Transition-state recrossing dynamics in activated rate processes

Eli Pollak* and Peter Talkner
Paul Scherrer Institute, CH-5232, Villigen, Switzerland
(Received 26 October 1994)

In the framework of the transition-state theory (TST), the rate of thermally activated escapes from a locally stable state in phase space is determined by the unidirectional flux through a conveniently chosen dividing surface. It is known that the occurrence of trajectories that recross this surface renders the true rate smaller than the TST rate by the so-called transmission factor. By means of a statistical theory we show how the mean number of recrossings can be related to the transmission factor. Formulas are derived for the average number of recrossings at the top of a parabolic barrier and through an energy surface in phase space. The former case is relevant for the spatial diffusion regime and the latter for the energy diffusion regime. The resulting transmission factors are in good agreement with the exact ones.

PACS number(s): 05.40.+j, 82.20.Db, 82.20.Fd

I. INTRODUCTION

An activated rate process is one in which a system changes from one stationary state to another by crossing a barrier located between the two states. The necessary energy to cross this barrier is supplied by the surrounding medium. At the same time, the medium exerts a drag on the system, preventing it from crossing the barrier. Kramers [1], in his famous paper of 1940, modeled this process in terms of a Langevin equation. The surrounding medium is modeled by a Gaussian random force with zero mean and memory, resulting in a damping term in the equation of motion with damping strength γ. He then proceeded to estimate the rate of escape and showed that the "standard" transition-state theory (TST) expression for the rate must be modified by a prefactor which in the strong damping limit is inversely proportional to the damping strength.

The standard TST expression [2] is obtained by placing a dividing surface at the barrier top of the potential of mean force felt by the system. The fact that the damping modifies the TST result implies that the assumption of no recrossing of the barrier, implicit in the TST result, is violated. This of course makes sense. Especially in the strong damping limit, the system is diffusing over the barrier top. This means that it must be recrossing it many times before ending up in the reactants or products zone.

Kramers original formulation has been generalized to include memory friction by Grote and Hynes [3] and others [4]. The resulting expression, when the friction is not too small, is again a product of a standard TST expression multiplied by a prefactor that is smaller than unity. In this spatial diffusion limit, the prefactor has been referred to as a correction factor for solvent induced recrossings of the barrier [5].

Recrossing occurs also in a different context. Consider the energy diffusion limited regime of the activated rate process. In this limit, the damping is very small and the rate limiting step is the rate at which the medium transfers to the system the energy needed to cross the barrier [1]. It is well known [2] that in this limit the rate is again a product of the standard TST result and a prefactor which is proportional to a small dimensionless parameter denoted δ, known as the energy loss parameter. This parameter is proportional to the product of the damping strength and the barrier height.

In this limit, it might seem that a good idea would be to change somewhat the dividing surface used in the TST. Instead of putting it at the barrier top, as appropriate for the spatial diffusion limit, one might consider using a dividing surface in energy space [6]. The rate determining step in this limit is obtaining the necessary energy to cross the barrier. Once this energy is obtained, the system reacts immediately so one might choose the dividing surface to be the system Hamiltonian at the barrier energy $V^{\ddagger}$. The only problem with this choice is that the resulting TST expression diverges if the friction is Ohmic [6,7]. There is nothing "wrong" with this divergence. The TST is a theory guaranteed to give an upper bound and ∞ is also an upper bound. Clearly the system must be recrossing this dividing surface an infinity of times too.

To date, almost all work dealing with activated rate processes was centered about estimates for the rate. The recrossing dynamics, which as sketched above is ubiquitous, was assumed to properly account for the prefactors. However, we are not aware of any direct analysis of the recrossing dynamics. This is the topic of this paper.

There is a way of essentially eliminating the recrossings in the spatial diffusion limit. As noted elsewhere [8], instead of choosing the dividing surface $q = 0$ (where q denotes the system reaction coordinate) one may use the dividing surface $\rho = 0$, where ρ is the unstable nor-

*Permanent address: Chemical Physics Department, Weizmann Institute of Science, 76100, Rehovot, Israel.

mal mode that diagonalizes the system bath Hamiltonian [9,11] at the barrier top. Along the unstable normal mode, if the barrier height is large compared to k_BT, there really are no recrossings and the TST estimate using this dividing surface is exact and identical to the theory of Kramers and Grote and Hynes [8].

One might thus be tempted to use the unstable mode also in the energy diffusion regime and choose as the dividing surface in energy space the effective Hamiltonian for the unstable mode at the barrier energy. This turns out to be better than the previously chosen surface along the system coordinate; the prefactor is proportional to $\sqrt{\delta}$ and is thus much smaller than unity, however still much larger than the correct answer, which is δ [6]. Obviously, there must be of the order of $\frac{1}{\sqrt{\delta}}$ recrossings of this surface. Is there a practical way of estimating the recrossings and thus obtaining a new estimate for the rate in the energy diffusion limited regime?

The question is not an idle one. In the presence of very long memory friction, the Kramers turnover theory derived by Pollak, Grabert, and Hänggi (PGH) [10] is not necessarily valid [12]. Any new methodology for estimating the rate might become useful for extension to the long memory case.

In Sec. II we review the formalism needed to estimate the average number of recrossings. A statistical theory is then used to relate the average number of recrossings to the reaction rate. The application to the parabolic barrier in the presence of memory friction is given in Sec. III. The energy diffusion limited regime is considered in Sec. IV. The TST result with a dividing surface in the energy space of the unstable normal mode as well as an estimate of the recrossing dynamics is given. We end with a discussion of the implications of the results to the long memory problem.

II. THE RATE AND THE RECROSSING DISTRIBUTION

A. The recrossing distribution

The total number of times $N_a[x(t)]$ that a trajectory $x(t)$ crosses the threshold a in the time interval $[0,\infty)$ is, by definition,

$$N_a[x(t)] = \int_0^\infty dt|\dot{x}(t)|\delta[x(t)-a]. \tag{2.1}$$

The overdot denotes differentiation with respect to time and δ is the Dirac delta function. If $x(t)$ is a stochastic process, the probability of finding a trajectory that crosses the threshold a altogether N times is given by

$$p_a(N) = \langle \delta_{N_a[x(t)],N} \rangle. \tag{2.2}$$

The angular brackets denote an average over the process and δ_{ij} is the Kronecker delta function. All moments of the distribution $p_a(N)$ may be generated from the characteristic function

$$\theta_a(k) = \sum_{N=0}^{\infty} e^{ikN} p_a(N) = \left\langle \exp\left(ik \int_0^\infty dt|\dot{x}(t)|\delta[x(t)-a] \right) \right\rangle , \tag{2.3}$$

where the second equality on the right-hand side follows from Eqs. (2.1) and (2.2).

