ACTIVATED RATE PROCESSES: A RELATION BETWEEN HAMILTONIAN AND STOCHASTIC THEORIES

by

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ABSTRACT

Kramers' treatment of activated rate processes is based on the Langevin equation of motion for the escaping particle. The stochastic dynamics may be cast equivalently as the dynamics of a particle interacting bilinearly with a bath of harmonic oscillators. This paper explores the connection between the solutions of Kramers' problem (and its generalization to include memory friction) obtained in the framework of these two approaches. We demonstrate their equivalence for the specific case of a parabolic barrier potential. The Hamiltonian representation is used to construct (a) a nontrivial eigenfunction of the Fokker-Planck equation which is generalized to include time dependent friction; (b) the 'Kramers' stationary flux distribution function; (c) the stochastic separatrix.

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1. Introduction

The classical representation of activated rate processes as described by Kramers [1] is in terms of a Fokker-Planck equation for the probability density function (pdf) $W(p,q,t)$ of the particle position (q) and momentum (p),

$$\frac{\partial W(p,q,t)}{\partial t} = LW(p,q,t). \tag{1.1}$$

The Fokker-Planck operator (L) has the form

$$L \equiv -\frac{\partial}{\partial q}p + \frac{\partial}{\partial p}\left[\gamma p + \frac{dV(q)}{dq}\right] + \frac{\gamma}{\beta}\frac{\partial^2}{\partial p^2}, \tag{1.2}$$

where $V(q)$ is the potential acting on the particle, γ is the damping coefficient, and $\beta = 1/k_B T$, where T is the temperature of the bath with which the particle interacts. The Fokker-Planck equation describes the time (t) evolution of the pdf $W(p,q,t)$ of the particle. Much effort has been expended in finding solutions of the partial differential equation (1.1), as described in standard textbooks [2]-[4].

It is also well understood that the Fokker-Planck equation may be derived from the stochastic Langevin equation of motion for the particle,

$$\ddot{q} + \frac{dV(q)}{dq} + \gamma\dot{q} = \xi(t), \tag{1.3}$$

where the dot denotes differentiation with respect to time and $\xi(t)$ is a δ-correlated Gaussian random force with zero mean, related to the damping by

$$\langle \xi(t)\xi(\tau)\rangle = \frac{2\gamma}{\beta}\delta(t-\tau). \tag{1.4}$$

For simplicity, we have assumed unit mass for the particle, or equivalently, the coordinate q and momentum $p = \dot{q}$ are mass weighted.

In an activated rate process, the potential V is assumed to have a well at some location $q = q_0$ and a barrier at a point $q = q^{\ddagger}$ that separates the well from a different well or a continuum. The theory of activated rate processes describes the effect of damping and temperature on the rate of escape of the particle. If $V(q) \to \infty$ sufficiently fast as $|q| \to \infty$, the Fokker-Planck operator has well defined eigenfunctions, W_n, and eigenvalues, $-\mu_n$. The time dependence is then exponential, with modes $W_n(p,q,t) = e^{-\mu_n t}W_n(p,q)$. The eigenfunction W_0, associated with the zero eigenvalue $\mu_0 = 0$, is the thermal equilibrium density $W_0 = \exp[-\beta(p^2/2 + V(q)]$. The standard methodology [2, 3, 4] for obtaining the rate is based on various approximations for nontrivial density functions, use of variational principles such as generalized Ritz principles for the Fokker-Planck operator [5, 6], and more recently, estimates of the mean first passage time to the stochastic separatrix [7]-[9]. All these approaches were based on studying the properties of the Fokker-Planck equation or the Langevin equation.

