing surface (in configuration space) may be written as

$$f = a_0 q + \sum_j a_j x_j - \rho_0 = 0 , \quad (2.12)$$

where ρ_0 denotes the distance of the dividing surface from the origin. A generalization of the Kramers-Grote-Hynes theory is obtained by minimizing the TST expression for the rate with respect to the coefficients $a_0, a_j, j = 1, ..., N$ and the shift ρ_0. The details are given explicitly in Ref. [29], here we summarize the results.

The TST expression for the rate (2.4) using the planar dividing surface (2.12) is

$$P_0 \equiv \frac{\Gamma}{\Gamma_{1D}} = \left(\frac{\beta A^2}{2\pi}\right)^{\frac{1}{2}} \int_{-\infty}^\infty dq \exp[-\beta V_{eff}(q, \rho_0)] , \quad (2.13)$$

where the effective potential has the form

$$V_{eff}(q, \rho_0) \equiv \frac{1}{2} A^2 C^2 (q - q_0)^2 + V(q). \qquad (2.14)$$

The effective frequency A and coupling constant C are expressed in terms of the coefficients of the planar dividing surface

$$A^2 = \left[\sum_j \frac{a_j^2}{\omega_j^2} \right]^{-1}, \qquad (2.15)$$

$$C = a_0 + \sum_j \frac{a_j c_j}{\omega_j^2}. \qquad (2.16)$$

The projection of the shift of the dividing surface onto the system coordinate q is defined as

$$q_0 = \frac{\rho_0}{C}. \qquad (2.17)$$

After varying with respect to the transmission coefficients $a_j, j = 1, ..., N$, one finds that the frequency A, coupling constant C, and transformation coefficient a_0 may all be expressed in terms of an effective barrier frequency $\lambda^{\ddagger}$:

$$A^2 = \frac{\lambda^{\ddagger^2}}{a_0 C - 1}, \qquad (2.18)$$

$$C = a_0 \left(1 + \frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}} \right), \qquad (2.19)$$

$$a_0^2 = 1 - \sum_j a_j^2 = \left[1 + \frac{1}{2} \left(\frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}} + \frac{\partial \hat{\gamma}(s)}{\partial s} \bigg|_{s = \lambda^{\ddagger}} \right) \right]^{-1}. \qquad (2.20)$$

At this point the transmission coefficient in Eq. (2.13) is a function of only two variables: the barrier frequency $\lambda^{\ddagger}$ and the shift q_0. Optimization with respect to these two variables has been carried out in Ref. [29]. Our interest here is not the end result of the variational procedure, but rather to bring the VTST result based on the planar dividing surface to a form which is identical to the one obtained in the generalized Ritz method.

To do this we define a new variable ω such that

$$\omega^2 \equiv \lambda^{\ddagger^2} \left[1 + \frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}} \right]. \qquad (2.21)$$

The variational parameter will now become the frequency ω instead of $\lambda^{\ddagger}$. We can use this frequency to define an effective nonlinear part of the potential $V_1(\omega, q_0, q)$

$$V_1(\omega, q_0, q) \equiv V(q) + \frac{1}{2} \omega^2 (q - q_0)^2 \qquad (2.22)$$

such that

$$V(q) = -\frac{1}{2} \omega^2 (q - q_0)^2 + V_1(\omega, q_0, q). \qquad (2.23)$$

The transmission probability (2.13) may be rewritten as

$$P(\omega, q_0) = \left(\frac{A^2}{A^2 C^2 - \omega^2} \right)^{\frac{1}{2}} \left(\frac{\beta(A^2 C^2 - \omega^2)}{2\pi} \right)^{\frac{1}{2}}$$
$$\times \int_{-\infty}^{\infty} dq e^{-\beta[\frac{1}{2}(A^2 C^2 - \omega^2)(q - q_0)^2 + V_1(\omega, q_0, q)]}. \qquad (2.24)$$

