Non-Markovian theory of activated rate processes. III. Bridging between the Kramers limits

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Kramers' theory of activated processes yields expressions for the steady-state escape rate in the large- and small-friction limits and for Markovian dynamics. The present work extends this theory to non-Markovian dynamics and to the whole friction range. Kramers' results are recovered in the appropriate limits.

I. INTRODUCTION

Kramers' approach to the theory of activated rate processes,[1] using a model of a Brownian particle moving in a one-dimensional potential well, has played a central role in many areas of science.[2] This approach starts from the Langevin equation

$$\ddot{x}=-\frac{1}{M}\frac{dV(x)}{dx}-\gamma\dot{x}+\frac{1}{M}R(t)\ , \tag{1.1}$$

where x is the coordinate of the particle of mass M moving in the potential $V(x)$, and where γ and R are the damping rate and the (stationary Gaussian) random force associated with the coupling to the thermal bath. γ and R are related by the fluctuation-dissipation theorem

$$\langle R(0)R(t)\rangle=2\gamma Mk_BT\delta(t),\ \ \langle R(t)\rangle=0 \tag{1.2}$$

where k_B is the Boltzmann constant and T is the temperature. The Langevin equation (1.1) is equivalent to the Fokker-Planck equation for the probability distribution $P=P(x,v,t)$

$$\frac{\partial P}{\partial t}=\frac{1}{M}\frac{dV(x)}{dx}\frac{\partial P}{\partial v}-v\frac{\partial P}{\partial x}+\gamma\left[\frac{k_BT}{M}\frac{\partial^2P}{\partial v^2}+\frac{\partial}{\partial v}(vP)\right]. \tag{1.3}$$

The objective is to find the steady-state escape rate r out of the potential well (Fig. 1). Kramers[1] has obtained different limiting results for this rate:

$$r\to\begin{cases}\dfrac{\omega_0\omega_B}{2\pi\gamma}\exp\left[\dfrac{-E_B}{k_BT}\right] & \text{as } \gamma\to\infty \quad (1.4a)\\[2ex] \gamma\dfrac{E_B}{k_BT}\exp\left[\dfrac{-E_B}{k_BT}\right] & \text{as } \gamma\to 0 \quad (1.4b)\end{cases}$$

where ω_0 and ω_B are the frequencies associated with the second derivative of the potential at the bottom of the well and at the barrier top, respectively, and where E_B is the well depth. Equation (1.4b) is valid only for a truncated harmonic potential. Note that $E_B \gg k_BT$ is necessary for the steady-state escape rate to be experimentally meaningful. Kramers has also derived an expression which is supposedly appropriate for "intermediate" values of γ

$$r=\frac{\omega_0}{2\pi\omega_B}\left\{\left[\left[\frac{\gamma}{2}\right]^2+\omega_B^2\right]^{1/2}-\frac{\gamma}{2}\right\}\exp\left[\frac{-E_B}{k_BT}\right]. \tag{1.5}$$

This expression yields (1.4a) for $\gamma \gg \omega_B$ while for $\gamma\to 0$ it goes to the transition state theory (TST) rate

$$r_{\rm TST}=\frac{\omega_0}{2\pi}\exp\left[\frac{-E_B}{kT}\right] \tag{1.6}$$

In applying the Kramers model to problems in molecular physics the Markovian assumption inherent in Eqs. (1.1) and (1.2) is a serious drawback. In many situations an internal time scale characterizing the system of interest is shorter than that of the surrounding thermal bath. In this case Eqs. (1.1) and (1.2) should be replaced by their non-Markovian analogs.

$$\ddot{x}=-\frac{1}{M}\frac{dV(x)}{dx}-\int_0^t d\tau Z(t-\tau)\dot{x}(\tau)+\frac{1}{M}R(t)\ , \tag{1.7}$$

$$\langle R(t_1)R(t_2)\rangle=Z(t_1-t_2)Mk_BT,\ \ \langle R(t)\rangle=0. \tag{1.8}$$

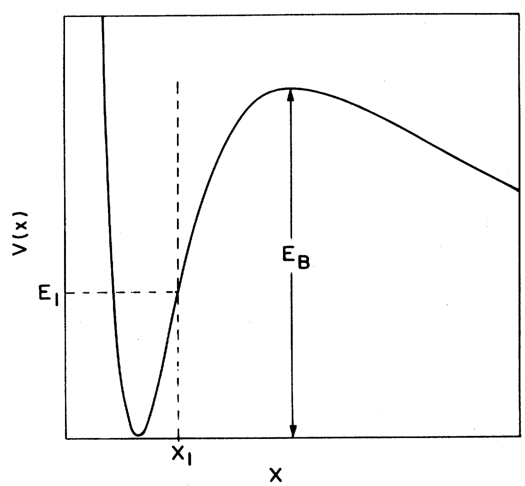

FIG. 1. A schematic representation of the potential well. x_1 and E_1 denote the position and energy associated with the matching point discussed in Sec. II.

The memory function $Z(t)$ is characterized by its Fourier-Laplace components

$$\hat{Z}_n(\omega)=\int_0^\infty dt\, Z(t)e^{-in\omega t} \tag{1.9}$$

with

$$\hat{Z}_0(\omega)=\int_0^\infty dt\, Z(t)=\gamma\ . \tag{1.10}$$

In addition, $Z(t)$ is associated with the correlation time τ_c which characterizes the time scale for its decay to zero. For specificity we shall often refer to the simple case

$$Z(t)=\frac{\gamma}{\tau_c}\exp\left[\frac{-t}{\tau_c}\right], \tag{1.11}$$

$$\hat{Z}_n(\omega)=\frac{\gamma}{1+in\omega\tau_c}\ . \tag{1.12}$$

Several workers have recently treated different aspects of the escape problem represented by Eqs. (1.7) and (1.8). Grote and Hynes,[3] and later Hanggi and Mojtabai[4] have treated the non-Markovian behavior associated with the barrier dynamics. This case corresponds to the limit where the escape process at the top of the potential barrier is considered to be the rate determining step, while the particles in the well are taken to be in an equilibrium Boltzmann distribution. This yields the result (1.5) in the Markovian limit. In the non-Markovian case the escape rate is obtained in the form[4]

$$r=\frac{\omega_0\lambda_0}{2\pi\omega_B}\exp\left[\frac{-E_B}{k_BT}\right], \tag{1.13}$$

where

$$\lambda_0=\lim_{t\to\infty}\left\{\left[\left[\frac{\bar{\gamma}(t)}{4}\right]^2+\bar{\omega}_B^2(t)\right]^{1/2}-\frac{\bar{\gamma}(t)}{2}\right\}, \tag{1.14}$$

$$\bar{\gamma}(t)=-\frac{d}{dt}\ln\Phi(t)\ , \tag{1.15}$$

$$\bar{\omega}_B^2(t)=-\theta(t)/\Phi(t)\ , \tag{1.16}$$

$$\Phi(t)=\dot{\rho}(t)\left[1+\omega_B^2\int_0^t d\tau\,\rho(\tau)\right]-\omega_B^2\rho^2(t)\ , \tag{1.17}$$

$$\theta(t)=\omega_B^2[\rho(t)\ddot{\rho}(t)-\dot{\rho}^2(t)]\ , \tag{1.18}$$

and where the function $\rho(t)$ is defined from

$$\rho(t)=\mathscr{L}^{-1}\left[\frac{1}{s^2-\omega_B^2+S\hat{Z}_1(-is)}\right] \tag{1.19}$$

with $\mathscr{L}^{-1}$ being the inverse Laplace transform. Note that by Eq. (1.9)

$$\hat{Z}_1(-is)=\int_0^\infty dt\, e^{-st}Z(t)$$

is the Laplace transform of $Z(t)$. In the Markovian limit

$$\rho(t)=\mathscr{L}^{-1}\left[\frac{1}{s^2-\omega_B^2+s\gamma}\right]$$

which may be used to show that $\bar{\gamma}(t)=\gamma$ and $\bar{\omega}_B^2(t)=\omega_B^2$ in this limit. It may also be shown (see Appendix A) that λ_0, Eq. (1.14), is the largest (real and positive) root of the equation

$$\lambda^2-\omega_B^2+\lambda\hat{Z}_1(-i\lambda)=0\ . \tag{1.20}$$

Equations (1.13) and (1.20) give the result in the form obtained originally by Grote and Hynes.[3]

Carmeli and Nitzan,[5] and Grote and Hynes,[6] have calculated the steady-state escape rate associated with the model of Eqs. (1.7) and (1.8) and Fig. 1 for the case in which the rate determining process is the energy accumulation in the well. In this case which corresponds to the $\gamma\to 0$ limit, the steady-state escape rate may be identified with the inverse mean first passage time to reach the escape energy. This limit is characterized by the reduced Fokker-Planck equation for the probability distribution $P(J,t)$ for the action variable J[5]

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial J}\left[\epsilon(J)\left[k_BT\frac{\partial P}{\partial J}+\omega(J)P\right]\right] \tag{1.21}$$

with $\epsilon(J)$ given by

$$\epsilon(J)=2M\sum_{n=1}^{\infty}n^2\,|\,x_n(J)\,|^2\mathrm{Re}\{\hat{Z}_n[\omega(J)]\}\ , \tag{1.22}$$

where x_n are the coefficients of the Fourier expansion of the deterministic motion [determined by Eq. (1.7) without the Z and R terms]

$$x=x(J,\varphi)=\sum_{n=-\infty}^{\infty}x_n(J)e^{in\varphi} \tag{1.23}$$

(φ is the angle variable). Equation (1.21) implies the following expression for the mean first passage time $\tau(J,J_0)$ to reach a point J on the action axis starting from a point J_0 and given that there is a reflecting barrier at $J=0$ (the bottom of the potential well):

$$\tau(J,J_0)=\frac{1}{k_BT}\int_{J_0}^{J}dJ'\frac{e^{E(J')/k_BT}}{\epsilon(J')}\int_0^{J'}dJ''e^{-E(J'')/k_BT}\ . \tag{1.24}$$

The escape rate is obtained using

$$r=\left[\int_0^{J_B}dJ_0P_{ss}(J_0)\tau(J,J_0)\right]^{-1}, \tag{1.25}$$

where $P_{ss}(J_0)$ is the steady-state distribution. From deep wells the latter may be approximated by a Boltzmann distribution. In the Markovian limit (1.25) may be shown to reduce to the Kramers result (1.4b) for the low-friction limit.