We are specifically interested in the number of recrossings of the threshold a. Let $p_t(x,\dot{x};a)$ denote the joint probability density that the particle initiated at a at time $t=0$ is found at time t at x with associated velocity $\dot{x}$. By definition, this probability density takes the form

$$p_t(x,\dot{x};a) = \frac{\langle \delta[x-x(t)]\delta[\dot{x}-\dot{x}(t)]\delta[a-x(0)] \rangle}{\langle \delta[a-x(0)] \rangle}. \tag{2.4}$$

The average number of recrossings of the threshold a is obtained by taking the first derivative of the characteristic function Eq. (2.3) with respect to k, at $k=0$. This gives [13]

$$\langle N_a \rangle = \int_0^\infty dt \int_{-\infty}^\infty dv|v|p_t(a,v;a). \tag{2.5}$$

This will be the working expression for the rest of this paper. The variable x will be either a coordinate q or an energy E of the system and the variable v will be the associated time derivative.

For the sake of completeness, we note that higher moments of the distribution may be obtained in a similar fashion. Specifically, the nth moment of the distribution may be written as

$$\langle N_a^n \rangle = \int_0^\infty dt_1 \cdots \int_0^\infty dt_n \int_{-\infty}^\infty dv_1 \cdots \int_{-\infty}^\infty dv_n |v_1| \cdots \times |v_n| p_{t_1,\ldots,t_n}[(a,v_1),\ldots,(a,v_n);a] , \tag{2.6}$$

where $p_{t_1,\ldots,t_n}[(a,v_1),\ldots,(a,v_n);a]$ is the joint probability distribution for a trajectory initiated at a to be at a, v_k at time t_k for $k=1,\ldots,n$.

Although the definitions are straightforward enough, there is a slight conceptual problem. Consider the activated rate process with Ohmic friction in the strong damping limit. In this case, the path of a given trajectory is continuous, but nowhere differentiable so that $\dot{x}$ is seemingly not well defined. We will circumvent this problem by evaluating all averages using a finite damping strength and considering the strong damping limit only at the end.

B. A statistical estimate of the rate

The average number of recrossings of a dividing surface gives an indication of the extent of validity of the TST estimate for the rate, but is insufficient for a precise evaluation. One must either obtain higher moments of the distribution, a nontrivial exercise, or one can resort to some simple statistical assumption.

We will adapt the unified statistical theory of Miller

[14–16] to the dissipative dynamics. To do so, we assume that on either side of the dividing surface, labeled c, there exist two additional surfaces, to the left and right of c, labeled l and r, respectively. These additional surfaces will have the property that any trajectory crossing them in the direction away from the central surface c will not recross the central surface. Furthermore, we will assume that the probability p that a trajectory leaving c towards the ith surface will immediately exit through surface i, for $i = l, r$, is the same. In other words, the dynamics with respect to the dividing surface c is determined locally and is symmetric with respect to either direction.

These assumptions are valid as long as one can assume that the fate of the trajectory is determined once its energy has changed by $\sim k_B T$ after crossing the dividing surface. A central assumption in any analytical theory of activated rate processes is that the barrier height is large with respect to $k_B T$ [2]. This implies that indeed the trapping is determined locally with respect to the dividing surface. Although the neighborhood on either side of the central surface c may be somewhat different, the usual smoothness of the potential ensures that such a difference will be small and so may be ignored.

At this point it becomes straightforward to adapt the unified statistical theory to our problem. We denote the total flux leaving the central dividing surface in either direction as $2F_c$, where $2F_c$ is the unidirectional flux estimated using the standard TST formula. This flux may be further subdivided such that

$$F_c = \sum_{N=0}^{\infty} F_c^N \ , \tag{2.7}$$

where F_c^N is the unidirectional flux that leaves the dividing surface and recrosses it N times before getting trapped at either the l or r surface. By definition, the average number of recrossings as defined in Sec. II A is

$$\langle N_c \rangle = \frac{1}{F_c} \sum_{N=1}^{\infty} N F_c^N . \tag{2.8}$$

Similarly one may subdivide the unidirectional flux F_i, $i = l, r$, that reaches c, leaving either l or r in the direction of the central surface c such that

$$F_i = \sum_{N=1}^{\infty} F_i^N , \quad i = l, r \tag{2.9}$$

where F_i^N is the flux leaving the surface $i = l, r$ in the direction of c, crosses the surface c altogether N times, and then reexits through either l or r. The assumed symmetry of the dynamics implies that $F_l^N = F_r^N$ for any N.

There is a clear relation between the distribution F_c^N and F_i^N, $i = r, l$:

$$2F_c^N = \sum_{M=N+1}^{\infty} (F_l^M + F_r^M) = 2 \sum_{M=N+1}^{\infty} F_l^M . \tag{2.10}$$

This relation is obtained by noting that any trajectory initiated on either the left or the right that crosses c, say, M times, contributes equal fluxes to all F_c^N for all $N < M$. The second equality on the right-hand side follows from the symmetry.

It now becomes evident that the flux F_c is related to the average number of times that trajectories initiated on either l or r recross the central surface c [15]:

$$\begin{aligned} \langle N_i \rangle &= \frac{1}{F_i} \sum_{N=1}^{\infty} N F_i^N = \frac{1}{F_i} \sum_{M=1}^{\infty} \sum_{N=M}^{\infty} F_i^N \\ &= \frac{1}{F_i} \sum_{M=0}^{\infty} F_c^M = \frac{F_c}{F_i}, \quad i = l, r \end{aligned} \tag{2.11}$$

where explicit use has been made of Eq. (2.10). Similarly one finds that the average number of recrossings $\langle N_c \rangle$ is related to the second moment of the average number of recrossings of trajectories initiated on either l or r [16]:

$$\langle N_c \rangle = \frac{\langle \frac{1}{2} N_i (N_i - 1) \rangle}{\langle N_i \rangle}, \quad i = l, r. \tag{2.12}$$

Our purpose is to obtain the net reactive flux through the central dividing surface. Clearly, only trajectories emanating from the left or the right that cross c an odd number of times are reactive. Thus the probability for reaction κ is

$$\kappa = \frac{1}{F_c} \sum_{N=0}^{\infty} F_i^{2N+1}, \quad i = l, r. \tag{2.13}$$

The statistical assumption is that any trajectory initiated on the surface c in the direction of surface i has a probability p of immediately exiting through i for both the left and right surfaces. It is a matter of straightforward algebra to see that the probability p_i^N of exiting through i after N crossings of c is

$$p_i^N = \frac{F_i^N}{F_i} = p(1-p)^{N-1}, \quad i = r, l. \tag{2.14}$$

One therefore finds that

$$\langle N_i \rangle = \frac{1}{p}, \quad i = l, r \tag{2.15}$$

$$\kappa = \frac{1}{p(2-p)}, \tag{2.16}$$

$$\langle N_c \rangle = \frac{1-p}{p}. \tag{2.17}$$

The last two equations give us the central result of this subsection. We can now express the correction to the TST result in terms of the average number of recrossings as

$$\kappa = \frac{1}{2\langle N_c \rangle + 1}. \tag{2.18}$$

This result has a very reasonable structure. As $\langle N_c \rangle \to \infty$ the probability of exiting through either the left or the right is the same and the TST expression must be modified by the average number of recrossings and a factor of $\frac{1}{2}$ reflecting the equal probability of exiting through the

left or the right. On the other hand, if $\langle N_c \rangle = 0$, then the TST is exact and the transmission factor κ is in fact unity.