It is a matter of some straightforward algebra, using Eqs. (2.18), (2.19), and (2.21) to see that

$$\frac{A^2}{A^2 C^2 - \omega^2} = \frac{\lambda^{\ddagger^2}}{\omega^2} \qquad (2.25)$$

and

$$\Omega^2(\omega) \equiv A^2 C^2 - \omega^2 = \left[\frac{a_0^2}{\lambda^{\ddagger^2}} - \frac{1}{\omega^2} \right]^{-1}. \qquad (2.26)$$

The transmission probability may now be rewritten as

$$P(\omega, q_0) \equiv \frac{\Gamma(\omega, q_0)}{\Gamma_{1D}}$$
$$= \frac{\lambda^{\ddagger}}{\omega} \left[\frac{\beta \Omega(\omega)^2}{2\pi} \right]^{\frac{1}{2}}$$
$$\times \int_{-\infty}^{\infty} dq e^{-\beta[\Omega(\omega)^2 (q - q_0)^2 / 2 + V_1(\omega, q_0, q)]}. \qquad (2.27)$$

This is the central result of this section. The transmission probability has been factorized into two parts. The first part is a Kramers-Grote-Hynes parabolic barrier term $(\frac{\lambda^{\ddagger}}{\omega})$. The second part is a shifted Gaussian average of the nonlinear part of the potential. Comparison of Eqs. (2.7) and (2.27) shows that the optimal planar dividing surface VTST is identical to a VTST which is based on the unstable normal mode dividing surface but such that the system parabolic barrier frequency and location become variational parameters. The transmission probability is a function of the two variables ω, q_0 and may be minimized with respect to them. This minimization will give *exactly* the same result as obtained by optimizing the transmission coefficient as given in Eq. (2.13) with respect to the transformation coefficient a_0 and shift ρ_0. For each planar dividing surface there exists a corresponding parabolic barrier frequency and shift. Optimizing the planar dividing surface is thus identical to optimizing the parabolic barrier frequency and shift.

In summary, we have demonstrated that the optimized planar dividing surface approach to VTST is identical to finding the best parabolic barrier representation for the rate. This is in a way very similar to the Bogoliubov-Feynman variational principle for the free energy where one often uses it to find the best harmonic oscillator representation for a nonlinear oscillator [35]. The optimized parabolic barrier representation depends explicitly on the friction and the nonlinearity in the potential.

III. THE RAYLEIGH QUOTIENT METHOD

We assume that the activated barrier crossing problem may be described in terms of a Fokker-Planck equation for the time evolution of the probability distribution of the particle in some generalized phase space. In Sec. IV we will be more specific, considering the explicit case of a GLE with exponential time-dependent friction. Here we first set up the terminology needed to obtain the Rayleigh quotient. This terminology is abstract and it is not necessary to be specific with respect to the system studied except for a few general properties. An important property which must be fulfilled is that of detailed balance. Then the Fokker-Planck operator L possesses a time reversal invariant equilibrium density P_{eq} such that

$$LP_{eq} = 0, \qquad P_{eq} = \tilde{P}_{eq} , \qquad (3.1)$$

where the tilde notation denotes the operation of time reversal. (Under this operation, coordinates remain invariant while momenta change sign.)

It is useful to define the transformed operator

$$L^* = P_{eq}^{-1} L P_{eq} \qquad (3.2)$$

and one may show that it coincides with the time reversed backward operator L^+:

$$L^* = \tilde{L}^+. \qquad (3.3)$$

For further details on all these relationships, see, for example, Refs. [8,9].

The operators L^* and L^+ act in the Hilbert space of phase space functions with finite second moments with respect to the equilibrium distribution. The scalar product of two functions of this Hilbert space is defined as

$$(f, g) = \langle fg \rangle_{eq} \qquad (3.4)$$

where the notation $\langle \ \rangle_{eq}$ serves to remind that the weighting function of the product is the equilibrium distribution P_{eq}. The operators L^* and L^+ are Hermitian conjugates with respect to this scalar product and their eigenvalues coincide.