Kramers' treatment of the escape problem, as well as generalizations of the Kramers theory like those described above, have considered separately cases governed by either well or barrier processes. Several works have tried to provide a unified theory. Skinner and Wolynes[7] have suggested an interpolation formula using Padé approximants based on expansion in powers of the friction. Visscher[8(a)] has investigated the Kramers model numerically and has suggested an analytical form that fits his results in the whole friction range. A similar approach was taken by Larson and Kostin.[8(b)] Risken Vollmer and Denk[9] have outlined an approach based on evaluating the eigenvalues of the Kramers equation. This approach is, however, difficult to implement. Matkowsky, Schuss, and Ben-Jacob[10] have suggested a form for the transition rate associated with a double potential well problem. Even though their form goes to the proper limits ($\sim\gamma$ for $\gamma\to 0$, $\sim 1/\gamma$ for $\gamma\to\infty$), the origin of the $\gamma\to 0$ behavior in their model is different from the one discussed here (and in the original Kramers' work). Büttiker *et al.*[11] have described a procedure which connects between the results (1.4b) and (1.6). All these works involve the Markovian approximation.

Recently[12] we have described a procedure which, in the Markovian limit, yields a unified expression for the steady-state escape rate and which for deep wells is valid in the entire friction range. In the present paper we extend our work to the non-Markovian situation, thus deriving a unified expression for the escape rate associated with Eqs. (1.7) and (1.8) which is valid for all frictions and which reduces to the previously obtained results of Grote and Hynes[3] and of Hanggi and Mojtabai[4] in the high viscosity limit, and to the results of Carmeli and Nitzan[5] and of Grote and Hynes[6] in the low viscosity limit.

In Sec. II we derived the unified result for the steady-state rate in the Markovian limit and provide some details of the procedure that are missing in the preliminary short publication.[12] The theory is extended in Sec. III to the non-Markovian case. Numerical results and discussion are given in Sec. IV.

II. STEADY-STATE RATE IN THE MARKOVIAN LIMIT

Starting from Eq. (1.3) in the steady state ($\partial P/\partial t=0$) we first divide our discussion into barrier and well dynamics and, after obtaining results for the steady-state probability distributions and for the fluxes appropriate to the two dynamical regimes, we join the solutions in a way that satisfies essential continuity requirements.

Consider barrier dynamics first. In this case we follow exactly Kramers' procedure.[1] The essential points in this procedure are as follows. Kramers approximates the potential near the barrier top ($x=0$) by a parabula

$$V(x)=E_B-\tfrac{1}{2}M\omega_B^2x^2 \tag{2.1}$$

and looks for a steady-state solution $P_B(x,v)$ (B denotes the barrier) to Eq. (1.3) of the form

$$P_B(x,v)=\exp\left[-\frac{Mv^2/2+V(x)}{k_BT}\right]F(x,v)\ . \tag{2.2}$$

Using Eqs. (1.3), (2.1), and (2.2), the "correction function" F is shown to satisfy the equation

$$\gamma\frac{k_BT}{M}\frac{\partial^2F}{\partial v^2}-\gamma v\frac{\partial F}{\partial v}-v\frac{\partial F}{\partial x}-\omega_B^2x\frac{\partial F}{\partial v}=0\ . \tag{2.3}$$

Kramers looks for a solution of the form $F(x,v)=F(u)$ with

$$u=v+\Gamma x \tag{2.4}$$

and finds that such a function $F(u)$ should satisfy the equation

$$\frac{k_BT}{M}\frac{d^2F}{du^2}+\alpha u\frac{dF}{du}=0 \tag{2.5}$$

with

$$\alpha=-\frac{\Gamma+\gamma}{\gamma} \tag{2.6}$$

provided that Γ satisfies the equation

$$\Gamma^2-\omega_B^2+\Gamma\gamma=0\ . \tag{2.7}$$

A general solution of Eq. (2.5) is

$$F(u)=F_1+F_2\int_0^u dz\exp\left[-\frac{\alpha Mz^2}{2k_BT}\right], \tag{2.8}$$

where F_1 and F_2 are constants to be determined. We look for a solution which vanishes for $x\to\infty$. For this to happen the integral in (2.8) should remain finite for $|u|\to\infty$. This implies that $\alpha>0$, namely, of the two roots of (2.7) only

$$\Gamma=-\left\{\frac{\gamma}{2}+\left[\left(\frac{\gamma}{2}\right)^2+\omega_B^2\right]^{1/2}\right\} \tag{2.9}$$

is relevant. Then the requirement $P_B(x,v)\to 0$ for $x\to\infty$ implies

$$F_1=-F_2\int_0^{-\infty}dz\exp\left[-\frac{\alpha Mz}{2k_BT}\right]=\left[\frac{\pi k_BT}{2\alpha M}\right]^{1/2}F_2\ . \tag{2.10}$$

Thus,

$$P_B(x,v)=F_2\left[\left[\frac{\pi k_BT}{2\alpha M}\right]^{1/2}+\int_0^{v-|\Gamma|x}dz\exp\left[-\frac{\alpha Mz^2}{2k_BT}\right]\right]\times\exp\left[-\frac{Mv^2/2+V(x)}{k_BT}\right]. \tag{2.11}$$

The current associated with this distribution is calculated using

$$j_B=\int_{-\infty}^{\infty}dv\,vP_B(x,v) \tag{2.12}$$

which may be evaluated [using Eqs. (2.1) and (2.11)] to give

$$j_B=F_2\left[\frac{k_BT}{M}\right]^{3/2}\left[\frac{2\pi}{\alpha+1}\right]^{1/2}\exp\left[\frac{-E_B}{k_BT}\right]. \tag{2.13}$$

This result is independent of the position x as expected of a steady-state current.

Before proceeding to consider the steady-state distribution in the well, P_W, we notice that Kramers' derivation of Eq. (1.5) is based on Eq. (2.13) where F_2 is determined from the requirement that the P_W is an equilibrium Boltzmann distribution obtained from (2.11) for $x\to-\infty$:

$$P_W(x,v)=P_B(x\to-\infty,v)=F_2\left[\frac{2\pi k_BT}{\alpha M}\right]^{1/2}\exp\left[-\frac{Mv^2/2+V(x)}{k_BT}\right]. \tag{2.14}$$

For a deep well the total number N of particles in the well is approximated by Kramers as

$$N=\int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dx\, P_W(x,v) \quad (2.15)$$

which, taking $V(x)=M\omega_0^2x^2/2$ in (2.14), results in

$$N=\frac{F_2}{\omega_0\sqrt{\alpha}}\left[\frac{2\pi k_B T}{M}\right]^{3/2} . \quad (2.16)$$

Equation (1.5) results from taking $r=j_B/N$, using Eqs. (2.6), (2.9), (2.13), and (2.16).

The inconsistency in Kramers' derivation which leads to the fact that Eq. (1.5) does not go over to (1.4b) as $\gamma\to 0$, is seen in that the current associated with the distribution (2.14) is zero, while in steady state the current should be the same everywhere [and therefore given by j_B of Eq. (2.13)]. For γ large enough Eq. (2.14) is nevertheless a good approximation for the well distribution which, for a deep enough well yields a good approximation for the total number of particles N, Eq. (2.16). For small friction the escape of particles over the barrier causes a distortion in the distribution even deep down in the well: Thermal relaxation due to the coupling with the thermal bath cannot "keep up" with this escape which depletes the well of the more energetic particles. In the extreme limit this thermal relaxation (i.e., energy accumulation in the well) becomes the rate determining step.

To take proper care of these effects we depart from Kramers' procedure by replacing Eq. (2.14) by a steady-state distribution in the well corresponding to the appropriate current. Our approach is based on the following observations:

(a) For most problems in molecular dynamics one may safely assume that deep in the well the oscillations are fast relative to other relevant time scales (e.g., γ, and for non-Markovian cases $\hat{Z}_n(\omega)$ and τ_c). This implies[1] that deep in the well Eq. (1.3) may be reduced to a Smoluchowski equation in the action J [the Markovian equivalent of (1.21)]

$$\frac{\partial P_W}{\partial t}=\gamma\frac{\partial}{\partial J}\left[\frac{J}{\omega(J)}\left[k_B T\frac{\partial P_W}{\partial J}+\omega(J)P_W\right]\right] , \quad (2.17)$$

where the action distribution function $P_W(J,t)$ is related to $P_W(x,v,t)$ by

$$P_W(x,v,t)=\frac{M}{2\pi}P_W(J,t) . \quad (2.18)$$

Equation (2.18) expresses the fact that because of the fast oscillations deep in the well the distribution is uniform $[(2\pi)^{-1}]$ in the phase. The mass M is the Jacobian of the $(x,v)\to(J,\varphi)$ transformation.[13]

(b) A steady state in the strict sense cannot exist in Kramer's model because the number of particles in the well decreases as particles escape. The rates (1.4)—(1.6) actually correspond to the quasi-steady-state situation which exists if the well is deep enough so that the escape is slow relative to the other time scales in the system. As a *mathematical* convenience it is possible to convert this into a real steady-state situation by providing a source at or near the bottom of the well. As long as the quasi-steady-state concept is valid, this source should not change any physical observable.