III. RECROSSINGS AND THE PARABOLIC BARRIER

A. Preliminaries

The generalized Langevin equation (GLE) for a one-dimensional system has the form

$$\ddot{q} + \frac{dV(q)}{dq} + \int^t dt' \gamma(t-t')\dot{q}(t') = \xi(t). \tag{3.1}$$

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 (3.1) is equivalent to the dynamics of the system bath Hamiltonian [9,17]

$$H = \frac{p_q^2}{2} + V(q) + \sum_j \frac{1}{2}\left[p_{x_j}^2 + \left(\omega_j x_j - \frac{c_j q}{\omega_j}\right)^2\right], \tag{3.2}$$

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 an 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 (3.1), with the identification that

$$\gamma(t) = \sum_j \frac{c_j^2}{\omega_j^2}\cos(\omega_j t). \tag{3.3}$$

The transition state theory uses the flux over population expression for the rate. The flux is the equilibrium unidirectional flux through the dividing surface and the population is the equilibrium population of reactants [18–20]:

$$\Gamma = \frac{\int dp_q dq \prod_j dp_{x_j} dx_j \delta(f)(\mathbf{p}\cdot\nabla f)\theta(\mathbf{p}\cdot\nabla f)e^{-\beta H}}{\int dp_q dq \prod_j dp_{x_j} dx_j \theta(-f)e^{-\beta H}}. \tag{3.4}$$

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 [21].

The standard choice for the dividing surface 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 (3.4) is known as the one-dimensional TST result

$$\Gamma_{1D} = (2\pi\beta)^{-\frac{1}{2}} \frac{e^{-\beta V(0)}}{\int dq \theta(-q) e^{-\beta V(q)}} \simeq \frac{\omega_a}{2\pi} e^{-\beta V^\ddagger}, \tag{3.5}$$

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

The Kramers-Grote-Hynes expression for the rate in the spatial diffusion limited regime may be derived from the TST formulation by noting that for a purely parabolic barrier

$$V_{PB}(q) = V(0) - \frac{1}{2}\omega^{\ddagger 2} q^2, \tag{3.6}$$

the Hamiltonian (3.2) is a bilinear form which may be diagonalized using a normal mode transformation [8]. In the diagonal form, one finds one unstable mode, denoted ρ, with associated momentum p_ρ, and barrier frequency $\lambda^\ddagger$. The N stable normal modes have coordinates and momenta y_j and p_{y_j}, respectively, and frequencies λ_j. The normal mode form of the Hamiltonian for the parabolic barrier is thus

$$H_{PB} = \frac{1}{2}(p_\rho^2 - \lambda^{\ddagger 2}\rho^2 + \sum_j [p_{y_j}^2 + \lambda_j^2 y_j^2]). \tag{3.7}$$

The normal mode barrier frequency $\lambda^\ddagger$ is the solution of the equation

$$\omega^{\ddagger 2} = \lambda^{\ddagger 2}\left(1 + \frac{\hat{\gamma}(\lambda^\ddagger)}{\lambda^\ddagger}\right), \tag{3.8}$$

where $\hat{\gamma}(s)$ denotes the Laplace transform of the friction kernel with frequency s.

The rate may be obtained by choosing the dividing surface $f = \rho = 0$. The resulting expression is [1,3,8]

$$\Gamma = \frac{\lambda^\ddagger}{\omega^\ddagger}\Gamma_{1D}. \tag{3.9}$$

The normal mode coordinates are an orthogonal transformation of the original system bath coordinates q, x_j, $j = 1, ..., N$, appearing in the equivalent Hamiltonian (3.2). The transformation matrix is denoted as $\mathbf{U}$ such that the system coordinate q may be expressed in terms of the normal modes as

$$q = u_{00}\rho + \sum_j u_{j0} y_j. \tag{3.10}$$

The matrix element u_{00} is given in terms of the Laplace transform of the time dependent friction as [10]

$$u_{00}^2 = \left[1 + \frac{1}{2}\left(\frac{\hat{\gamma}(\lambda_\infty^\ddagger)}{\lambda_\infty^\ddagger} + \left.\frac{\partial\hat{\gamma}(s)}{\partial s}\right|_{s=\lambda_\infty^\ddagger}\right)\right]^{-1}. \tag{3.11}$$

It is also convenient to define a normal mode friction function [10] as

$$K(t) = \sum_j u_{j0}^2 \cos(\lambda_j t). \tag{3.12}$$

This friction function is related to the velocity autocorrelation function of the parabolic barrier

$$\langle p_q(t) p_q \rangle = \frac{1}{\beta}[u_{00}^2 \cosh(\lambda^\ddagger t) + K(t)]. \tag{3.13}$$

The Laplace transform of the velocity autocorrelation function is

$$\int_0^\infty dt e^{-st} \langle p_q(t) p_q(0) \rangle = \frac{1}{\beta} \frac{s}{-\omega^{\ddagger 2} + s^2 + s\hat{\gamma}(s)}. \tag{3.14}$$

The combination of Eqs. (3.13) and (3.14) shows that the normal mode friction function is well defined in the continuum limit in terms of Laplace transforms of the time dependent friction. Finally, it is useful to define a collective bath mode frequency Ω^2 as

$$\Omega^{-2} \equiv \frac{\sum_j \frac{u_{j0}^2}{\lambda_j^2}}{1 - u_{00}^2} = \frac{1}{1 - u_{00}^2} \left(\frac{u_{00}^2}{\lambda^{\ddagger 2}} - \frac{1}{\omega^{\ddagger 2}} \right) , \tag{3.15}$$

where the second equality on the right-hand side follows from properties of the normal mode transformation; see, for example, [11].

B. The average number of recrossings

To estimate the average number of recrossings at the barrier top of the parabolic barrier potential ($q = 0$) one must know the joint probability distribution $p_t(q, v; 0)$ [cf. Eq. (2.4)] for the particle to be at the barrier and have velocity v at the time t. First we note that the denominator of Eq. (2.4) is, in our case,

$$\langle \delta[q(0)] \rangle = 1. \tag{3.16}$$

The averaging is over the thermal distribution of the initial values of the Hamiltonian. The result is easily obtained by using the Hamiltonian in the original system bath coordinates as in Eq. (3.2).