Since the two operators are not themselves Hermitian, their spectrum in principle is complex and is contained in the left half of the complex plane. The Hilbert space allows for a bra-ket notation. If $|h\rangle$ is an eigenvector of the operator L^* with eigenvalue μ then $\langle \tilde{h}|$ is the bra in the adjoint space associated with the complex conjugate eigenvalue μ^*. The eigenfunction h =const is always a trivial eigenfunction with zero eigenvalue. For an activated rate process, the rate constant is the eigenvalue whose negative real part is closest to zero.

The Rayleigh quotient is defined as

$$\mu[h] = \frac{(\tilde{h}, L^* h)}{(\tilde{h}, h)}. \qquad (3.5)$$

Clearly, if $|h\rangle$ is an eigenfunction, then μ is the associated eigenvalue. The important point is the variational

property. Just as in the usual Ritz method, it is easy to show that if $|f\rangle$ is an approximate eigenfunction, such that $|h\rangle = |f\rangle + |\delta f\rangle$, then the error in the estimate of the eigenvalue will be of the order of $(\delta f, \delta f)$. It is this variational property which makes the Rayleigh quotient so useful. If, furthermore, the operator L^* is Hermitian (as is the case in the Smoluchowski limit), then one can show that the Rayleigh quotient is an upper bound to the absolute magnitude of the eigenvalue closest to zero.

IV. APPLICATION TO EXPONENTIAL MEMORY FRICTION

In this section we will consider the Rayleigh quotient method for the case of an exponential time-dependent friction kernel

$$\gamma(t) = \frac{\gamma}{\tau} e^{-t/\tau} , \qquad (4.1)$$

where τ is the correlation time of the memory friction and γ is the static friction coefficient [$\hat{\gamma}(0) = \gamma$]. The restriction to a single exponent is mainly for the purpose of convenience and clarity of presentation.

For the single exponent case, the GLE Eq. (2.1) may be rewritten as a Markovian process by introducing an auxiliary variable z [36,37]. This leads to a three-dimensional phase space and the set of equations

$$\dot{q} = v ,$$

$$\dot{v} = -\frac{dV(q)}{dq} + z , \qquad (4.2)$$

$$\dot{z} = -\frac{\gamma}{\tau} v - \frac{1}{\tau} z + \left(\frac{\gamma}{\tau^2 \beta} \right)^{\frac{1}{2}} \xi(t) ,$$

where $\xi(t)$ is a Gaussian white noise

$$\langle \xi(t) \rangle = 0, \qquad \langle \xi(t)\xi(t') \rangle = 2\delta(t - t'). \qquad (4.3)$$

The equivalent Fokker-Planck equation for the joint probability density $P(q, v, z, t)$ is

$$\frac{\partial}{\partial t} P(q, v, z, t) = LP(q, v, z, t) , \qquad (4.4)$$

where the Fokker-Planck operator L is

$$L = -\frac{\partial}{\partial q} v + \frac{\partial}{\partial v} \left[\frac{dV(q)}{dq} - z \right]$$

$$+ \frac{\partial}{\partial z} \left[\frac{\gamma}{\tau} v + \frac{1}{\tau} z \right] + \frac{\gamma}{\tau^2 \beta} \frac{\partial^2}{\partial z^2}. \qquad (4.5)$$

The equilibrium probability density $P_{eq}(q, v, z,)$ satisfies the stationary Fokker-Planck equation

$$LP_{eq} = 0. \qquad (4.6)$$

Its explicit form is

$$P_{eq}(q, v, z) = Z^{-1} \exp(-\beta\phi) , \qquad (4.7)$$

where ϕ is a generalized energy function in the extended phase space

$$\phi(q, v, z) = \frac{1}{2}v^2 + V(q) + \frac{\tau}{2\gamma}z^2. \qquad (4.8)$$

The constant Z assures normalization of the probability distribution P_{eq}. The process defined by the Langevin equation (4.2) satisfies the principle of detailed balance since the auxiliary variable z and the coordinate q transform evenly under time reversal while the velocity v is odd.