An alternate representation of the stochastic differential equation is obtained by describing the particle dynamics in terms of a Hamiltonian in which the particle is bilinearly coupled to a harmonic bath [10]. The equivalent Hamiltonian has the form

$$H = \frac{p^2}{2} + V(q) + \sum_j \left[\frac{p_{x_j}^2}{2} + \frac{1}{2}(\omega_j x_j - \frac{c_j}{\omega_j} q)^2 \right], \tag{1.5}$$

where the bath (mass weighted) modes have coordinates x_j, momenta p_j, and frequencies ω_j. Each bath oscillator is bilinearly coupled to the system through the coupling coefficient c_j. This Hamiltonian is related to the stochastic Langevin equation by noting that the equation of motion of each bath oscillator is just that of a forced oscillator in which the forcing function is dependent only on the system coordinate q. This allows for an explicit equation of motion for the system coordinate which has the same form as the (generalized) Langevin equation,

$$\ddot{q} + \frac{dV(q)}{dq} + \int^t d\tau \gamma(t-\tau)\dot{q}(\tau) = \xi(t), \tag{1.6}$$

in which the time dependent friction is

$$\gamma(t) = \sum_j \frac{c_j^2}{\omega_j^2} \cos(\omega_j t). \tag{1.7}$$

The random force, $\xi(t)$, depends on the initial positions and momenta of all the bath variables. If this initial distribution is chosen from the canonical ensemble, $\exp(-\beta H)$, then the random force is Gaussian and its autocorrelation function is related to the time dependent friction by the fluctuation-dissipation theorem. For the Langevin equation, the time dependent friction is Ohmic, $\gamma(t) = 2\gamma\delta(t)$. Obtaining the Langevin dynamics from the Hamiltonian implies a representation of the friction function as a periodic function, whose cosine Fourier series is well defined, for example $\gamma_\tau(t) = 2\gamma \sum_{n=-\infty}^{n=\infty} \delta(t + n\tau)$, and then taking an ever increasing period τ. For a given period, τ, the Hamiltonian representation of the dynamics is accurate for times t less than τ.

Although this representation would seem at first glance to cause enormous difficulties, it has been shown in recent work [11, 12] that direct analysis of the Hamiltonian dynamics can lead to vast simplifications. Specifically, one can use classical variational transition state theory to estimate the rate for finite barrier heights[11, 12], cusped potentials [12], space dependent friction problems [13], and anisotropic friction in the multidimensional case [14]. The Hamiltonian dynamics has been used to derive a Kramers turnover theory for the rate [15], valid for all values of the damping constant γ. It has also been used as a starting point for a perturbation theory expansion to derive exact finite barrier corrections to the rate of reaction [16].

What has not been done to date is to establish the relation between the detailed dynamics of the Hamiltonian representation on the one hand and the dynamics as determined from the Fokker-Planck equation or the stochastic differential equation on the other. While it has been shown that the rates, when known, are identical, it has not been shown for example how one may derive the eigenfunctions of the Fokker-Planck operator directly from the Hamiltonian representation. Similarly, one would think that there should be a way to relate the stochastic separatrix and the Hamiltonian dynamics.

In this paper we start exploring the connection between the two approaches. We deal exclusively with the dynamics of a parabolic barrier potential, for which everything is presumably known. The Fokker-Planck equation can be solved analytically [2] and the Hamiltonian dynamics is separable [17]. ¿From the point of view of each separate approach, there is nothing new, however, the relationship between the two very different solutions is new and we believe interesting. For example, the Hamiltonian approach can deal with memory friction as easily as with Ohmic friction. The Fokker-Planck equation is well defined only for Ohmic friction. However, from the Hamiltonian approach we can derive a distribution function in the q, p phase space which decays exponentially for *any* time dependent friction. On a conceptual basis, the analysis presented in this paper also indicates why the variational transition state theory for the rate is so much more powerful and useful than other methods.

In Section 2, we review briefly the Hamiltonian dynamics for the parabolic barrier potential. We then show in Section 3 how these dynamics may be exploited for a direct construction of a nontrivial eigenfunction. In Section 4, the "Kramers" stationary flux distribution function is derived, and in Section 5, we construct the stochastic separatrix. We end with a discussion, indicating how the present results may be used for further development of the theory of activated rate processes.