To obtain the numerator of Eq. (2.4) one must in principle know the time dependence of the coordinate q. A straightforward way of obtaining the distribution is to use the trivial time dependence of the normal modes of the Hamiltonian. The separability of the parabolic barrier Hamiltonian in the normal modes implies that

$$\rho(t) = \rho(0) \cosh(\lambda^\ddagger t) + \frac{p_\rho(0)}{\lambda^\ddagger} \sinh(\lambda^\ddagger t). \tag{3.17}$$

Similarly the time dependence of each of the stable modes is

$$y_j(t) = y_j(0) \cos(\lambda_j t) + \frac{p_{y_j}}{\lambda_j} \sin(\lambda_j t), \qquad j = 1, ..., N. \tag{3.18}$$

In this case, it is convenient to use the normal mode form of the Hamiltonian while performing the averaging. The δ functions are easily handled by using their Fourier expansion, for example,

$$\delta[q - q(t)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\kappa e^{i\kappa\{u_{00}[\rho - \rho(t)] + \sum_j u_{j0}[y_j - y_j(t)]\}}. \tag{3.19}$$

The resulting integrals are Gaussian integrals. After some straightforward algebra one finds

$$p_t(q, v; 0) = \frac{\beta}{2\pi\sqrt{A}} e^{\frac{-\beta}{2A}(v\dot{L} - q)^2} e^{-\frac{\beta}{2}[v^2 - \omega^{\ddagger 2} q^2]}. \tag{3.20}$$

Here we have used the following notation:

$$L \equiv \sum_j \frac{u_{j0}^2}{\lambda_j^2} \cos(\lambda_j t) - \frac{u_{00}^2}{\lambda^{\ddagger 2}} \cosh(\lambda^\ddagger t), \tag{3.21}$$

$$A \equiv \omega^{\ddagger 2} L^2 - \dot{L}^2 - \frac{1}{\omega^{\ddagger 2}}. \tag{3.22}$$

The function $L(t)$ may be obtained from the velocity autocorrelation function [cf. Eq. (3.12)] by a double integration over time. A specific example, using Ohmic friction, will be given in the following subsection.

The average number of recrossings is now obtained by integrating the distribution over the velocity and the time [cf. Eq. (2.5)]

$$\langle N_{q=0} \rangle_{\mathrm{PB}} = \frac{1}{\pi} \int_0^\infty dt \frac{\sqrt{A(t)}}{A(t) + \dot{L}(t)^2}. \tag{3.23}$$

This is the central result of this section. For any time dependent friction, obtaining the average number of recrossings for the parabolic barrier involves an integration over a known time dependent function. We have used here the Hamiltonian formulation to derive the average. One may also derive the same result directly from the GLE as sketched in Appendix A.

C. Recrossing and Ohmic friction

Ohmic friction is instantaneous in time:

$$\gamma(t) = 2\gamma\delta(t) , \tag{3.24}$$

where γ is the damping constant. Kramers's equation [Eq. (3.8)] is quadratic with two solutions. The positive solution gives the unstable mode barrier frequency

$$\lambda^\ddagger = \left(\frac{\gamma^2}{4} + \omega^{\ddagger 2} \right)^{\frac{1}{2}} - \frac{\gamma}{2}. \tag{3.25}$$

The modulus of the negative solution is

$$\lambda_+ = \left(\frac{\gamma^2}{4} + \omega^{\ddagger 2} \right)^{\frac{1}{2}} + \frac{\gamma}{2} \tag{3.26}$$

and appears also in the normal mode friction function $K(t)$; cf. Eq. (3.12).

The projection matrix element u_{00} [cf. Eq. (3.11)] is

$$u_{00}^2 = \left(1 + \frac{\gamma}{2\lambda^\ddagger}\right)^{-1} = \frac{2\lambda^\ddagger}{\lambda_+ + \lambda^\ddagger} \tag{3.27}$$

and the collective bath mode frequency Eq. (3.15) turns out to be simply

$$\Omega^2 = \omega^{\ddagger 2}. \tag{3.28}$$

The Ohmic normal mode friction function is found to be [22]

$$K(t) = \frac{u_{00}^2}{2\lambda^\ddagger}(\lambda_+ e^{-\lambda_+|t|} - \lambda^\ddagger e^{-\lambda^\ddagger|t|}). \tag{3.29}$$

One then finds that the function $L(t)$ [cf. (Eq. 3.21)] is

$$L(t) = \frac{1}{\lambda^\ddagger + \lambda_+}\left(\frac{1}{\lambda^\ddagger}e^{\lambda^\ddagger t} + \frac{1}{\lambda_+}e^{-\lambda_+ t}\right). \tag{3.30}$$

We were not able to integrate Eq. (3.23) analytically for all values of the damping strength. Instead, in Table I we provide results from numerical integration for the average number of recrossings as well as for the rate as predicted by the statistical theory expression Eq. (2.18). One notes that for the whole friction range, the error in the statistical theory is at most 50% even though the Kramers prefactor itself varies by orders of magnitude.

One may understand this behavior better by analyzing the average number of recrossings in the strong and weak damping limits. In the strong damping limit defined by $\frac{\gamma}{\omega^\ddagger} \gg 1$ the function $L(t)$ is well approximated as $L(t) \sim \frac{1}{\omega^{\ddagger 2}} e^{\frac{\omega^{\ddagger 2}}{\gamma}t}$ and the average number of recrossings is

$$\langle N_{q=0}\rangle_{\mathrm{PB},\frac{\gamma}{\omega^\ddagger}\gg 1} = \frac{1}{2}\frac{\gamma}{\omega^\ddagger}. \tag{3.31}$$

One then finds that $\kappa \to \frac{\omega^\ddagger}{\gamma}$, which is the exact answer.

The situation is somewhat different when the damping becomes weak. In this case one can show that

$$\langle N_{q=0}\rangle_{\mathrm{PB},\frac{\gamma}{\omega^\ddagger}\ll 1} = \left(\frac{\gamma}{\omega^\ddagger}\right)^{\frac{1}{2}}\frac{2}{\pi}\int_0^1 dz \frac{(1 - z^4 + 4z^2 \ln z)^{\frac{1}{2}}}{(1-z^2)^2}$$
$$\sim 0.717\left(\frac{\gamma}{\omega^\ddagger}\right)^{\frac{1}{2}}. \tag{3.32}$$

The statistical theory for the rate in the weak damping limit has a leading order term which goes as the square root of the damping, while the exact result is linear in the damping.

This analysis shows that the statistical theory is accurate in the strong damping limit, but not so when the damping becomes weak. The central assumption of the statistical theory is that the probability of immediate exit from the dividing surface is the same for all trajectories. In the weak damping limit, this is not the case, as trajectories with a velocity which is of the order of $\sqrt{k_b T}$ and higher will immediately leave the dividing surface without returning. Only those trajectories initiated with small enough velocity will feel the frictional force and thus may recross.