The spectrum of the Fokker-Planck operator has a large gap due to a separation of time scales. The barrier crossing process is usually much slower than all other "fast" relaxational processes. When the potential has locally stable reactant and product states, the Fokker-Planck operator (with natural boundary conditions) has a zero eigenvalue whose eigenfunction is the equilibrium distribution [cf. Eqs. (4.7) and (4.8)]. The eigenvalue μ_1 whose real part is closest to zero is related to the rate; $-\mu_1$ is the sum of the forward and backward rates. If one imposes absorbing boundary conditions at the products well, then the zero eigenvalue disappears and the eigenvalue closest to zero gives the escape rate from the appropriately defined reactants well.

The rate may now be estimated from the Rayleigh quotient by demanding that all trial functions obey the relevant absorbing boundary condition. The explict form of the operator L^* for the exponential memory friction case is seen to be

$$L^* = -v\frac{\partial}{\partial q} + \left[\frac{dV(q)}{dq} - z\right]\frac{\partial}{\partial v}$$
$$+ \left[\frac{\gamma}{\tau}v - \frac{1}{\tau}z\right]\frac{\partial}{\partial z} + \frac{\gamma}{\tau^2\beta}\frac{\partial^2}{\partial z^2}. \qquad (4.9)$$

If the potential $V(q)$ is a purely parabolic barrier, located around q_0 such that

$$V_{pb}(q) = -\frac{1}{2}\omega^2(q - q_0)^2 , \qquad (4.10)$$

then following Kramers [1] one finds that the operator L^*_{pb} has a nontrivial eigenfunction ζ associated with a zero eigenvalue whose form is

$$\zeta(q, v, z) = \left(\frac{\beta\omega^2}{2\pi}\right)^{\frac{1}{2}} \int_{u_<}^{\infty} \exp\left(-\frac{1}{2}\beta\omega^2 u^2\right) du. \quad (4.11)$$

The lower limit of integration is

$$u_< = \frac{(\lambda^{\ddagger}\gamma/\omega^2)^{\frac{1}{2}}}{1 - \frac{\lambda^{\ddagger^2}}{\omega^2}}\left[q - q_0 - \frac{\lambda^{\ddagger}}{\omega^2}v + \frac{\tau}{\gamma}\left(1 - \frac{\lambda^{\ddagger^2}}{\omega^2}\right)z\right] . \quad (4.12)$$

The frequency $\lambda^{\ddagger}$ is the solution of the Kramers-Grote-Hynes equation [1,12] [cf. Eq. (2.21)], which for exponential time-dependent friction takes the form

$$\lambda^{\ddagger^3} + \frac{1}{\tau}\lambda^{\ddagger^2} - \left(\omega^2 - \frac{\gamma}{\tau}\right)\lambda^{\ddagger} - \frac{\omega^2}{\tau} = 0. \qquad (4.13)$$

We will henceforth refer to the function ζ as the "Kramers function." It is evident that the function ζ obeys the correct boundary conditions. It is unity in the reactants well and goes to zero in the products region. For a fixed value of the parameters τ, γ of the exponential time-dependent friction, the Kramers function ζ depends on the barrier frequency ω and location q_0. It therefore may be used as a trial function in the Rayleigh quotient, where these two parameters will be considered as variational parameters. The true potential $V(q)$ may always be rewritten as a sum of a parabolic barrier potential and a remainder, as in Eq. (2.23). The rate expression will take the form

$$\Gamma[\omega, q_0] = -\mu[\zeta] = -\frac{(\tilde{\zeta}, L^*\zeta)}{(\tilde{\zeta}, \zeta)}. \qquad (4.14)$$