2. Hamiltonian dynamics for a parabolic barrier

When the potential function is that of a parabolic barrier

$$V(q) = -\frac{1}{2}\omega^{\ddagger^2} q^2, \tag{2.1}$$

where $\omega^{\ddagger}$ is the barrier frequency, the Hamiltonian (1.5) is a quadratic form and thus may be cast in terms of normal modes

$$H = \frac{1}{2}p_\rho^2 - \frac{1}{2}\lambda^{\ddagger^2}\rho^2 + \sum_j \frac{1}{2}\left[p_{y_j}^2 + \lambda_j^2 y_j^2\right]. \tag{2.2}$$

Here, ρ denotes the unstable normal mode, which is the analog of the system coordinate q, and reduces to it in the zero damping limit. Similarly, y_j denotes the j-th stable normal mode. The normal modes are related to the original system and bath coordinates, $q, \underline{x}$, via an orthogonal transformation matrix $\mathbf{U}$, such that

$$q = u_{00}\rho + \sum_j u_{j0}y_j, \qquad p = u_{00}p_\rho + \sum_j u_{j0}p_{y_j}. \tag{2.3}$$

The details of this transformation have been worked out in various places [17, 18, 19], so that here we summarize the main results which will be of interest in the next sections.

Denoting the Laplace transform by a "hat", one may easily see that the Laplace transform of the time dependent friction, as represented in Eq.(1.7), is

$$\hat{\gamma}(s) = s \sum_j \frac{c_j^2}{\omega_j^2} \frac{1}{\omega_j^2 + s^2}. \tag{2.4}$$

One finds that the unstable mode parabolic barrier frequency, $\lambda^{\ddagger}$, is just the usual Kramers-Grote-Hynes frequency [1, 20]

$$\frac{\lambda^{\ddagger}}{\omega^{\ddagger}} = \left[1 + \frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}}\right]^{-\frac{1}{2}}. \tag{2.5}$$

The transformation matrix element that gives the projection of the system coordinate on the unstable mode may also be expressed in terms of the Laplace transform of the time dependent friction as [15]

$$u_{00}^2 = \left[1 + \frac{1}{2}\left(\frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}} + \frac{\partial \hat{\gamma}(s)}{\partial s}\Big|_{s=\lambda^{\ddagger}}\right)\right]^{-1}. \tag{2.6}$$

One may define an effective bath frequency, Ω, as [21]

$$\Omega^{-2} \equiv \sum_j \frac{u_{j0}^2}{\lambda_j^2} = \frac{u_{00}^2}{\lambda^{\ddagger^2}} - \frac{1}{\omega^{\ddagger^2}}, \tag{2.7}$$

where the last equality on the right hand side of the equation may be proved from properties of the normal mode transformation [19]. Since the three quantities, $\lambda^{\ddagger}$, u_{00}, and Ω, are all expressed in terms of Laplace transforms of the time dependent friction, they are well defined in the continuum limit. We also note that, as shown in [17], the product over all normal mode frequencies is identical to the product over all original frequencies,

$$\lambda^{\ddagger} \prod_j \lambda_j = \omega^{\ddagger} \prod_j \omega_j. \tag{2.8}$$

For the specific case of Ohmic friction,

$$\gamma(t) = 2\gamma\delta(t), \tag{2.9}$$

which is the main case of interest in this paper, the explicit solution for all the three quantities $\lambda^{\ddagger}$, u_{00}, and Ω, is simple, specifically,

$$u_{00}^{-2} = 1 + \frac{\gamma}{2\lambda^{\ddagger}} \tag{2.10}$$

and

$$u_1^2 \Omega^2 = \omega^{\ddagger^2}, \tag{2.11}$$

where we have used the notation

$$u_1^2 \equiv 1 - u_{00}^2. \tag{2.12}$$

Since the Hamiltonian in the normal mode form is separable, the solution for the time dependence of each of the modes in terms of the initial conditions (denote by a 0 subscript) is simple. For the unstable mode one has

$$\rho(t) = \rho_0 \cosh(\lambda^{\ddagger} t) + \frac{p_{\rho 0}}{\lambda^{\ddagger}} \sinh(\lambda^{\ddagger} t) \tag{2.13}$$

and for the j-th stable mode

$$y_j(t) = y_{j0} \cos(\lambda_j t) + \frac{p_{y_{j0}}}{\lambda_j} \sin(\lambda_j t) \tag{2.14}$$

In the normal mode form, the question of crossing the barrier becomes trivial. If the energy in the unstable mode is greater than zero and the momentum is positive, the trajectory proceeds from reactants (negative ρ) to products (positive ρ). However, the system is observed in the physical phase space q, p and thus the question remains of how does the motion of the normal modes reflect in the physical space. This is dealt with in detail in the next section.