One may construct a more sophisticated theory in which one first evaluates the average number of recrossings for an initial given momentum on the dividing surface, next uses the statistical theory to estimate a momentum dependent transmission coefficient, and then one must average over all initial momenta. This option will be discussed further in Sec. V. We note though that in the strong damping limit, the friction is so high that the statistical assumption is valid for a large enough range of momenta and one obtains the correct rate.

TABLE I. Average number of recrossings and statistical rates for Ohmic friction and a parabolic barrier.

$\frac{\gamma}{\omega^\ddagger}$	$\langle N_{q=0}\rangle_{\mathrm{PB}}$	κ	$\frac{\lambda^\ddagger}{\omega^\ddagger}$
0.02	0.102	0.831	0.990
0.2	0.328	0.604	0.905
1.0	0.810	0.382	0.618
2.0	1.295	0.279	0.414
10	5.118	0.0890	0.0990
20	9.947	0.0479	0.0499
200	98.87	0.00498	0.00499

IV. RECROSSINGS IN THE ENERGY DIFFUSION LIMIT

A. TST with an energy dependent dividing surface

In the energy diffusion limited regime, the natural candidate for a dividing surface is the energy needed to cross the barrier. The TST expression based on such a surface was derived in Ref. [6]; here we review briefly the relevant results.

To construct a theory valid also for memory friction it is advisable to construct the energy surface in the normal mode representation. The potential $V(q)$ may always be rewritten as

$$V(q) = -\frac{1}{2}\omega^{\ddagger 2}q^2 + V_1(q)\ , \tag{4.1}$$

thus defining the nonlinear part of the potential $V_1(q)$. It follows that the full Hamiltonian may be written as

$$H = V_1(u_{00}\rho + u_I\sigma) + H_{\mathrm{PB}}\ , \tag{4.2}$$

where σ and u_I are defined as

$$u_I\sigma \equiv \sum_j u_{j0}y_j, \qquad u_I^2 \equiv 1 - u_{00}^2 \tag{4.3}$$

and H_{PB} has been defined in Eq. (3.7). The weak damping limit is obtained when $u_I^2 \ll 1$.

The dividing surface must have the property that any reactive trajectory must cross it before escaping. A dividing surface f that has this property is the one-dimensional Hamiltonian governing the motion of the unstable normal mode in the limit of weak coupling:

$$f(\rho, p_\rho) \equiv E_\rho\theta(-\rho) = [\tfrac{1}{2}(p_\rho^2 - \lambda^{\ddagger 2}\rho^2) + V_1(u_{00}\rho)]\theta(-\rho). \tag{4.4}$$

A reaction may occur only if $f > 0$. If $f < 0$, the particle cannot cross the dividing configuration $\rho = 0$. The unit step function limits the dividing surface to the reactants region taken to be at negative ρ.

Inserting this expression into the TST rate expression [cf. Eq. (3.4)] leads to the following estimate for the rate:

$$\Gamma = \Gamma_{1D}\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}P_{ED} , \tag{4.5}$$

where the energy diffusion transmission factor P_{ED} is found to be

$$P_{ED} = \frac{u_{00}\beta^{\frac{3}{2}}\Omega}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\sigma\int_{-\infty}^{0}d\rho|V_1'(u_{00}\rho+u_I\sigma)-V_1'(u_{00}\rho)|e^{-\beta[\frac{1}{2}\Omega^2\sigma^2+V_1(u_{00}\rho+u_I\sigma)-V_1(u_{00}\rho)]} \times\theta[\tfrac{1}{2}\lambda^{\ddagger 2}\rho^2 - V_1(u_{00}\rho)] , \tag{4.6}$$

where $V_1'(q) \equiv \frac{dV_1(q)}{dq}$ and the frequency Ω has been defined in Eq. (3.15).

In the weak damping limit, this expression may be further simplified. The leading term in an expansion in the small parameter u_I is

$$P_{ED} \simeq u_I\left(\frac{2\beta}{\pi\Omega^2}\right)^{\frac{1}{2}}\int_{-\infty}^{0}d\rho|V_1''(u_{00}\rho)| \times\theta[\tfrac{1}{2}\lambda^{\ddagger 2}\rho^2 - V_1(u_{00}\rho)]. \tag{4.7}$$

The linear dependence of this term on u_I implies that it is substantially larger than the exact result, which goes as u_I^2. On the other hand, the result does go to zero in the limit of no coupling and is finite at any finite value of the damping. The purpose of this section is to demonstrate that the overestimate of the rate inherent in this expression is a result of recrossing and that a suitable estimate of the recrossing dynamics allows one to recover the correct result.

B. Recrossings in the energy diffusion limit

Without loss of generality, we will assume that the barrier height of the potential is taken as zero on the energy scale. Since the dividing surface is an energy surface, the stochastic variable $x(t)$ becomes, in our case, the energy $E_\rho(t)$ defined as

$$E_\rho(t) = \frac{1}{2}[p_\rho(t)^2 - \lambda^{\ddagger 2}\rho^2(t)] + V_1[u_{00}\rho(t)] \tag{4.8}$$

and the probability distribution function [cf. Eq. (2.4)] is

$$p_t(0,\dot{E}_\rho;0) = \frac{\langle\delta[E_\rho(t)]\delta[\dot{E}_\rho(t)-\dot{E}_\rho]\delta[E_\rho(0)]\rangle}{\langle\delta[E_\rho(0)]\rangle}. \tag{4.9}$$

To explicitly evaluate the distribution function it is necessary to know the time dependence of the energy $E_\rho(t)$ in the unstable normal mode. In general this is a daunting task; however, in the weak coupling limit, one may use the same perturbation theory as in the PGH theory [10]. The zeroth order equation of motion for the unstable normal mode is

$$\ddot{\rho} - \lambda^{\ddagger 2}\rho = -u_{00}V_1'(u_{00}\rho) \equiv F(t), \tag{4.10}$$

while the first order equation of motion for any of the stable modes is

$$\ddot{y}_j + \lambda_j^2 y_j^2 = -u_{j0}V_1'(u_{00}\rho) = \frac{u_{j0}}{u_{00}}F(t). \tag{4.11}$$

In other words, within the context of first order perturbation theory, the equations of motion of the stable normal modes are identical to forced oscillator equations in which the forcing function $F(t)$ as defined in Eq. (4.10) is determined by the zeroth order equation of motion for the unstable normal mode.