We thus use Eq. (2.17) and, in addition, assume that a source exists at the bottom of the well such that the distribution $P_W(J)$ at $0\le J\le J_0$ is fixed and given by a Boltzman form[14]

$$P_W(J)=A_0 e^{-E(J)/k_B T}, \quad 0\le J\le J_0 . \quad (2.19)$$

This imposes a boundary condition on Eq. (2.17). For the result to be meaningful the final rate should not depend on the choice of J_0 and A_0. We look for a steady-state $(\partial P_W/\partial t=0)$ solution in the form

$$P_W(J)=F(J)e^{-E(J)/k_B T} \quad (2.20)$$

and [using $dE(J)/dJ=\omega(J)$] obtain for $F(J)$

$$\frac{d}{dJ}\left[\frac{\gamma J}{\omega(J)}e^{-E(J)/k_B T}\frac{dF}{dJ}\right]=0 \quad (2.21)$$

whose general solution, which corresponds to (2.19), is

$$F(J)=A_0-A\int_{J_0}^{J} dJ'\frac{\omega(J')}{\gamma J'}e^{E(J')/k_B T} . \quad (2.22)$$

We anticipate the following steps by introducing a point $J=J_1>J_0$ (corresponding to $E=E_1$) and redefining

$$\frac{A_0}{A}=B+\int_{J_0}^{J_1} dJ\frac{\omega(J)}{\gamma J}e^{E(J)/k_B T} \quad (2.23)$$

so that [using (2.20), (2.22), and (2.23)]

$$P_W(J)=Ae^{-E(J)/k_B T}\left[B+\int_{J}^{J_1} dJ'\frac{\omega(J')}{\gamma J'}e^{E(J')/k_B T}\right] . \quad (2.24)$$

The steady-state current in J space is obtained from (2.24) using

$$j_W=-\frac{\gamma J}{\omega(J)}\left[k_B T\frac{dP_W}{dJ}+\omega(J)P_W\right] \quad (2.25)$$

which yields

$$j_W=Ak_B T . \quad (2.26)$$

We now turn to the task of piecing together the two distributions P_B [Eq. (2.11)] and P_W [Eq. (2.24)]. We assume that there exists a region in phase space (x,v) in which both results are valid. Since P_B is valid for x large enough while P_W is valid for J (or E) small enough, we may assume that there is a point in this region with $v=0$. We thus carry our adjoining procedure at the point x_1, $v_1=0$ (Fig. 1) and denote the corresponding action and energy by J_1 and E_1 [thus identifying the previously arbitrary point J_1 in (2.23)]. These are related to each other by

$$E_1=\int_0^{J_1} dJ\,\omega(J) \quad (2.27)$$

and

$$E_1=V(x_1)=E_B-\tfrac{1}{2}M\omega_B^2x_1^2 . \quad (2.28)$$

The "transition point" (x_1,E_1) is to be determined together with the parameters F_2, A, and B of Eqs. (2.11) and

(2.24) from the continuity requirements. These are taken to be

$$j_B = j_W\ , \tag{2.29}$$

$$\frac{M}{2\pi} P_W(J_1) = P_B(x_1, v=0)\ , \tag{2.30}$$

$$\left[\frac{\partial}{\partial E} P_B(x, v=0)\right]_{x=x_1} = \frac{M\omega(E_1)}{2\pi}\left[\frac{\partial}{\partial E} P_W(E)\right]_{E=E_1} . \tag{2.31}$$

Equation (2.29) expresses the fact that in steady state the number of particles crossing per unit time the line $E=E_1$ (Fig. 1) in the upward direction (increasing energy) should be the same as the number of particles crossing per unit time the line $x=x_1$ (Fig. 1) in the outward direction (increasing x). This, in fact, is true for any horizontal and perpendicular lines in Fig. 1. Equations (2.30) and (2.31) are conditions on the continuity of the distribution at the point (x_1, E_1), taken along the $v=0$ direction which, as noted above, is the most likely direction for overlapping of P_B and P_W. The factors M and $M\omega(E)$ appearing in (2.30) and (2.31) are the Jacobians of the $(x,v)\to(J,\varphi)$ and $(x,v)\to(E,\varphi)$ transformations, respectively.

Using Eqs. (2.11), (2.13), (2.24), and (2.26), Eqs. (2.29) and (2.30) yield

$$F_2 = AM^{3/2}\left[\frac{\alpha+1}{2\pi k_B T}\right]^{1/2} e^{E_B/k_B T}\ , \tag{2.32}$$

$$B = \pi(1+\mathrm{erf}\{[(\alpha+1)(E_B-E_1)/k_B T]^{1/2}\}) \times \left[\frac{\alpha+1}{\alpha}\right]^{1/2} e^{E_B/k_B T}\ , \tag{2.33}$$

and Eq. (2.31) leads to

$$\exp\left[-\alpha\frac{E_B-E_1}{k_B T}\right] = \frac{k_B T}{\gamma J_1(\alpha+1)\sqrt{\pi}}\left[\alpha\frac{E_B-E_1}{k_B T}\right]^{1/2} . \tag{2.34}$$

Equation (2.34) may be used to determine the transition point energy E_1. It is easy to show [using the fact that J_1 monotonously increases while $(E_B-E_1)^{1/2}$ monotonically decreases with E_1] that Eq. (2.34) must have a single real and positive solution E_1. With E_1 known, Eqs. (2.32) and (2.33) determine the parameters F_2 and B, leaving A to be determined from the normalization condition. The procedure and the approximations used to carry out this normalization are described in Appendix B. There we show that the number N defined by

$$N = \int_{-\infty}^{0} dx \int_{-\infty}^{\infty} dv\, P(x,v) \tag{2.35}$$

with $P(x,v)$ given by Eqs. (2.11) or (2.18) and (2.24) in the appropriate regimes is well approximated by

$$N = Ak_B T[\tau(J_1,J_0) + Sr_K^{-1}]\ , \tag{2.36}$$

where

$$S = \frac{\omega_0}{k_B T}\int_0^{E_B} \frac{dE}{\omega(E)} e^{-E/k_B T} \times \left[\frac{1+R}{2}\eta(E_1-E) + \eta(E-E_1)\right] \tag{2.37}$$

with

$$R = \mathrm{erf}([(\alpha+1)(E_B-E_1)/k_B T]^{1/2}) \tag{2.38}$$

and with $\eta(E)$ being the step function (1 for $E>0$ and 0 for $E>0$). In Eq. (2.38) erf denotes the error function, r_K is the Kramers rate given by r of Eq. (1.5), and

$$\tau(J_1,J_0) = \frac{1}{k_B T}\int_{J_0}^{J_1} dJ \frac{\omega(J)}{\gamma J} e^{E(J)/k_B T} \times \int_0^J dJ' e^{-E(J')/k_B T} \tag{2.39}$$

is the mean first passage time to reach J_1 [in a process governed by Eq. (2.17)] starting from J_0 ($J_1 > J_0 > 0$) given a reflecting barrier at $J=0$. τ is the Markovian equivalent of the result (1.24).

The steady-state escape rate is now obtained as the normalized net current, $r=j/N$. Using Eq. (2.26) we obtain

$$r = [\tau(J_1,J_0) + Sr_K^{-1}]^{-1} \tag{2.40}$$

which is our final result for the escape rate in the Markovian case. To investigate its behavior as a function of the friction γ we refer to Fig. 2 which shows the typical behavior of E_1 as a function of γ. For large γ, $E_1\to 0$ and $\tau(J_1,J_0)\to 0$. At the same time $R\to 1$ and [using $E_B \gg k_B T$, $\int_0^{E_B} dE\,\omega^{-1}(E)\exp(-E/k_B T) \sim k_B T/\omega_0$] $S\to 1$ and we get $r\to r_K$. For small γ, $E_1\to E_B$ so that $r\to[\tau(J_B,J_0) + (2r_K)^{-1}]^{-1}$. However, for a deep well $\tau(J_B,J_0)$ dominates so that $r\to\tau(J_B,J_0)^{-1}$. For the model $V(x)=\frac{1}{2}M\omega_0^2(x-x_0)^2$, $x<0$ and $V(x)=0$, $x\geq 0$ (truncat-

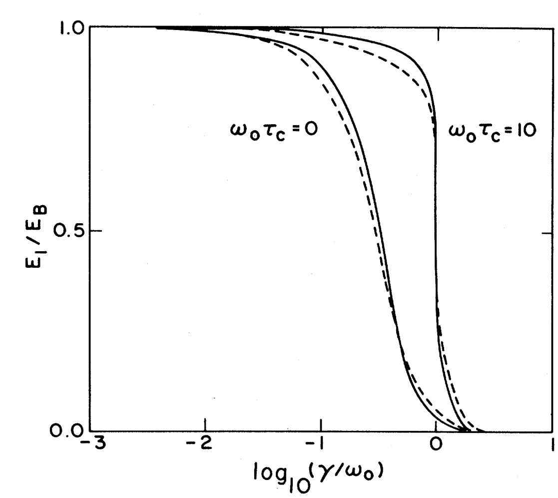

FIG. 2. E_1/E_B vs $\log_{10}(\gamma/\omega_0)$ calculated from Eq. (4.7) in the Markovian limit ($\omega_0\tau_c=0$) and in the non-Markovian case ($\omega_0\tau_c=10$). Solid lines: $E_B=10k_B T$. Dashed lines: $E_B=4k_B T$.

ed harmonic potential), it is easy to show[1] that $\tau(J_B,J_0)^{-1}$ reduces to the result (1.4b) independent of J_0. [For $E_0=E(J_0)\ll E_B$.] Our result (2.40) thus reduces properly to the Kramers results in the appropriate limits. We defer more discussion of this result to Sec. V and turn now to consider the non-Markovian case.