3. An Eigenfunction

As noted in the Introduction, the time dependence of the eigenfunctions of the Fokker-Planck operator is that of a single exponent. For the parabolic barrier, the lowest nonzero eigenvalue is just the normal mode barrier frequency $\lambda^{\ddagger}$. It is shown below that this is not a mere coincidence. In fact, when considering the normal mode representation, one understands that if the initial conditions of the unstable mode are chosen such that

$$\lambda^{\ddagger} \rho_0 - p_{\rho_0} = 0 \tag{3.1}$$

then for any time t,

$$\rho(t) = \rho_0 e^{+\lambda^{\ddagger} t}, \qquad p_\rho(t) = p_{\rho_0} e^{+\lambda^{\ddagger} t}. \tag{3.2}$$

The time dependence of the physical coordinate and momentum is on the average the same exponential time dependence as implied by eqs. (2.3). Thus one should expect the eigenfunction to be represented by the projection onto the physical phase space of all points which obey the fundamental relation as in Eq.(3.1). In this section, we quantify these ideas and show that they are correct.

A function $P(q,p,t)$ is defined as

$$P(\tilde{q}, \tilde{p}, t) = \mathrm{Tr} \left\{ \frac{\delta(q(t) - \tilde{q}) \delta(p(t) - \tilde{p}) \delta(\lambda^{\ddagger} \rho_0 - p_{\rho_0}) e^{-\beta H}}{\mathrm{Tr} \left\{ \delta(q - \tilde{q}) \delta(p - \tilde{p}) e^{-\beta H} \right\}} \right\}. \tag{3.3}$$

The time dependence of $q(t), p(t)$ is known exactly for the Hamiltonian dynamics in terms of the initial conditions and is given by a combination of eqs.(2.3), (2.13), and (2.14). The trace implies an integration over all initial coordinates and momenta and may be performed either in the $q, \underline{x}$ representation, using the form of the Hamiltonian given in Eq.(1.5) or in the $\rho, \underline{y}$ representation using the normal mode Hamiltonian (2.2).

Instead of performing the trace operation over the initial conditions, one may use the invariance of the volume element in phase space to perform the integration over the volume element at time t. One must then express the initial conditions for the unstable mode ρ_0, p_{ρ_0} in terms of the unstable coordinate and momentum at time t. By virtue of eqs.(3.1) and (3.2) and properties of the δ function, one finds that

$$\delta(\lambda^{\ddagger}\rho_0 - p_{\rho_0}) = e^{-\lambda^{\ddagger}t}\delta\left[\lambda^{\ddagger}\rho(t) - p_\rho(t)\right]. \tag{3.4}$$

It immediately follows that the time dependence of the distribution is as designed,

$$P(q,p,t) = e^{-\lambda^{\ddagger}t}P(q,p,0). \tag{3.5}$$

It is thus reasonable to expect that $P(q,p,0)$ is related to the eigenfunction associated with the eigenvalue $-\lambda^{\ddagger}$ of the Fokker-Planck equation in the case of Ohmic friction. It is just a matter of some algebra to demonstrate the explicit relation.

The denominator in Eq.(3.3) is easily evaluated in the $q, \underline{x}$ representation, since the integration over all the bath modes is just a simple Gaussian integration. One finds that

$$\mathrm{Tr}\left\{\delta(q-\tilde{q})\delta(p-\tilde{p})e^{-\beta H}\right\} = \prod_j \left(\frac{2\pi}{\beta\omega_j}\right) e^{-\beta\frac{1}{2}(\tilde{p}^2 - \omega^{\ddagger^2}\tilde{q}^2)}. \tag{3.6}$$

For the numerator, it is convenient to use the normal mode representation, this implies expressing the system coordinate q and momentum p in terms of the normal modes, as given in eqs.(2.3). The integrals may be reduced to simple Gaussian integration by using the Fourier expansion of the δ function. For example,

$$\delta(q-\tilde{q}) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\kappa e^{i\kappa(u_{00}\rho + \sum_j u_{j0}y_j - \tilde{q})}. \tag{3.7}$$