The total energy of the bath at any time t is defined as

$$E_B(t) = \frac{1}{2}\sum_j[p_{y_j}^2(t) + \lambda_j^2 y_j^2(t)]. \tag{4.12}$$

The energy gained (or lost) by the bath at any time t relative to its initial energy can be decomposed into a systematic energy loss $\Delta(t)$ and a Gaussian random energy loss δ_t [10]:

$$E_B(t) - E_B(0) = \Delta(t) + \delta_t , \tag{4.13}$$

$$\Delta(t) = \frac{1}{2u_{00}^2}\int_0^t\int_0^t dt'dt''F(t')K(t'-t'')F(t'') , \tag{4.14}$$

$$\delta_t = \frac{1}{u_{00}}\sum_j u_{j0}[p_{y_j}(0)F_{jc}(t) - \lambda_j y_j(0)F_{js}(t)] , \tag{4.15}$$

$$F_{jc}(t) \equiv \int_0^t dt'F(t')\cos(\lambda_j t'), \qquad F_{js}(t) \equiv \int_0^t dt'F(t')\sin(\lambda_j t'). \tag{4.16}$$

It is also useful to note the identity

$$\Delta(t) = \frac{1}{2u_{00}^2} \sum_j u_{j0}^2 [F_{jc}^2(t) + F_{js}^2(t)]. \tag{4.17}$$

The energy gained by the bath in the time interval $[0, t]$ is also the energy lost by the unstable mode so that

$$E_\rho(t) - E_\rho(0) = -[\Delta(t) + \delta(t)]. \tag{4.18}$$

At this point all the necessary ingredients are available for evaluating the probability distribution function $p_t(0, \dot{E}_\rho; 0)$. As usual, the Dirac δ functions are handled through their Fourier representations. The averaging is over the zeroth order Hamiltonian, which is a Gaussian with respect to the bath variables. The linearity of the random part of the energy loss $\delta(t)$ with respect to the bath variables ensures that one will remain only with Gaussian integrals.

After integration over all the bath variables and Dirac δ functions one obtains the following result:

$$p_t(0, \dot{E}_\rho; 0) = \frac{\beta}{2^{3/2}\pi} \frac{\int_{-\infty}^{\infty} d\rho \int_{-\infty}^{\infty} dp_\rho \delta[E_\rho(0)] B(t)^{-\frac{1}{2}} e^{-\frac{1}{2}\beta\Delta(t)\{\frac{1}{2} + B(t)^{-1}[\dot{E}_\rho + \frac{1}{2}\dot{\Delta}(t)]^2\}}}{\int_{-\infty}^{\infty} d\rho \int_{-\infty}^{\infty} dp_\rho \delta[E_\rho(0)]} \tag{4.19}$$

where the time dependent function $B(t)$ is found to be

$$\begin{aligned} B(t) &= \frac{u_I^2}{u_{00}^2}\Delta(t)F^2(t) - \frac{1}{2}\dot{\Delta}(t)^2 \\ &= \frac{1}{2u_{00}^4}\int_0^t dt' \int_0^t dt'' F(t)F(t')[u_I^2 K(t'-t'') \\ &\quad - K(t-t')K(t-t'')]F(t'')F(t). \end{aligned} \tag{4.20}$$

To obtain the average number of recrossings one must still integrate over the phase space of the unstable mode, the time, and the rate of change of the energy ($\dot{E}_\rho$); cf. Eq. (2.5). The integration over the energy rate may be done analytically, leading to an error function whose argument in the weak damping limit is small, of the order of u_I. Keeping only the lowest order term gives the substantially simplified result

$$\begin{aligned} &2\int_0^\infty d\dot{E}_\rho \dot{E}_\rho p_t(0, \dot{E}_\rho; 0) \\ &\simeq \frac{1}{\sqrt{2\pi}} \frac{\int_{-\infty}^{\infty} d\rho \int_{-\infty}^{\infty} dp_\rho \delta[E_\rho(0)] \frac{B(t)^{\frac{1}{2}}}{\Delta(t)} e^{-\frac{1}{4}\beta\Delta(t)}}{\int_{-\infty}^{\infty} d\rho \int_{-\infty}^{\infty} dp_\rho \delta[E_\rho(0)]}. \end{aligned} \tag{4.21}$$

The remaining integrations over time and the phase space of the unstable mode cannot in general be evaluated analytically. To make further progress one must resort to further approximation. At very short times, the energy loss $\Delta(t) \sim t^2$. However, the short time contribution to the integral is negligible, the exponent decays only on a time scale which is inversely proportional to the energy loss, and in the weak coupling limit this is a long time compared to the inverse well frequency.

By considering motion in the well as harmonic, one expects that except for short times, the energy loss $\Delta(t)$ will increase approximately linearly with time so that

$$\Delta(t) \sim \langle \dot{\Delta} \rangle_{E_\rho(0)} t, \tag{4.22}$$

$$\dot{\Delta}(t) \sim \langle \dot{\Delta} \rangle_{E_\rho(0)}. \tag{4.23}$$

The angular brackets denote an average over the initial conditions of the unstable mode at the energy of the dividing surface. This average is identical also to a time average over one period of the motion of the unstable normal mode so the averages themselves become time independent.

The only remaining problematic term is the square of the forcing function $F^2(t)$, which appears in the time dependent function $B(t)$; cf. Eq. (4.20). Although this term will in general oscillate as a function of the initial conditions, it will not grow with time. As a zeroth order approximation we will replace it too by its phase space average turning it into a constant in time

$$F(t)^2 \sim \langle F^2 \rangle_{E_\rho(0)}. \tag{4.24}$$

At this point we note that the function $B(t)$ takes the form

$$B(t) \sim \langle \dot{\Delta} \rangle \left[\frac{u_I^2}{u_{00}^2} \langle F^2 \rangle t - \frac{1}{2}\langle \dot{\Delta} \rangle \right], \tag{4.25}$$

where we have suppressed the subscript $E_\rho(0)$ to simplify the notation. While the first term on the right-hand side of Eq. (4.25) grows without bound in time, the second term stays constant and is also of the order of u_I^2. We will ignore it since in the weak coupling limit the main contribution to the recrossing does not come from short times. A more careful analysis of the short time behavior of $B(t)$ and the energy loss $\Delta(t)$ is presented in Appendix B.

With these approximations at hand, the remaining time integration is a simple Gaussian integral and one finds that the average number of recrossings of the energy surface in the weak coupling limit is

$$\langle N_E \rangle = \frac{2u_I}{u_{00}\langle \dot{\Delta} \rangle} \left(\frac{\langle F^2 \rangle}{2\pi\beta} \right)^{\frac{1}{2}}. \tag{4.26}$$

This is the main result of this section. One notes that the rate of energy loss goes as u_I^2, so that the average number of recrossing diverges as $\frac{1}{u_I}$.