III. STEADY-STATE RATE IN THE NON-MARKOVIAN CASE

For the non-Markovian case described by Eqs. (1.7) and (1.8) we again consider first separately the barrier and the well dynamics and after that join the solutions in a way similar to that described in the Markovian case. For the barrier dynamics we follow the formulation of Hanggi and Majtabai[4] which is based on the generalized Fokker-Planck equation obtained by Adelman[15] for Eqs. (1.7) and (1.8) with a parabolic potential. Using Eq. (2.1) this equation takes the form

$$\frac{\partial P}{\partial t}=-\overline{\omega}_B^2 x\frac{\partial P}{\partial v}-v\frac{\partial P}{\partial x}+\overline{\gamma}\frac{\partial}{\partial v}(vP)+\overline{\gamma}\frac{k_BT}{M}\frac{\partial^2 P}{\partial v^2}+\frac{k_BT}{M}\left[\frac{\overline{\omega}_B^2}{\omega_B^2}-1\right]\frac{\partial^2 P}{\partial x\,\partial v}\,, \quad (3.1)$$

where $\overline{\gamma}=\gamma(t)$ and $\overline{\omega}_B^2=\overline{\omega}_B^2(t)$ are the functions of time defined by Eqs. (1.15)—(1.19). In looking for a steady-state solution to Eq. (3.1) Hanggi and Mojtabai consider the long-time limit of the functions $\overline{\omega}_B^2$ and $\overline{\gamma}$. However, it may be shown that these functions, though bounded, do not always have a long-time limit. We are therefore forced to proceed more cautiously using the observation [Ref. 4(b) and Appendix A] that the limit defined by Eq. (1.14) does exist. We again look for a solution of the form

$$P(x,v,t)=F(x,v,t)\exp\left[-\frac{Mv^2/2+V(x)}{k_BT}\right] \quad (3.2)$$

[with $V(x)$ given by (2.1)] and seek for F the form

$$F(x,v,t)=F(u,t),\quad u=v+\Gamma x\,. \quad (3.3)$$

Inserting (3.3) and (3.2) in (3.1) we get

$$\frac{\partial F}{\partial t}=-\frac{k_BT}{M}(\overline{\lambda}+\Gamma)\frac{\partial^2 F}{\partial u^2}+\overline{\lambda}\left[v-\frac{\omega_B^2}{\overline{\lambda}}x\right]\frac{\partial F}{\partial u}\,, \quad (3.4)$$

where

$$\overline{\lambda}(t)=-\left[\overline{\gamma}(t)+\Gamma\frac{\overline{\omega}_B^2(t)}{\omega_B^2}\right]. \quad (3.5)$$

We further require [as our choice for Γ in (3.3)] that

$$\lim_{t\to\infty}\overline{\lambda}(t)=-\frac{\omega_B^2}{\Gamma}\,. \quad (3.6)$$

To prove that this requirement is possible we have to show that this limit exists. This is done in Appendix C where we further show that

$$\lim_{t\to\infty}\overline{\lambda}(t)=\lambda_0\,, \quad (3.7)$$

where λ_0 [defined in (1.14)] is identified (Appendix A) as the largest root of Eq. (1.20). In what follows we shall use the relations

$$\lambda_0=\left[\left[\frac{\overline{\gamma}}{2}\right]^2+\overline{\omega}_B^2\right]^{1/2}-\frac{\overline{\gamma}}{2} \quad (3.8)$$

and

$$\Gamma=-\frac{\omega_B^2}{\lambda_0}=-\left\{\frac{\overline{\gamma}}{2}+\left[\left[\frac{\overline{\gamma}}{2}\right]^2+\overline{\omega}_B^2\right]^{1/2}\right\}\frac{\omega_B^2}{\overline{\omega}_B^2} \quad (3.9)$$

with the understanding that the long-time limit has been taken.

Equations (3.5)—(3.9) imply that Eq. (3.4) admits a long-time steady-state solution which satisfies the equation

$$\frac{k_BT}{M}\frac{\partial^2 F}{\partial u^2}+\overline{\alpha}u\frac{\partial F}{\partial u}=0 \quad (3.10)$$

with

$$\overline{\alpha}=\frac{\omega_B^2}{\Gamma^2-\omega_B^2}\,. \quad (3.11)$$

These results are identical in form to the expressions obtained in the Markovian limit [Eqs. (2.5) and (2.6)] [note that Eqs. (2.6) and (2.7) imply $\alpha=\omega_B^2/(\Gamma^2-\omega_B^2)$]. In this limit $\overline{\omega}_B^2\to\omega_B^2$, $\overline{\gamma}\to\gamma$, and Γ of Eq. (3.9) becomes indeed identical to its Markovian equivalent [Eq. (2.9)]. We note, however, that in the general non-Markovian case we cannot ascertain that $\overline{\alpha}>0$ [thus making the solution of (3.10) physically relevant] or that this is the only relevant solution. (See Appendix C.) We proceed with the assumption that this is indeed so.

Since Eqs. (3.10) and (3.11) are identical to their Markovian counterparts, the calculation of P_B and of j_B proceeds as before, yielding

$$P_B(x,v)=F_2\left[\left[\frac{\pi k_BT}{2M\overline{\alpha}}\right]^{1/2}+\int_0^{v-|\Gamma|x}dz\exp\left[-\frac{\overline{\alpha}Mz^2}{2k_BT}\right]\right]\times\exp\left[-\left[\frac{M}{2}v^2+V(x)\right]/k_BT\right] \quad (3.12)$$

and

$$j_B=F_2\left[\frac{k_BT}{M}\right]^{3/2}\left[\frac{2\pi}{\overline{\alpha}+1}\right]^{1/2}\exp(-E_B/k_BT) \quad (3.13)$$

with Γ and $\overline{\alpha}$ given by Eqs. (3.9) and (3.11).

Turning now to the well dynamics we again assume that deep in the well the frequency is high enough so that in the action-angle representation the angle distribution is uniform and that the Smoluchowski equation for $P_W(J,t)$ is valid. Instead of Eq. (2.17) we now have to use Eq. (1.21) which differs from its Markovian counterpart in that the function $\gamma J/\omega(J)$ is replaced by $\epsilon(J)$ defined by Eq. (1.22). P_W satisfies Eq. (2.18) and, adopting the same source trick as in Sec. II, we take it also to satisfy the boundary condition (2.19). With the change $\gamma J/\omega(J)\rightarrow\epsilon(J)$ the calculation proceeds as in Sec. II and we get

$$P_W(J)=Ae^{-E(J)/k_BT}\left[B+\int_J^{J_1}dJ'\frac{1}{\epsilon(J')}e^{E(J')/k_BT}\right] \quad (J>J_0) \qquad (3.14)$$

and using

$$j_W=-\epsilon(J)\left[k_BT\frac{dP_W(J)}{dJ}+\omega(J)P_W(J)\right] \qquad (3.15)$$

Eq. (3.14) leads to

$$j_W=Ak_BT\ . \qquad (3.16)$$

Equations (3.14)—(3.16) are the non-Markovian counterparts of Eqs. (2.24)—(2.26).

To determine the constants F_2, A, and B and the transition point [$x=x_1$, $v=0$, $E=E_1$, $J=J_1$ with E_1 and J_1 satisfying Eqs. (2.27) and (2.28)] we again use the continuity requirements (2.29)—(2.31) and the normalization condition. Equations (2.29) and (2.30) now yield the analogs ($\bar\alpha$ replaces α) of Eqs. (2.32) and (2.33)

$$F_2=AM^{3/2}\left[\frac{\bar\alpha+1}{2\pi k_BT}\right]^{1/2}e^{E_B/k_BT}\ , \qquad (3.17)$$

$$B=\pi(1+\operatorname{erf}\{[(\bar\alpha+1)(E_B-E_1)/k_BT]^{1/2}\})\left[\frac{\bar\alpha+1}{\bar\alpha}\right]^{1/2}\times e^{E_B/k_BT} \qquad (3.18)$$

while Eq. (2.31) leads to the analog of (2.34) [which may also be obtained directly from (2.34) by replacing $\gamma J/\omega(J)$ by $\epsilon(J)$]

$$\exp\left[-\bar\alpha\frac{E_B-E_1}{k_BT}\right]=\frac{k_BT}{\epsilon(J_1)\omega(J_1)(\bar\alpha+1)\sqrt{\pi}}\times\left[\bar\alpha\frac{E_B-E_1}{k_BT}\right]^{1/2}. \qquad (3.19)$$

For the normalization factor N [Eq. (2.35)] we now get (see Appendix B)

$$N=Ak_BT[\tau_{NM}(J_1,J_0)+Sr_{K,NM}^{-1}]\ , \qquad (3.20)$$

where S is given by Eqs. (2.37) and (2.8) with α replaced by $\bar\alpha$, $r_{K,NM}$ is the non-Markovian analog of the Kramers rate, Eqs. (1.13) and (1.14), and $\tau_{NM}(J_1,J_0)$, the non-Markovian analog of the τ appearing in (2.39), is given by Eq. (2.24).

The steady-state escape rate is obtained from

$$r=\frac{j_W}{N} \qquad (3.21)$$

leading to the analog of Eq. (2.40)

$$r=[\tau_{NM}(J_1,J_0)+Sr_{K,NM}^{-1}]^{-1}\ . \qquad (3.22)$$

This, with $r_{K,NM}$ and τ_{NM} given by Eqs. (1.13), (1.14), and (1.24), respectively, is our final result for the escape rate in the non-Markovian case.

IV. RESULTS AND DISCUSSION

Our final result is represented by the remarkably simple expression for the escape rate

$$r=[\tau(J_1,J_0)+Sr_k^{-1}]^{-1}\ , \qquad (4.1)$$

where

$$\tau(J_1,J_0)=\begin{cases}\dfrac{1}{k_BT}\displaystyle\int_{J_0}^{J_1}dJ\frac{\omega(J)}{\gamma J}\exp\left[\frac{E(J)}{k_BT}\right]\times\int_0^J dJ'\exp\left[-\frac{E(J')}{k_BT}\right] & \text{(Markovian)} \quad (4.2a)\\[2ex] \dfrac{1}{k_BT}\displaystyle\int_{J_0}^{J_1}dJ\frac{1}{\epsilon(J)}\exp\left[\frac{E(J)}{k_BT}\right]\times\int_0^J dJ'\exp\left[-\frac{E(J')}{k_BT}\right] & \text{(non-Markovian)} \quad (4.2b)\end{cases}$$

$$r_K=\frac{\omega_0\lambda_0}{2\pi\omega_B}\exp(-E_B/k_BT)\ , \qquad (4.3)$$

$$\lambda_0=\begin{cases}\left[\left[\dfrac{\gamma}{2}\right]^2+\omega_B^2\right]^{1/2}-\dfrac{\gamma}{2} & \text{(Markovian)} \quad (4.4a)\\[2ex] \lim\limits_{t\to\infty}\left\{\left[\left[\dfrac{\bar\gamma(t)}{2}\right]^2+\bar\omega_B^2\right]^{1/2}-\dfrac{\bar\gamma(t)}{2}\right\} & \text{(non-Markovian)} \quad (4.4b)\end{cases}$$

$$S=\frac{\omega_0}{k_BT}\int_0^{E_B}\frac{dE}{\omega(E)}\exp\left[-\frac{E}{k_BT}\right]\left[\frac{1+R}{2}\eta(E_1-E)+\eta(E-E_1)\right]\ , \qquad (4.5)$$

$$R=\begin{cases}\operatorname{erf}\{[(\alpha+1)(E_B-E_1)/k_BT]^{1/2}\} & \text{(Markovian)} \quad (4.6a)\\ \operatorname{erf}\{[(\bar\alpha+1)(E_B-E_1)/k_BT]^{1/2}\} & \text{(non-Markovian)}\ . \quad (4.6b)\end{cases}$$

The functions $\bar\gamma(t)$ and $\bar\omega_B^2(t)$ and the parameters α and $\bar\alpha$ were defined in previous sections [Eqs. (1.15)—(1.19) (2.6)—(2.7), and (3.8)—(3.11)]. λ_0 is most easily determined as the largest positive root of Eq. (1.20) (note that λ_0 is identical to the "reactive frequency" λ_r of Grote and Hynes[3]). It should be noted that using the equivalent variables J (action) or E (energy) in the integrals of Eqs. (4.2) and (4.5) is done merely for convenience of presentation, and that $\omega(E)$ denotes the frequency at energy E which is equal to $\omega(J)$ for $J=J(E)$.