As long as the location of the barrier q_0 is not too far in the region of the well or too far out in the products region, the denominator in Eq. (4.14) will give the usual population of the well

$$(\tilde{\zeta}, \zeta) = \frac{1}{Z}\int_{-\infty}^{0} dq \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dz e^{-\beta[\frac{v^2}{2} + V(q) + \frac{\tau}{\gamma}z^2]}$$
$$= \frac{1}{\beta}\left(\frac{2\pi\gamma}{\beta\tau}\right)^{\frac{1}{2}}\frac{1}{Z\Gamma_{1D}}, \qquad (4.15)$$

where Γ_{1D} has been defined in Eq. (2.5).

It is now a matter of some lengthy algebra, whose details are given in Appendix A, to show that the explicit expression for the rate obtained from the Rayleigh quotient using the Kramers function takes the form

$$P(\omega, q_0) \equiv \frac{\Gamma(\omega, q_0)}{\Gamma_{1D}} = \frac{\lambda^{\ddagger}}{\omega}\langle\langle e^{-\beta V_1(\omega, q_0, q)}\rangle\rangle. \qquad (4.16)$$

The double angular brackets denote a Gaussian average over the coordinate q such that $\langle\langle q\rangle\rangle = q_0$ and $\langle\langle(q - q_0)^2\rangle\rangle = \beta^{-1}\Omega(\omega)^{-2}$. For exponential memory friction, the frequency Ω [cf. Eq. (2.26)] is related to the friction parameters through the relation

$$\Omega(\omega)^2 = \omega^2\frac{2\lambda^{\ddagger^3}\tau + \lambda^{\ddagger^2} + \omega^2}{(\omega^2 - \lambda^{\ddagger^2})(2\lambda^{\ddagger}\tau + 1)}. \qquad (4.17)$$

Equation (4.16) is the central result of this paper since it is identical to the expression obtained using the optimal planar dividing surface VTST; cf. Eq. (2.27). The identity of the two approaches proves that for the restricted Kramers class of trial functions, the Rayleigh quotient provides an upper bound to the rate. This result follows from the upper bound property of the VTST method. We know of no other way of proving this bounding property except in the Smoluchowski limit.

V. DISCUSSION

In transition state theory, the rate is estimated through the ratio of a unidirectional flux to the population of reactants. The Rayleigh quotient method is based upon the spectral properties of the Fokker-Planck operator. Formally, these are very different methods. However, both have a variational property. Transition state theory gives an upper bound to the rate. The Rayleigh quotient method in the Smoluchowski limit also bounds the rate from above. These similarities motivated the present paper in which we attempted to understand the common grounds of the two approaches. We have demonstrated a restricted identity. If VTST is limited to optimal planar dividing surfaces and the Rayleigh quotient method is limited using only Kramers functions as trial functions, then the two methods are identical.

The identity has been demonstrated here only for exponential memory friction. However, it remains true, as long as the memory friction appearing in the generalized Langevin equation can be expanded as a series of exponentials. If this is the case, one has a well defined Fokker-Planck operator and one may construct the Kramers function associated with a parabolic barrier. The proof of the identity in the presence of a number of exponential terms becomes much more tedious, since each exponent introduces an additional degree of freedom. However, the structure of the quotient remains the same, one will still find that the rate is a Gaussian average of the "nonlinear potential" V_1. It is interesting to note that the rate expression obtained using the optimal planar dividing surface VTST is obtained for arbitrary memory friction.

The physics of the identity of the two methods is rather clear. In the optimal planar dividing surface method, the planarity of the dividing surface implies that one is really fitting the best possible parabolic barrier approximation to the dynamics. The class of Kramers functions is a class of functions also constructed from parabolic barriers. The "physics" of the two (restricted) methods is thus the same.