The rate in the energy diffusion limit is now obtained by combining the TST result [Eq. (4.6)] with the statistical correction [Eq. (2.18)] to find

$$\Gamma = \Gamma_{1D} \frac{\lambda^\ddagger}{\omega^\ddagger} \Upsilon \,, \tag{4.27}$$

$$\Upsilon = 2\beta \langle \dot{\Delta} \rangle \left(\frac{u_{00}^2}{\Omega^2 \langle F^2 \rangle} \right)^{\frac{1}{2}} \times \int_{-\infty}^{0} d\rho |V_1''(u_{00}\rho)| \theta[\tfrac{1}{2}\lambda^{\ddagger 2}\rho^2 - V_1(u_{00}\rho)]. \tag{4.28}$$

The depopulation factor Υ is now linear in the rate of energy loss $\dot{\Delta}$, as it should be.

C. An example: A cubic potential with Ohmic friction

Since the rate expression derived in the previous subsection does not "look" like the usual known result for the energy diffusion limited rate, it is instructive to consider a concrete case and show that it is essentially identical. Consider the case of a cubic potential

$$V(q) = -\frac{1}{2}\omega^{\ddagger 2} q^2 \left(1 + \frac{q}{q_0}\right). \tag{4.29}$$

The barrier height is

$$V^\ddagger = \frac{2}{27}\omega^{\ddagger 2} q_0^2. \tag{4.30}$$

For Ohmic friction, the Kramers depopulation factor in the weak damping limit ($\frac{\gamma}{\omega^\ddagger} \ll 1$) is

$$\Upsilon_{\text{Kramers}} = \frac{36}{5}\frac{\gamma}{\omega^\ddagger}\beta V^\ddagger. \tag{4.31}$$

The TST transmission factor [cf. Eq. (4.6)] in this same limit is

$$P_{\text{ED}} = \frac{3}{4}\left(\frac{15}{2\pi}\right)^{\frac{1}{2}} \Upsilon_{\text{Kramers}}^{\frac{1}{2}}. \tag{4.32}$$

To obtain an estimate for the average number of recrossings, we make the simplifying assumption that the potential in the well region may be approximated as a harmonic potential with the same frequency as the cubic oscillator. With this assumption, the rate of energy loss is $\dot{\Delta} \simeq \gamma V^\ddagger$. The squared average of the force is $\langle F^2 \rangle \simeq 81 \frac{V^{\ddagger 2}}{q_0^2}$ and the mean number of crossings turns out to be

$$\langle N_E \rangle \sim \frac{6}{\Upsilon_{\text{Kramers}}^{\frac{1}{2}}} \left(\frac{6}{5\pi}\right)^{\frac{1}{2}}. \tag{4.33}$$

It follows that the depopulation factor based on the statistical theory and the mean number of crossing is

$$\Upsilon \sim \tfrac{5}{32}\Upsilon_{\text{Kramers}}. \tag{4.34}$$

We thus find that a TST with an energy dependent dividing surface in conjunction with a correction factor based on the mean number of recrossings does give (up to a factor 5/32) the correct rate in the weak damping limit. Given the crudity of some of the approximations used, this is a very reasonable result.

V. DISCUSSION

The importance of recrossings of a dividing surface was always well appreciated by anyone who considered the theory of activated rate processes. In this paper we have demonstrated that one can actually evaluate the number of recrossings and use them to obtain good estimates for rate constants. In the strong damping limit, we find the exact answer for the rate using a combination of the TST, a statistical theory, and the mean number of recrossings. Similarly in the energy diffusion limit, apart from a numerical factor of order unity, we obtain the correct rate.

We believe though that the present framework can be substantially improved upon. As already noted in Sec. III, there really is no need to assume that the mean number of recrossings is the same for each initial condition. In the spatial diffusion limit, one understands that the number of crossings will be reduced substantially as one increases the initial momentum. Similarly, in the energy diffusion limited regime one understands that if one initiates the particle close to the barrier with momentum in the direction of the barrier, the number of crossings will be quite small as the particle will probably escape immediately. If though one starts it at the same point but with momentum towards the direction of the well, the number of recrossings will be large. Numerically, there really is no hinderance in evaluating the mean number of recrossings as a function of the initial conditions and only then averaging.

Especially for the energy diffusion limited regime, we have made no attempt to optimize the energy dependent dividing surface. In the weak damping limit one would expect that the surface used is reasonable. But as the damping increases, one understands that particles finding themselves at the turning point opposite the barrier will need more energy to escape than particles in the region of the barrier. One could change the structure of the dividing surface such that it is initially just the energy surface, but changes gradually to become the usual dividing surface in the spatial diffusion limit. In this way one would construct a turnover theory whose structure is quite different from the standard (PGH) turnover theory.

All this is interesting not only from an academic point of view. One of the failings of the PGH theory is that it does not treat accurately cases with very long memory friction. The PGH theory estimates the rate by assuming that only the dynamics at the barrier energy is important. If memory friction is long compared to the typical oscillation period in the well, this assumption breaks down. In the present approach, there is no difficulty in

lowering the energy of the energy dependent dividing surface, searching for the true bottleneck, and then estimating the effects of recrossings.

ACKNOWLEDGMENTS

We gratefully acknowledge Dr. Alexander Starobinetz for his comments on this work and the support of this research by the Julius Baer Stiftung.

APPENDIX A: AVERAGE NUMBER OF RECROSSINGS FROM THE GLE

In this appendix we rederive the expression (3.23) for the average number of recrossings for a parabolic barrier without using the equivalent Hamiltonian formulation of the GLE. When trajectories are started precisely on top of the barrier with a velocity chosen from a Boltzmann distribution, the joint probability density of the coordinate and the momentum remains Gaussian for all times due to the linearity of the GLE and the Gaussian nature of the fluctuating forces. It therefore reads

$$p_t(q,p_q;0)=\frac{1}{2\pi\sqrt{D(t)}}\exp\left\{-\frac{\langle p_q(t)^2\rangle q^2-2\langle q(t)p_q(t)\rangle qp_q+\langle q(t)^2\rangle p_q^2}{2D(t)}\right\}, \tag{A1}$$

where

$$D(t)=\langle q(t)^2\rangle\langle p_q(t)^2\rangle-\langle q(t)p_q(t)\rangle^2 \tag{A2}$$

and $\langle q(t)^2\rangle$, $\langle p_q(t)^2\rangle$, and $\langle q(t)p_q(t)\rangle$ denote the second moments of $q(t)$ and $p_q(t)$. Inserting (A1) into Eq. (2.5) and integrating over p_q yields, for the number of barrier recrossings,

$$\langle N_0\rangle=\frac{1}{\pi}\int_0^\infty dt\frac{\sqrt{D(t)}}{\langle q(t)^2\rangle}. \tag{A3}$$