The "transition energy" E_1 and the corresponding action J_1 are obtained as solutions to the equations

$$\exp\left[-\alpha\frac{E_B-E_1}{k_BT}\right]=\frac{k_BT}{\gamma J_1(\alpha+1)\sqrt{\pi}}\left[\alpha\frac{E_B-E_1}{k_BT}\right]^{1/2} \quad \text{(Markovian)} \tag{4.7a}$$

$$\exp\left[-\bar{\alpha}\frac{E_B-E_1}{k_BT}\right]=\frac{k_BT}{\epsilon(J_1)\omega(J_1)(\bar{\alpha}+1)\sqrt{\pi}}\times\left[\bar{\alpha}\frac{E_B-E_1}{k_BT}\right]^{1/2} \quad \text{(non-Markovian)}\,. \tag{4.7b}$$

Finally the function $\epsilon(J)$ is given by

$$\epsilon(J)=2M\sum_{n=1}^{\infty}n^2|X_n(J)|^2\text{Re}\{\hat{Z}_n[\omega(J)]\} \tag{4.8a}$$

and may be shown (Appendix D) to be identical to

$$\epsilon(J)=\frac{M}{\omega^2(J)}\int_0^\infty dt\,Z(t)\langle v(0)v(t)\rangle\,, \tag{4.8b}$$

where the correlation function $\langle v(0)v(t)\rangle$ corresponds to the isolated system (no coupling to the heath bath) and $\langle\cdots\rangle$ denotes averaging over the initial phases.

The result (4.1) has the expected form of an overall rate associated with two consecutive rate processes. $\tau(J_1,J_0)$ is the mean first passage time to reach the point j_1 starting from the source point J_0 in the well, while r_K^{-1} is the time associated with the transition over the barrier. The transition point between the two regimes is the solution E_1 (or J_1) of Eq. (4.7). This is a function of the systems parameters. In particular, it varies between E_B and zero as the friction γ (or the magnitude of the function ϵ) increase from zero to ∞ (see Fig. 2).

The following points regarding these results should be noticed:

(a) The result (4.1) yields all the previously derived Kramers limits. To see this consider first the Markovian case. In the low viscosity limit ($\gamma\to 0$) $E_1\to E_B$. Equations (4.3)–(4.5) yield[16]

$$Sr_K^{-1}\to\frac{\pi}{\omega_0}\exp(E_B/k_BT) \tag{4.9}$$

while Eq. (4.2) leads to $\tau(J_1,J_0)\to\tau(J_B,J_0)$,

$$\tau(J_B,J_0)=\frac{1}{k_BT}\int_{J_0}^{J_B}dJ\frac{\omega(J)}{\gamma J}\exp\left[\frac{E(J)}{k_BT}\right]\times\int_0^J dJ'\exp\left[-\frac{E(J')}{k_BT}\right] \tag{4.10}$$

which may be evaluated approximately[1] by noticing that (for deep wells, $E_B\gg k_BT$) the largest contribution to the integral comes from the neighborhood of $J=J_B$. Replacing

$$\frac{1}{J}\int_0^J dJ'\exp\left[\frac{-E(J')}{k_BT}\right]$$

by its $J=J_B$ value and evaluating it approximately as

$$\frac{1}{J_B}\int_0^{J_B}dJ'\exp\left[-\frac{E(J)}{k_BT}\right]\simeq\frac{1}{J_B\omega_0}\int_0^{E_B}dE\exp\left[-\frac{E}{k_BT}\right]\simeq\frac{k_BT}{J_B\omega_0}$$

we get

$$\tau(J_B,J_0)\simeq\frac{1}{\gamma J_B\omega_0}\int_{E_0}^{E_B}dE\exp\left[\frac{E}{k_BT}\right]\simeq\frac{k_BT}{\gamma J_B\omega_0}e^{E_B/k_BT}\,. \tag{4.11}$$

Comparing this to (4.9) we see that for $\gamma\to 0$, τ makes the dominant contribution to Eq. (4.1) and the rate is given by

$$r\to\tau^{-1}(J_B,J_0)\simeq\gamma\frac{\omega_0J_B}{k_BT}\exp\left[-\frac{E_B}{k_BT}\right]\,. \tag{4.12}$$

This is a generalization of Eq. (1.4b) ($\omega_0J_B=E_B$ for the truncated harmonic-oscillator model).

In the high viscosity limit ($\gamma\to\infty$) $E_1\to 0$, $R\to 1$, Eq. (4.5) becomes

$$S=\frac{\omega_0}{k_BT}\int_0^{E_B}dE\frac{1}{\omega(E)}\exp(-E/k_BT)\simeq 1\,,$$

τ becomes small and negligible relative to r_K^{-1}, and we recover the familiar Kramers expression $r=r_K$ with r_K given by Eq. (4.3).

In the non-Markovian case the situation is very much the same. In the low friction limit the rate again approaches $\tau^{-1}(J_B,J_0)$ now given by Eq. (1.24).[17] For very deep wells this may be shown[5,6] to yield again Eq. (4.12), where the non-Markovian effects disappear. For wells which are not too deep the full expression (1.24) for τ has to be used and non-Markovian effects may be appreciable.[5,6] In the high friction limit similar arguments as above lead to $r=r_K$, now given by Eqs. (4.3) and (4.4b).

(b) The result, at least for low friction, appears to formally depend on the source point J_0 that was chosen arbitrarily with the condition $E_0=E(J_0)\ll E_B$. In fact, there is no dependence on J_0 for those cases where the steady-state rate is physically meaningful (i.e., where the escape time scale is much longer than the time scale for thermal relaxation in the well). In this case if $\tau(J_1,J_0)$ in Eq. (4.1) is not negligible [i.e., if $E_1=E(J_1)\gg k_BT$] then it is also much larger than the thermal relaxation time. It is therefore independent of the starting point J_0 because starting from any point on the J_0 surface a trajectory will first thermally relax [on a time scale short relative to $\tau(J_1,J_0)$].

We have checked this point numerically for the potential of Fig. 1 for the Markovian case and also for the non-Markovian model, Eqs. (1.10)–(1.12), for several values of γ and τ_c. This was done by calculating $\tau(J_1,J_0)$ for fixed J_1 and different values of J_0 in the range $0,\ldots,\frac{1}{2}J_1$. For $E_1=E(J_1)=4k_BT$ the variation in $\tau(J_1,J_0)$ is about 5% in this range while for $E_1=10k_BT$

the variation is $\sim 0.1\%$.

(c) Comparing Eqs. (4.9) and (4.11) we may get a simple condition for the validity of the low friction result (4.12)

$$\frac{\pi \gamma J_B}{k_B T} \ll 1 . \tag{4.13}$$

In the truncated harmonic-oscillator model ($\omega_0 J_B = E_B$) this yields

$$\frac{\pi}{\omega_0} \gamma E_B \ll k_B T . \tag{4.14}$$

Noting that $E_B = 2\langle E_{kB} \rangle$, where $\langle E_{kB} \rangle$ is the average kinetic energy at the barrier, and that $\gamma \langle E_k \rangle$ is the rate of energy loss due to thermal relaxation, Eq. (4.14) states that the amount of energy damped during one period of oscillation should be much less than $k_B T$. For the Morse oscillator $\gamma J_B = (\gamma/\omega_0)/(E_B/2)$ (where ω_0 is the well bottom frequency) and the interpretation of (4.13) is not as simple. However, quite generally, it is seen that the behavior is determined by the dimensionless parameter $\gamma J_B / k_B T$ so that departure from the low friction limit occurs on increasing either γ or E_B ($= \int_0^{J_B} dJ\, \omega(J)$). This conclusion is valid also when Eq. (4.12) cannot be used and the more rigorous expression (4.10) (or its non-Markovian analog) is needed.

(d) The transition rate theory (TST) rate is obtained as the zero friction limit for r_K, Eq. (4.3). Equation (4.1) and the above discussion imply that the rate r approaches zero for both $\gamma \to 0$ and $\gamma \to \infty$ and thus goes through a maximum for some intermediate γ. Denoting this maximum by $r_{\max}$, it is easy to see that $r_{\max} \le r_{\rm TST}$ (see also Figs. 4 and 5 below). This follows from the fact that r_K, Eq. (4.3) is a decreasing function of γ while S approaches 1 (as $R \to 1$ when $E_B - E_1$ becomes large relative to $k_B T$) faster than r_K attains its maximum value ($= r_{\rm TST}$). $r_{\max}$ will be larger (hence closer to $r_{\rm TST}$) for larger E_B. The reason for this is that for larger E_B the range of validity of the approximation which neglects τ relative to $S r_K^{-1}$ in Eq. (4.1) extends to lower values of γ and that, for large E_B, $S \to 1$ (Ref. 18) and r_K becomes equal to $r_{\rm TST}$ [Eq. (1.6)]. Thus, the transition state theory result is obtained from Eq. (4.1) by taking first the large E_B limit, then the small γ limit, while the result (4.12) is approached as $\gamma \to 0$ for fixed E_B. As seen in the computations described below, for large ranges of parameters $r_{\max}$ and, of course, the actual rate r are appreciably smaller than $r_{\rm TST}$ in agreement with observation made in many previous works.[19]

(e) The dependence of the rate r on the friction (γ or generally Z), namely, the linear dependence on γ and on γ^{-1} for $\gamma \to 0$ and for $\gamma \to \infty$, respectively, is related to the presence of the two consecutive processes. The rate of energy accumulation in the well is proportional to γ which measures the strength of coupling of the system to the surrounding thermal bath. For low friction this becomes the rate determining step. For high friction the barrier crossing becomes the rate determining step and it becomes inversely proportional to the friction.