Integration over all bath coordinates and momenta leaves one with the interim result

$$P(\tilde{q},\tilde{p},0) = \frac{\beta\Omega}{2\pi u_1}\prod_j\left(\frac{\omega_j}{\lambda_j}\right) \times \tag{3.8}$$

$$\int_{-\infty}^{\infty} d\rho\, dp_\rho\, \delta(\lambda^{\ddagger}\rho - p_\rho)\exp\left(-\frac{\beta}{2}\left[\Omega^2\frac{\lambda^{\ddagger^2}}{\omega^{\ddagger^2}}(\rho - u_{00}\tilde{q}\frac{\omega^{\ddagger^2}}{\lambda^{\ddagger^2}})^2 + \frac{1}{u_1^2}(p_\rho - u_{00}\tilde{p})^2\right]\right).$$

The remaining two integrations are now straightforward. Using the identities (2.5, (2.7), (2.8), (2.10)-(2.12), and rearranging, one finds

$$P(\tilde{q},\tilde{p},0) = (\frac{\beta}{2\pi})^{\frac{1}{2}}\left[\frac{\lambda^{\ddagger}}{u_{00}^2\hat{\gamma}(\lambda^{\ddagger})}\right]^{\frac{1}{2}}\exp\left[-\frac{\beta}{2}\frac{\lambda^{\ddagger}}{\hat{\gamma}(\lambda^{\ddagger})}(\tilde{p} - \frac{\omega^{\ddagger^2}}{\lambda^{\ddagger}}\tilde{q})^2\right]. \tag{3.9}$$

The eigenfunction of the Fokker-Planck operator is the product of P with the equilibrium distribution (see [22])

$$W(q,p) = P(q,p,0)e^{-\frac{\beta}{2}(p^2-\omega^{\ddagger 2} q^2)} \tag{3.10}$$

It is a matter of algebra to show that this function is indeed the eigenfunction of a Fokker-Planck like operator,

$$L = -\frac{\partial}{\partial q}p + \frac{\partial}{\partial p}\left[\hat{\gamma}(\lambda^{\ddagger})p + \frac{dV(q)}{dq}\right] + \frac{\hat{\gamma}(\lambda^{\ddagger})}{\beta}\frac{\partial^2}{\partial p^2} \tag{3.11}$$

For Ohmic friction $\hat{\gamma}(\lambda^{\ddagger}) = \gamma$ and so Eq.(3.10) is just the standard Fokker-Planck operator. However, by utilizing the microscopic dynamics which is valid also for memory friction, we find that we may define a new operator, whose eigenfunction is $W(q,p)$ with eigenvalue $-\lambda^{\ddagger}$ which in turn obeys the Kramers-Grote-Hynes equation (2.5).

4.Kramers' stationary flux distribution function

In his original paper, Kramers determined the escape rate of the activated particle in the spatial diffusion limit by finding a distribution function $F(q,p)$ which has the property that the flux associated with it is stationary and that it obeys the boundary condition which is that deep in the reactants region it is just the equilibrium distribution function. For the Fokker-Planck operator, Eq.(1.2), the current operator has components

$$J_q = p, \qquad J_p = -(\gamma p + \frac{dV(q)}{dq}) - \frac{\gamma}{\beta}\frac{\partial}{\partial p} \tag{4.1}$$

The stationarity condition takes the form

$$\frac{\partial F}{\partial t} = 0 = -\nabla \cdot \underline{J}F. \tag{4.2}$$

As shown by Kramers [1], for the parabolic barrier

$$F(q,p) = e^{-\frac{\beta}{2}(p^2-\omega^{\ddagger 2} q^2)}\frac{1}{\sqrt{\pi}}\int_{-\infty}^{(\frac{\beta\lambda^{\ddagger}}{2\gamma})^{\frac{1}{2}}(p-\frac{\omega^{\ddagger 2}}{\lambda^{\ddagger}}q)} e^{-y^2}\,dy. \tag{4.3}$$

When considering the Hamiltonian dynamics, the flux operator in the full phase space, in the normal mode representation, has the components

$$J_\rho = \dot{\rho}, \qquad J_{p_\rho} = \dot{p}_\rho, \tag{4.4}$$

and similarly for each of the stable modes,

$$J_{y_j} = \dot{y}_j, \qquad J_{p_{y_j}} = \dot{p}_{y_j}. \tag{4.5}$$

Here the dot denotes time differentiation, the time dependence is determined from Hamilton's equations of motion. The stationarity condition takes the form

$$\nabla \cdot \underline{J} F = 0, \tag{4.6}$$

where F is a distribution function and the gradient operator is in the full phase space.