For a parabolic barrier the GLE (3.1) becomes

$$\dot{\mathbf{r}}(t)=R\mathbf{r}(t)+\int_0^t ds\Gamma(t-s)\mathbf{r}(s)+\mathbf{f}(t)\ , \tag{A4}$$

where $\mathbf{r}(t)$ denotes the vector with components $q(t)$ and $p_q(t)$, $\mathbf{f}(t)$ is another vector with components 0 and $\xi(t)$, and R and $\Gamma(t)$ are matrices describing the instantaneous rate of change and memory damping, respectively,

$$R=\begin{pmatrix}0 & 1\\ \omega^{\ddagger 2} & 0\end{pmatrix} \tag{A5}$$

and

$$\Gamma(t)=\gamma(t)\begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}. \tag{A6}$$

The formal solution of the GLE (3.1) reads, in terms of the initial condition $\mathbf{r}(0)$,

$$\mathbf{R}(t)=G(t)\mathbf{r}(0)+\int_0^t dsG(t-s)\mathbf{f}(s)\ , \tag{A7}$$

where the matrix $G(t)$ is the Green's function of the GLE satisfying

$$\dot{G}(t)=RG(t)+\int_0^t ds\Gamma(t-s)G(s) \tag{A8}$$

with the identity matrix I as the initial condition

$$G(0)=I. \tag{A9}$$

An equivalent equation of motion is obtained by means of a Laplace transform of Eq. (A8), subsequent multiplication with the Laplace transform $\hat{G}(z)$ of the Green's function and $\hat{G}(z)^{-1}$ from the left and right, respectively, and finally a Laplace backtransform. It reads

$$\dot{G}(t)=G(t)R+\int_0^t dsG(s)\Gamma(t-s). \tag{A10}$$

For the second moment of $q(t)$ one finds, with Eq. (A7),

$$\langle q(t)^2\rangle=\left\langle\left(G_{qq}(t)q+G_{qp_q}(t)p_q+\int_0^t dsG_{qp_q}(t-s)F(s)\right)^2\right\rangle \tag{A11}$$

$$=\beta^{-1}\left(G_{qp_q}(t)^2+\int_0^t dt'\int_0^t ds'G_{qp_q}(t-t')\times G_{qp_q}(t-s')\gamma(t'-s')\right)\ , \tag{A12}$$

where G_{ij} denotes the ij component of the Green's function and we used the initial conditions

$$\langle q^2\rangle=\langle qp_q\rangle=0, \tag{A13}$$

$$\langle p_q^2\rangle=\beta^{-1}, \tag{A14}$$

the fluctuation dissipation theorem, and the fact that q and p_q are uncorrelated with the fluctuating forces $\xi(s)$ at later times s.

The double integral on the right-hand side of Eq. (A12) is conveniently split into two parts with $t'<s'$ and $t'>s'$ both giving the same contribution. Hence one finds

$$\int_0^t dt' \int_0^t ds' G_{qp_q}(t-t')G_{qp_q}(t-s')\gamma(t'-s')$$

$$= 2\int_0^t dt' \int_0^{t-t'} du G_{qp_q}(t-t')G_{qp_q}(t-t'-u)\gamma(u) \ , \tag{A15}$$

where $u = t' - s'$. Using the qq and the qp_q component of Eq. (A10), the integrals in Eq. (A15) can be performed, yielding, for $\langle q(t)^2 \rangle$,

$$\langle q(t)^2 \rangle = \omega^{\ddagger -2}\beta^{-1}\left[G_{qq}(t)^2 - 1\right] . \tag{A16}$$

Similarly $\langle q(t)p_q(t) \rangle$ and $\langle p_q(t)^2 \rangle$ can also be expressed in terms of the qq component of the Green's function

$$\langle q(t)p_q(t) \rangle = \omega^{\ddagger -2}\beta^{-1}\dot{G}_{qq}(t)G_{qq}(t) \ , \tag{A17}$$

$$\langle p_q(t)^2 \rangle = \beta^{-1}\left[\omega^{\ddagger -2}\dot{G}_{qq}(t)^2 + 1\right] . \tag{A18}$$

Accordingly, $D(t)$ becomes [cf. Eq. (A3)]

$$D(t) = \omega^{\ddagger -2}\beta^{-1}\left[G_{qq}(t) - \omega^{\ddagger -2}\dot{G}_{qq}(t) - 1\right] . \tag{A19}$$

Finally, it remains to express $G_{qq}(t)$ through $L(t)$. Comparing Eqs. (3.12) and (3.13) with (3.21) one finds

$$\langle p_q(t)p_q \rangle = -\beta^{-1}\ddot{L}(t). \tag{A20}$$

With Eqs. (A7), (A13), and (A14) the momentum correlation function becomes

$$\langle p_q(t)p_q \rangle = \beta^{-1}G_{p_qp_q}(t)$$
$$= \omega^{\ddagger -2}\beta^{-1}\ddot{G}_{qq}(t) \ , \tag{A21}$$

where the qp_q component of Eq. (A8) and the qq component of Eq. (A10) were used. With the initial values $\dot{L}(0) = 0$ and $L(0) = -\omega^{\ddagger -2}$, which follow from Eqs. (3.21) and (3.15), $G_{qq}(t)$ becomes

$$G_{qq}(t) = -\omega^{\ddagger 2}L(t) \ . \tag{A22}$$

Combining Eqs. (A16), (A19), and (A22) with (A3) yields, with Eq. (3.23), the desired result.

APPENDIX B: SHORT TIMES IN THE ENERGY DIFFUSION LIMIT

The purpose of this appendix is to note that the average number of recrossings is well defined also in the energy diffusion limited regime. A cursory glance at Eq. (4.21) would suggest that since the energy loss is zero at short times, the ratio $\frac{\sqrt{B(t)}}{\Delta(t)}$ diverges at least as $\frac{1}{t}$. In fact this is not the case. An inspection of Eqs. (3.12) and (4.14) shows that at short times

$$\Delta(t) \sim \frac{u_I^2 F(0)^2}{2u_{00}^2}t^2\left[1 + t\left(\frac{\dot{F}(0)}{F(0)} + \frac{\dot{K}(0)}{2u_I^2}\right) + O(t^2)\right], \tag{B1}$$

where $\dot{F}(0) \equiv \frac{dF(t)}{dt}\big|_{t=0}$. Note that in the continuum limit, even though the friction function $K(t)$ is symmetric, its derivative $\dot{K}(0) = \frac{dK(t)}{dt}\Big|_{t=0^\dagger}$ may be finite [see, for example, the case of Ohmic friction and Eq. (3.29)].

Inserting this result into the definition of $B(t)$ [cf. Eq. (4.20)] leads to the conclusion that

$$B(t) \sim O(t^3) \ , \tag{B2}$$

so that in the short time limit, the ratio $\frac{\sqrt{B(t)}}{\Delta(t)}$ goes to $1/\sqrt{t}$ and Eq. (4.21) is well behaved.

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