For a double well appropriate for modeling isomerization processes there is another mechanism that makes the rate linear in γ for small γ—the back scattering of unrelaxed particles from the far wall of the product well. This effect has been investigated numerically by Montgomery, Chandler, and Berne[20] and will be discussed within the present formalism in a separate publication.[21]

(f) A simple approximation to (4.1) may be tried. In this approximation we replace $\tau(J_1,J_0)$ by the Kramers approximation

$$\tau(J_1,J_0) \simeq \frac{k_B T}{\gamma J_1 \omega_0} \exp(E_1/k_B T) \quad \text{(Markovian)} \tag{4.15a}$$

noting that the same kind of approximation also leads to

$$\tau(J_1,J_0) \simeq \frac{k_B T}{\epsilon(J_1)\omega(J_1)\omega_0} \exp(E_1/k_B T) \quad \text{(non-Markovian)} . \tag{4.15b}$$

We also replace S by 1, noting that it takes this value if γ is large enough for the $S r_K^{-1}$ term to dominate Eq. (4.1). With these approximations we get

$$r_1 = \left[\frac{k_B T}{\epsilon(J_1)\omega(J_1)\omega_0} e^{E_1/k_B T} + \frac{2\pi\omega_B}{\lambda_0 \omega_0} e^{E_B/k_B T} \right]^{-1} , \tag{4.16}$$

where λ_0 is given by (4.4) and where the factor $\epsilon(J_1)\omega(J_1)$ goes to γJ_1 in the Markovian limit. Comparing results based on (4.16) to those obtained using Eq. (4.1) we have seen that Eq. (4.16) provides a reasonable approximation (error less than 20%) in the Markovian limit; however, it seems to fail in non-Markovian cases.

To further investigate the dependence of the steady-state rate on the parameters characterizing the system we have carried numerical computations of Eq. (4.1). This involves numerical integrations of Eq. (4.2) and of Eqs. (4.5) and (4.6) and a numerical solution (by iteration) of Eq. (4.7) to find E_1. All these are simple numerical procedures. In the non-Markovian case we also have to obtain λ_0 [by solving Eq. (1.20)] and $\epsilon(J)$. The procedure used for the latter is described in Appendix D.

The potential used for these calculations is

$$V(x) = D \left[\exp\left[-\frac{x}{a} \right] - \exp\left[-\frac{x}{b} \right] \right]^2 \tag{4.17}$$

for which we have taken $a/b = 20$. This implies $E_B = 0.658D$ and $\omega_0/\omega_B = 5.236$. This potential is shown in Fig. 1. In Fig. 2 we show the results for E_1 as a function of the friction γ obtained from Eqs. (4.7) for the Markovian case, $\omega_0 \tau_c = 0$, and for the non-Markovian model, Eqs. (1.10)–(1.12) with $\omega_0 \tau_c = 10$. As seen in Fig. 2, E_1 is close to E_B for low friction and is decreased abruptly to zero in the range $\gamma \sim 0.1 \cdots 1.0\omega_0$.

Non-Markovian effects enter into our results in the barrier functions, Eq. (1.14)–(1.20), and in the well function $\epsilon(J)$, Eqs. (1.22) and (D5). The former were investigated by Grote and Hynes.[6] Figure 3 depicts the behavior of the function $\epsilon(J)\omega(J)/\gamma J$ (which is unity in the Markovian limit) calculated for the potential of Fig. 1 and the model (1.10)–(1.12). We see that the deviation of this function from its Markovian limit are large through almost all the energy range. It should be noted, however, that for cases where the escape is dominated by the dynamics very close

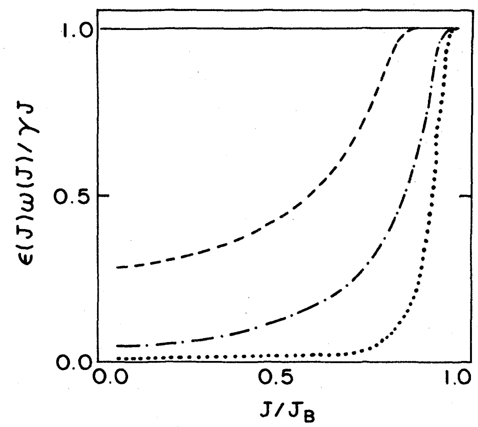

FIG. 3. $\epsilon(J)\omega(J)/\gamma J$ vs J/J_B. Solid line: $\omega_0\tau_c=0$. Dashed line: $\omega_0\tau_c=2$. Dotted-dashed line: $\omega_0\tau_c=4$. Dotted line: $\omega_0\tau_c=10$.

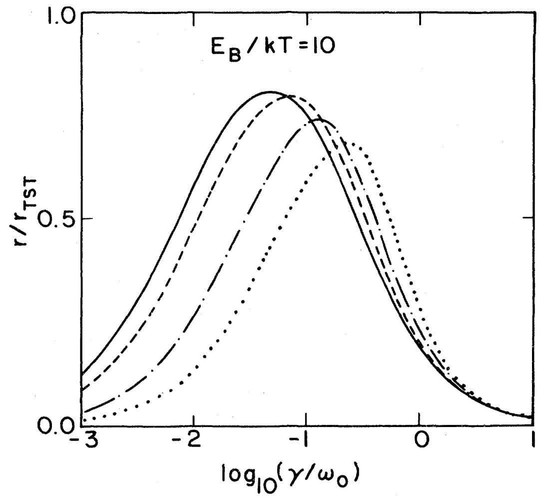

FIG. 5. Same as for Fig. 4 with $E_B=10k_BT$.

to the barrier top (very deep wells and friction not too small) this will not affect the escape rate (but will have strong effects on the rate of energy relaxation in the well).

Figures 4 and 5 display the behavior of the escape rate, Eq. (4.1) as a function of the friction for the potential (4.17) with barrier energies $4k_BT$ and $10k_BT$ and for different values of the correlation time τ_c. These results display the features discussed above. We have also compared some of our results in Fig. 4 to numerical simulations using stochastic classical trajectories based on Eqs. (1.7) and (1.8). Excellent agreement with the analytical results is obtained. Similar agreement in the non-Markovian low viscosity case has been obtained previously.[5]

The numerical results obtained above (Figs. 4 and 5) show that the range of weak dependence on the friction γ may be as large as one decade of the friction. This explains the success of transition state theory which, with a corrective "steric" factor can account for many condensed phase reactions. As seen from the present result this correction factor is not necessarily steric in origin. To go from the friction scale used in this study to the experimental viscosity scale is a rather ambiguous process which involves some bold assumptions.[22] If we adopt the simplest hard-sphere relation $\gamma=n\pi\eta R/M$, where n is an integer depending on the (slip or stick) boundary condition on the particle's surface and where η is the solvent's viscosity, we obtain $\gamma\sim10^{12}-10^{14}$ sec^{-1} for a range of normal solvents at normal temperature. Typical values of the parameters characterizing the potential surface are $\omega_0\sim10^{14}-10^{15}$ sec^{-1} and $\omega_B\sim10^{12}-10^{14}$ sec^{-1}. In addition to this, it should be kept in mind that the actual time scale for thermal relaxation is determined not by γ but by $\hat{Z}(\omega)$ [where ω is the local frequency, i.e., $\omega(J)$ in the well and ω_B during the barrier crossing] which is less than γ and which, deep in the well, may be in fact orders of magnitude smaller than γ.[23] Unfortunately, no reliable results for $\hat{Z}(\omega)$ in liquids exist in the molecular frequency range.[24]

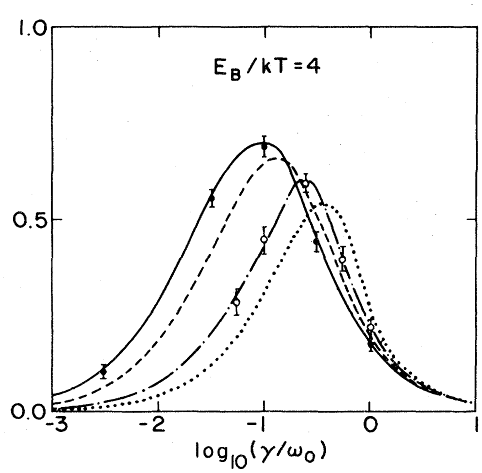

FIG. 4. Escape rate r as a function of friction γ for a particle moving in the potential (4.17) with $a/b=20$ (implying $E_B=0.6580$ and $\omega_0/\omega_B=5.236$) and with $E_B=4k_BT$. Solid line: $\omega_0\tau_c=0$. Dashed line: $\omega_0\tau_c=2$. Dotted-dashed line: $\omega_0\tau_c=4$. Dotted line: $\omega_0\tau_c=10$. Circles with error bars are results of numerical simulations based on the Langevin equation (1.7). Closed circles: $\omega_0\tau_c=0$. Open circles: $\omega_0\tau_c=4$.