From a mathematical point of view, the identity of the two restricted methods implies that the Rayleigh method, when restricted to the class of Kramers functions leads to an upper bound to the rate. This is not a trivial statement. In the Smoluchowski limit, the Fokker-Planck operator is Hermitian and the bounding property is just the usual result of the Ritz variational principle. But the Fokker-Planck operator in phase space is not Hermitian and so the Ritz methodology does not lead to a bound, only a variational principle. We find it interesting that we are using variational transition state theory to derive bounding properties for operators that are not Hermitian.

We have restricted ourselves in this paper to memory friction. It is known [17] that in the presence of exponential memory and space-dependent friction, one may also introduce an auxiliary variable which leads to a well defined Fokker-Planck operator. In this case, one may again use VTST to find the optimal planar dividing surface [31]. One then finds that, in addition to the two variational parameters ω and q_0, one must add another parameter which defines an effective (averaged) friction. It is also possible to construct the Kramers function for the parabolic barrier, in which the barrier frequency, location, and effective friction are treated as parameters. Here, the relation of both methods is not known yet.

Finally we note that the two approaches are not equivalent. The Rayleigh quotient method, when used with a large enough basis set, will in principle lead to the exact rate [8,9]. The VTST method in the presence of a nonlinear potential will in general *never* give the exact rate since one ignores successive recrossings of the dividing surface. The VTST method though has the advantage that it is more tractable and it has a bounding property. Perhaps most importantly, unless the temperature is too high, recrossings occur with low probability and the VTST estimate for the rate is very good as also confirmed by a number of numerical studies [30–32,38].

APPENDIX

In this appendix we outline the derivation of the central result of this paper as given in Eq. (4.16). As noted in Sec. IV, the Kramers function has the property that $L_{pb}^* \zeta = 0$; therefore one easily notes that

$$L^* \zeta = -\left(\frac{\beta \omega^2}{2\pi}\right)^{\frac{1}{2}} \frac{dV_1(\omega, q_0, q)}{dq} \frac{du_<}{dv} e^{-\frac{\beta}{2}\omega^2 u_<^2}. \quad (A1)$$

It therefore follows that

$$(\tilde{\zeta}, L^* \zeta) = -\frac{1}{Z}\left(\frac{\beta \omega^2}{2\pi}\right)^{\frac{1}{2}}$$

$$\times \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dz \tilde{\zeta} \frac{dV_1(\omega, q_0, q)}{dq} \frac{du_<}{dv}$$

$$\times e^{-\frac{\beta}{2}[\omega^2 u_<^2 + v^2 + \frac{\tau}{\gamma} z^2 - \omega^2(q-q_0)^2]} e^{-\beta V_1(\omega, q_0, q)}.$$

$$(A2)$$

Further progress may be made by changing variables from q, v, z to q, u, y such that

$$v = u + \lambda^{\ddagger}(q - q_0) , \qquad (A3)$$

$$z = y + \lambda^{\ddagger}u + (\lambda^{\ddagger^2} - \omega^2)(q - q_0). \qquad (A4)$$

With this change of variables and use of the Kramers-Grote-Hynes equation (4.13), one finds that

$$(\tilde{\zeta}, L^*\zeta) = -\frac{1}{Z\beta}\left(\frac{\beta\omega^2}{2\pi}\right)^{\frac{1}{2}}\frac{\lambda^{\ddagger}}{\omega}\frac{\lambda^{\ddagger}\tau + 1}{(\gamma\lambda^{\ddagger})^{\frac{1}{2}}}$$

$$\times \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dy\tilde{\zeta}\left[\frac{d}{dq}e^{-\beta V_1(\omega,q_0,q)}\right]$$

$$\times e^{-\frac{\beta}{2}\frac{1+\lambda^{\ddagger}\tau}{\tau}(\frac{\omega^2}{\lambda^{\ddagger}}u^2+\tau y^2)}. \qquad (A5)$$

After integrating by parts with respect to the variable q, one is left with two Gaussian integrals over the variables u and y. These are readily performed and after some manipulation [including use of Eq. (4.17)] one finds the desired result Eq. (4.16).

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