Of course, all this is just notation for the fact that any function in phase space which is constant along a classical trajectory will be stationary. Thus for example the Hamiltonian itself is stationary. However, Kramers was interested not only in a stationary flux, but he imposed the boundary condition which is that the flux is associated with particles which were initiated in the infinite past in the reactant region. Following Pechukas [23], we define the characteristic function of points in phase space χ_r which is unity on all phase space points of a trajectory which was initiated in the infinite past at reactants and is zero otherwise. By definition, χ_r is stationary. The distribution function associated with the characteristic function χ_r, projected onto the physical phase space is then

$$F_r(\tilde{q}, \tilde{p}) = N \mathrm{Tr} \left[\delta(q - \tilde{q}) \delta(p - \tilde{p}) e^{-\beta H} \chi_r \right], \tag{4.7}$$

where N is a normalization constant and the Tr operation is over the whole phase space.

For the purely parabolic barrier the dynamics is trivial and so we know the explicit form of the characteristic function

$$\chi_r = \theta(p_\rho - \lambda^{\ddagger} \rho). \tag{4.8}$$

where $\theta(x)$ is the unit step function. It is now a matter of repeating the same algebra as in the previous section to find that the desired function is simply

$$F_r(\tilde{q}, \tilde{p}) = e^{-\frac{\beta}{2}(\tilde{p}^2 - \omega^{\ddagger 2} \tilde{q}^2)} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\left[\frac{\beta}{2} \frac{\lambda^{\ddagger}}{\hat{\gamma}(\lambda^{\ddagger})}\right]^{\frac{1}{2}} (\tilde{p} - \frac{\omega^{\ddagger 2}}{\lambda^{\ddagger}} \tilde{q})} e^{-y^2} \, dy. \tag{4.9}$$

It is easy to see that for Ohmic friction this result reduces to Kramers function. Moreover, using the same generalization of the Fokker-Planck operator to include memory friction as in the previous section one finds that

$$LF(q, p) = 0, \tag{4.10}$$

where the operator L is defined in Eq.(3.11). It is the same Fokker-Planck operator as in Eq.(1.2), but generalized to include the memory friction case.

For the purely parabolic barrier, the eigenvalue $\mu = 0$ is degenerate, as both the equilibrium and the stationary flux distributions are eigenfunctions. Of course the equilibrium distribution is a nonnormalizable function. In addition, the equilibrium net flux through any surface vanishes while the net flux associated with the Kramers distribution is constant but not zero. As is well known, in the presence of nonlinearities, the degeneracy is removed.

5. The stochastic separatrix

The stochastic separatrix is defined as a curve in the particle phase space (q,p) from which the particle reaches products with a probability of $\frac{1}{2}$ [7]-[9]. To construct the stochastic separatrix we, construct a function $T(\tilde{q},\tilde{p})$ which is defined as the probability that a particle initiated at phase space point $\tilde{q},\tilde{p}$ reaches products in the limit that the time goes to ∞. The stochastic separatrix is a curve in phase space defined by the condition

$$T(\tilde{q},\tilde{p})=\frac{1}{2}. \tag{5.1}$$

To obtain the "transmission probability function" T, one only needs to consider the dynamics of the unstable mode. Positive values of ρ are defined as the products region, negative values are defined as reactants. Denote the energy in the unstable mode as E_ρ,

$$2E_\rho \equiv p_\rho^2 - \lambda^{\ddagger^2}\rho^2. \tag{5.2}$$

Any trajectory initiated with $E_\rho > 0, p_\rho > 0$ necessarily makes it to products as time tends to ∞. Similarly, any trajectory initiated with $E_\rho < 0, \rho > 0$, makes it to products at large times. Barring the set of measure zero, $E_\rho = 0$, no other initial condition will lead to products as the time goes to ∞. Therefore the transmission probability function is the projection of these two conditions onto the physical phase space. Explicitly,