There have been in recent years a number of experimental works[25–27] in which chemical reaction rates were studied as functions of pressure and solvent viscosity. Most relevant to the present work are the results of Velsko, Waldeck, and Fleming[26(a)] on the isomerization rate of 3.3′ diethyloxadicarbocyanine iodide which were interpreted using non-Markovian barrier dynamics[22,26,28] and the results of Hasha, Eguchi, and Jonas[27] which have demonstrated for the conformational isomerization of cyclohexane that the rate indeed goes through a maximum as a function of the solvent viscosity, as implied by Eq. (4.1) or the approximation (4.16). A fuller discussion of these results should, however, be made in terms of a double well model.[21]

V. CONCLUSION

In this paper we have derived a general expression for the escape rate of a particle out of a potential well. Our result, Eq. (4.1), is valid for Markovian as well as for non-Markovian dynamics and throughout all the friction range. A simple approximation to (4.1), Eq. (4.16), has been shown to be quite accurate for most applications. These results should be useful as simple models for chemical reactions in condensed phases. The formalism used in the present work is applicable also for more complicated situations (double well, location dependent friction and multimode dynamics). Work in these directions is currently in progress.

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APPENDIX A

Here we show that λ_0 appearing in Eq. (1.14),

$$\lambda_0=\lim_{t\to\infty}\left\{\left[\left[\frac{\bar{\gamma}(t)}{2}\right]^2+\bar{\omega}_B^2(t)\right]^{1/2}-\frac{\bar{\gamma}(t)}{2}\right\}, \quad \text{(A1)}$$

is the largest (real and positive) root of [Eq. (1.20)]

$$\lambda^2-\omega_B^2+\lambda\hat{Z}_1(-i\lambda)=0 . \quad \text{(A2)}$$

This result was previously obtained by Hanggi and is stated without proof in Eq. (4.20) of Ref. 4(b). The roots of these equations are poles of $\hat{\rho}(\lambda)$ [Eq. (1.19)]

$$\hat{\rho}(\lambda)=\frac{1}{\lambda^2-\omega_B^2+\lambda\hat{Z}_1(-i\lambda)} . \quad \text{(A3)}$$

The same poles govern the motion of a particle moving according to the equation of motion

$$\ddot{x}=\omega_B^2x-\int_0^t d\tau Z(t-\tau)\dot{x}(\tau) . \quad \text{(A4)}$$

For this motion, on an inverted parabolic potential we expect the real part of some of the poles to be positive. The imaginary part of the root with the largest positive real part should vanish (otherwise the long-time motion would appear as oscillation between the two sides of the potential barrier). Turning to the calculation of the right-hand side (rhs) of Eq. (A1) we first assume that Eq. (A3) may be written in the following form:

$$\hat{\rho}(\lambda)=\sum_{n=0}\sum_{m=1}^{M_N}\frac{C_{n,m}}{(\lambda-\lambda_n)^m} , \quad \text{(A5)}$$

where M_n is the multiplicity of the nth pole. The poles are in a decreasing order of their real part:

$$\lambda_0>\mathrm{Re}\lambda_1\geq\mathrm{Re}\lambda_2>\cdots . \quad \text{(A6)}$$

The function $\rho(t)$ may be obtained by taking the inverse Laplace transform of Eq. (A5)

$$\rho(t)=\sum_{n=0}\sum_{m=1}^{M_n}\frac{C_{n,m}}{(m-1)!}t^{m-1}e^{\lambda_n t} . \quad \text{(A7)}$$

We now use Eq. (A7) in Eqs. (1.15)–(1.18) where we keep in the above expansion only leading terms at a long enough time. The procedure described below indicates that the following terms should be considered:

$$\rho(t)\to(B_1t^{M_0-1}+B_2t^{M_0-2})e^{\lambda_0 t}+B_3t^{M_1-1}e^{\lambda_1 t}+B_4t^{M_2-1}e^{\lambda_2 t} , \quad \text{(A8)}$$

where

$$B_1=C_{0,M_0}/(M_0-1)! ,$$
$$B_2=C_{0,M_0-1}/(M_0-2)! ,$$
$$B_3=C_{1,M_1}/(M_1-1)! ,$$
$$B_4=C_{2,M_2}/(M_2-1)! . \quad \text{(A9)}$$

Note that the term involving t^{M_0-2} in the rhs of Eq. (A8) appears only if $M_0>1$.

We distinguish between three different cases: case 1—$M_0=1$ and $\lambda_1=\lambda_2^*$; case 2—$M_0=1$ and $\mathrm{Re}\lambda_1>\mathrm{Re}\lambda_2$, $\mathrm{Im}\lambda_1=0$; case 3—$M_0>1$. For these three cases we evaluate $\bar{\gamma}(t)$ and $\bar{\omega}_B^2(t)$ in the limit $t\to\infty$.

Case 1:

In this case $M_1=M_2$ and $B_3=B_4$ and we denote

$$\lambda_1=\mu+i\nu . \quad \text{(A10)}$$

using this in Eq. (A8) we get

$$\rho(t)\to B_1e^{\lambda_0 t}+2e^{\mu t}t^{M_1-1}\mathrm{Re}(B_3e^{i\nu t}) \quad \text{(A11)}$$

and when we use Eq. (A11) to evaluate Eqs. (1.17) and (1.18) we find

$$\Phi(t)\to2\omega_B^2B_1e^{(\lambda_0+\mu)t}t^{M_1-1}\mathrm{Re}\left[\frac{B_3(\lambda_0-\lambda_1)^2}{\lambda_0\lambda_1}e^{i\nu t}\right] , \quad \text{(A12)}$$

$$\Theta(t)\to2\omega_B^2B_1e^{(\lambda_0+\mu)t}t^{M_1-1}\mathrm{Re}(B_3(\lambda_0-\lambda_1)^2e^{i\nu t}) . \quad \text{(A13)}$$

Inserting the last results into Eqs. (1.15) and (1.16) we get

$$\bar{\gamma}(t)\to-[\lambda_0+\mu-\nu D(t)] , \quad \text{(A14)}$$

$$\bar{\omega}_B^2(t)\to-\lambda_0[\mu-\nu D(t)] , \quad \text{(A15)}$$

where

$$D(t)=\frac{\mathrm{Im}\left[\frac{B_3(\lambda_0-\lambda_1)^2}{\lambda_0\lambda_1}e^{i\nu t}\right]}{\mathrm{Re}\left[\frac{B_3(\lambda_0-\lambda_1)^2}{\lambda_0\lambda_1}e^{i\nu t}\right]} . \quad \text{(A16)}$$

Note that $\bar{\gamma}(t)$ and $\bar{\omega}_B^2(t)$ do not approach any limit since $D(t)$ oscillates.

Case 2:

In this case the leading terms of Eq. (A8) are

$$\rho(t)\to B_1e^{\lambda_0 t}+B_3t^{M_1-1}e^{\lambda_1 t} . \quad \text{(A17)}$$

Using this for Eq. (1.17) and (1.18) we find

$$\Phi(t)\to\omega_B^2\frac{B_1B_3(\lambda_0-\lambda_1)^2}{\lambda_0\lambda_1}t^{M_1-1}e^{(\lambda_0+\lambda_1)t}, \quad (A18)$$

$$\Theta(t)\to\lambda_0\lambda_1\Phi(t). \quad (A19)$$

Inserting the last results into Eq. (1.15) and (1.16) we get

$$\overline{\gamma}(t)\to-(\lambda_0+\lambda_1), \quad (A20)$$

$$\overline{\omega}_B^2(t)\to-\lambda_0\lambda_1. \quad (A21)$$

Case 3:

In this case only the first two terms of the rhs of Eq. (A8) remain

$$\rho(t)\to(B_1t^{M_0-1}+B_2t^{M_0-2})e^{\lambda_0 t}. \quad (A22)$$

From Eqs. (1.17) and (1.18) we get

$$\Phi(t)\to\left[\frac{\omega_B}{\lambda_0}(M_0-1)B_1t^{M_0-2}e^{\lambda_0 t}\right]^2, \quad (A23)$$

$$\Theta(t)\to\lambda_0^2\Phi(t). \quad (A24)$$

By substituting Eqs. (A23) and (A24) into Eqs. (1.15) and (1.16) we obtain

$$\overline{\gamma}(t)\to-2\lambda_0, \quad (A25)$$

$$\overline{\omega}_B^2(t)\to-\lambda_0^2. \quad (A26)$$

In all these cases [Eqs. (A14) and (A15) (A20) and (A21), and (A25) and (A26)] we get

$$\left[\left[\frac{\overline{\gamma}(t)}{2}\right]^2+\overline{\omega}_B^2(t)\right]^{1/2}-\frac{\overline{\gamma}(t)}{2}\to\lambda_0 \quad (A27)$$

which is the desired result.

APPENDIX B

Here we calculate approximately the normalization factor

$$N=\int_{-\infty}^{0}dx\int_{-\infty}^{\infty}dv\,P(x,v). \quad (B1)$$

We use the expressions derived in Sec. III (non-Markovian case) from which the Markovian counterparts may be easily obtained by replacing $\overline{\alpha}$ by α and $\epsilon(J)$ by $\gamma J/\omega(J)$. Thus,

$$P(x,v)=\begin{cases}\frac{M}{2\pi}P_W(J), & J\le J_1\\ P_B(x,v), & x\ge x_1\end{cases} \quad (B2)$$

where $P_W(J)$ and $P_B(x,v)$ are given by

$$P_W(J)=\begin{cases}A_0e^{-E(J)/k_BT}, & J\le J_0\\ Ae^{-E(J)/k_BT}\left[B+\int_J^{J_1}\frac{dJ'}{\epsilon(J')}e^{E(J)/k_BT}\right], & J_0\le J\le J_1\end{cases} \quad (B3)$$

where

$$A_0=A\left[B+\int_{J_0}^{J_1}\frac{dJ}{\epsilon(J)}e^{E(J)/k_BT}\right] \quad (B4)$$

and

$$P_B(x,v)=F_2\left[\left[\frac{\pi k_BT}{2M\overline{\alpha}}\right]^{1/2}+\int_0^{v-|\Gamma|x}dz\exp\left[-\frac{\overline{\alpha}Mz^2}{2k_BT}\right]\right]\times\exp[-E(x,v)/k_BT], \quad (B5)$$

where

$$E(x,v)=\frac{Mv^2}{2}+V(x). \quad (B6)$$

F_2 and B are given in terms of A by Eqs. (3.17) and (3.18). The required normalization factor will be calculated as a sum of three terms

$$N=N_W+N_B+N'. \quad (B7)$$

N_W is the contribution from the $J<J_1$ region

$$N_W=\int dx\int dv\,P(x,v)\eta(E_1-E(x,v)) \quad (B8)$$

[$\eta(E)=1$ for $E>0$, $\eta(E)=0$ for $E\le0$]. Using Eq. (B2) this may also be written in the form (note that $dx\,dv\to1/M dJ\,d\varphi$)

$$N_W=\int_0^{J_1}dJ\,P_W(J). \quad (B9)$$

N_B is the contribution from the barrier region

$$N_B=\int_{x_1}^{0}dx\int_{-\infty}^{\infty}dv\,P_B(x,v). \quad (B10)$$

N' is the contribution from the region $E>E_1$, $x<x_1$

$$N'=\int_{-\infty}^{x_1}dx\int_{-\infty}^{\infty}dv\,P(x,v)\eta(E(x,v)-E_1). \quad (B11)$$

This is the most problematic contribution since we do not actually have an expression for $P(x,v)$ in this region.