$$T(\tilde{q},\tilde{p})=\mathrm{Tr}\left\{\frac{\delta(q(t)-\tilde{q})\delta(p(t)-\tilde{p})\left[\theta(E_\rho)\theta(p_\rho)+\theta(-E_\rho)\theta(\rho)\right]e^{-\beta H}}{\mathrm{Tr}\delta(q-\tilde{q})\delta(p-\tilde{p})e^{-\beta H}}\right\}. \tag{5.3}$$

As in the previous section, it is convenient to carry out the integrations in the normal mode space. The integration over all the bath variables is identical to that in the previous section so that one can immediately write down the interim result as in Eq.(3.8), except that the δ function is replaced by the sum of the products of step functions appearing in Eq.(5.3). The result is

$$T(\tilde{q},\tilde{p})=(\frac{\beta}{2\pi})^{\frac{1}{2}}(\frac{\lambda^\ddagger}{\hat{\gamma}(\lambda^\ddagger)})^{\frac{1}{2}}\int_{-(\tilde{p}+\frac{\omega^{\ddagger^2}}{\lambda^\ddagger}\tilde{q})}^{\infty} dv e^{-\frac{\beta}{2}\frac{\lambda^\ddagger}{\hat{\gamma}(\lambda^\ddagger)}v^2}. \tag{5.4}$$

¿From the definition of the stochastic separatrix we find that $T=\frac{1}{2}$ on the line

$$\tilde{p}_{ss}+\frac{\omega^{\ddagger^2}}{\lambda^\ddagger}\tilde{q}_{ss}=0. \tag{5.5}$$

This result is correct for arbitrary memory friction, since the normal mode barrier frequency $(\lambda^\ddagger)$ is a solution of the Kramers-Grote-Hynes equation (2.5). In the Ohmic limit, this is identical to the results derived in [9]. Note again the ease with which we have derived the stochastic separatrix for arbitrary memory friction.

6. Discussion

The Hamiltonian representation of the dynamics of a particle moving on a parabolic barrier in the presence of time dependent friction and an external Gaussian random force has been used to derive stationary distribution functions and separatrices in the physical (q, p) phase space. In the limit of Ohmic friction, these become the known separatrices and eigenfunctions of the Fokker-Planck operator. We have seen that knowledge of the deterministic separatrix of the unstable normal mode (ρ) is really all that counts. The rest is just projection of the normal mode dynamics onto the physical phase space, taking into account the correct thermal averaging over initial conditions.

Interestingly, the Hamiltonian approach for the parabolic barrier is more efficient than the direct approach based on the Fokker-Planck operator since it allows immediate extension of all results to include memory friction. This is not a mere artifact of the parabolic barrier case. An important aspect of the parabolic barrier is that it provides a useful point of departure for a perturbation theory which takes into account the nonparabolic part of the potential. For example, one may use the perturbation theory presented in [16] together with the approach presented here, to obtain perturbation expansions of Kramers' function and the stochastic separatrix even in the presence of memory and space dependent friction.

The Hamiltonian approach for the parabolic barrier, seems to suggest a useful generalization of the Fokker-Planck operator to the memory friction case (cf Eq. 3.11). This operator does not in general describe the full dynamics for the memory friction case. However, it does suggest that one can usefully define Fokker-Planck like operators which provide a good representation for specific properties.

Perhaps the most interesting result of the present paper is the insight it gives into the dynamics underlying the stationary distribution functions. We have seen that it is necessary to understand the dynamics in all of phase space, in order to construct the eigenfunctions. Equivalently, the stochastic separatrix may be found only if one knows the fate of each trajectory. This is a much more severe restriction than the one used in bounding the rate with the use of variational transition state theory (VTST), In VTST, all that is needed is the instantaneous velocity of each trajectory as it crosses a dividing surface. This is a much weaker demand leading to a substantially more powerful theory of reaction rates. Of course, the weaker demand has its price, the VTST approach only gives an upper bound to the rate. However, experience has shown that often this upper bound is very good.

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