Evaluation of N_W: Inserting Eqs. (B3) and (B4) into (B9) we get

$$N_W=AB\int_0^{J_1}dJ\,e^{-E(J)/k_BT}+A\int_{J_0}^{J_1}\frac{dJ}{\epsilon(J)}e^{E(J)/k_BT}\int_0^{J_1}dJ\,e^{-E(J)/k_BT}+A\int_{J_0}^{J_1}dJ\,e^{-E(J)/k_BT}\int_J^{J_1}\frac{dJ'}{\epsilon(J')}e^{E(J')/k_BT}.$$

Integrating the third term in this expression by parts it can be shown to be equal to

$$A\int_{J_0}^{J_1}\frac{dJ}{\epsilon(J)}e^{E(J)/k_BT}\int_{J_0}^{J}dJ'e^{-E(J')/k_BT}.$$

Adding the second and third terms together we finally obtain

$$N_W=AB\int_0^{J_1}dJ\,e^{-E(J)/k_BT}+Ak_BT\tau, \quad (B12)$$

where

$$\tau=\frac{1}{k_BT}\int_{J_0}^{J_1}\frac{dJ}{\epsilon(J)}e^{E(J)/k_BT}\int_0^J dJ' e^{-E(J')/k_BT} \quad \text{(B13)}$$

is the mean first passage time to reach J_1, starting from J_0 $(0<J_0<J_1)$ given a reflecting barrier at $J=0$.

Evaluation of N_B: First calculate the function $C(x)\equiv\int_{-\infty}^{\infty}dv\,P_B(x,v)$. Using Eqs. (B5) and (B6) it takes the form

$$C(x)=F_2 e^{-V(x)/k_BT}\left[\frac{\pi k_BT}{M(\bar\alpha)^{1/2}}+L(x)\right], \quad \text{(B14)}$$

where

$$L(x)=\int_{-\infty}^{\infty}dv\exp\left[-\frac{Mv^2}{2k_BT}\right]\times\int_0^{v-|\Gamma|x}dz\exp\left[-\frac{\bar\alpha Mz^2}{2k_BT}\right]. \quad \text{(B15)}$$

$L(x)$ is calculated by first evaluating its derivative

$$\frac{dL(x)}{dx}=-|\Gamma|\int_{-\infty}^{\infty}dv\exp\left[-\frac{Mv^2}{2k_BT}\right]\times\exp\left[-\frac{\bar\alpha M(v-|\Gamma|x)^2}{2k_BT}\right]. \quad \text{(B16)}$$

The v integral may be evaluated to give

$$\frac{dL(x)}{dx}=-|\Gamma|\left[\frac{2\pi k_BT}{M(\bar\alpha+1)}\right]^{1/2}\exp\left[-\frac{M\bar\alpha\Gamma^2x^2}{2k_BT(\bar\alpha+1)}\right]. \quad \text{(B17)}$$

From (B15) it follows that $L(x=0)=0$ [the integrand in (B15) is then an odd function of v]. Therefore, by integrating (B17) we get

$$L(x)=-\frac{\pi k_BT}{M(\bar\alpha)^{1/2}}\text{erf}\left[\left[\frac{M\bar\alpha\Gamma^2}{2k_BT(\bar\alpha+1)}\right]^{1/2}\right]=\frac{\pi k_BT}{M(\bar\alpha)^{1/2}}\text{erf}\left[\left[\frac{M\bar\alpha\Gamma^2x^2}{2k_BT(\bar\alpha+1)}\right]^{1/2}\right] \quad \text{for } x<0\,. \quad \text{(B18)}$$

Finally we use Eq. (3.11) to show that $\bar\alpha\Gamma^2/(\bar\alpha+1)=\omega_B^2$. Equations (B14) and (B18) then give

$$C(x)=F_2\frac{\pi k_BT}{M(\bar\alpha)^{1/2}}e^{-V(x)/k_BT}\times\left\{1+\text{erf}\left[\left[\frac{M\omega_B^2x^2}{2k_BT}\right]^{1/2}\right]\right\} \quad \text{(B19)}$$

for which N_B is obtained as

$$N_B=\int_{-|x_1|}^{0}dx\,C(x)\,. \quad \text{(B20)}$$

Evaluation of N'. As noted above the exact form of the distribution $P(x,v)$ is not known in the $x<x_1$, $E>E_1$ region. However, an approximate expression for N' valid for deep enough wells may be obtained using the observation that for low friction $E_1\gg k_BT$ [E_1, the solution of Eq. (3.19), is depicted in Fig. 2] and N' (as well as N_B) is negligible relative to N_W, while for large friction (where E_1 is smaller and N' may contribute significantly) the distribution in the $x<x_1$, $E>E_1$ region (as well as in the $E<E_1$ region) may be taken as the Boltzman distribution from $P_B(x,v)$ for $x\to-\infty$ [Eq. (2.14) with α replaced by $\bar\alpha$]. This leads to

$$N'=F_2\left[\frac{2\pi k_BT}{M\alpha}\right]^{1/2}\int_{-\infty}^{x_1}dx\int_{-\infty}^{\infty}dv\exp\left[-\frac{E(x,v)}{k_BT}\right]\times\eta(E(x,v)-E_1)\,. \quad \text{(B21)}$$

Using now Eqs. (B7), (B12), (B19), (B20), (B21), and (3.18) we obtain

$$N=Ak_BT\tau+A\left[\frac{\bar\alpha+1}{\bar\alpha}\right]^{1/2}e^{E_B/k_BT}M(I_1+I_2+I_3) \quad \text{(B22)}$$

with

$$I_1=\frac{\pi}{M}(1+\text{erf}\{[(\bar\alpha+1)(E_B-E_1)/k_BT]^{1/2}\})\times\int_0^{J_1}dJ\,e^{-E(J)/k_BT}\,, \quad \text{(B23)}$$

$$I_2=\int_{-\infty}^{x_1}dx\int_{-\infty}^{\infty}dv\exp[-E(x,v)/k_BT]\eta[E(x,v)-E_1]\,, \quad \text{(B24)}$$

$$I_3=\left[\frac{\pi k_BT}{2M}\right]^{1/2}\int_{x_1}^{0}dx\exp[-V(x)/k_BT]\times\left\{1+\text{erf}\left[\left[\frac{M\omega_B^2x^2}{2k_BT}\right]^{1/2}\right]\right\}. \quad \text{(B25)}$$

Consider first I_1. Denote

$$R=\text{erf}\{[(\bar\alpha+1)(E_B-E_1)/k_BT]^{1/2}\} \quad \text{(B26)}$$

and note that

$$2\pi\int dJ\,f(J)=M\int dx\int dv\,f[J(x,v)]\,.$$

Therefore,

$$I_1=\frac{1+R}{2}\int_{-\infty}^{0}dx\int_{-\infty}^{\infty}dv\exp[-E(x,v)/k_BT]\times\eta(E_1-E(x,v))\,. \quad \text{(B27)}$$

Next consider I_3. We remind ourselves that the term containing $I_3(N_B)$ may contribute significantly to the total sum N only for large enough γ (small E_1; this is a similar argument used before to evaluate N'). In the x integral appearing in I_3 the close neighborhood of x_1 contributes dominantly and if

$$(\tfrac{1}{2})M\omega_B^2 x_1^2 = E_B - E_1 \gg k_B T$$

we may replace the error function in I_3 by unity. Hence,

$$I_3 \simeq \left[\frac{2\pi k_B T}{M}\right]^{1/2} \int_{x_1}^{0} dx \exp[-V(x)/k_B T]$$
$$= \int_{x_1}^{0} dx \int_{-\infty}^{\infty} dv \exp[-E(x,v)/k_B T] \ . \tag{B28}$$

Note that since x_1 is the lower limit in the x integration the energy range in the latter integral is automatically limited to $E(x,v) > E_1$. From Eqs. (B28) and (B24) we obtain

$$I_2 + I_3 = \int_{-\infty}^{0} dx \int_{-\infty}^{\infty} dv \exp[-E(x,v)/k_B T] \times \eta(E(x,v) - E_1) \tag{B29}$$

and also using (B27) together with the transformation

$$\int dx \int dv = \frac{1}{M} \int dJ \int d\varphi = \frac{2\pi}{M} \int \frac{dE}{\omega(E)}$$

(for an integrand which depends on E only), noting also that for $E_B \gg k_B T$ we can limit the E integration to $E \le E_B$, we get

$$I_1 + I_2 + I_3 = \frac{2\pi}{M} \int_0^{E_B} \frac{dE}{\omega(E)} e^{-E/k_B T} \left[\frac{1+R}{2}\eta(E_1 - E) + \eta(E - E_1)\right] . \tag{B30}$$

Finally, we use Eq. (B22) and the identity

$$\left[\frac{\bar{\alpha}+1}{\bar{\alpha}}\right]^{1/2} = \frac{\omega_B}{\left[\left[\dfrac{\bar{\gamma}}{2}\right]^2 + \bar{\omega}_B^2\right]^{1/2} - \dfrac{\bar{\gamma}}{2}} \tag{B31}$$

together with

$$r_{K,NM} = \frac{\omega_0}{2\pi\omega_B} \left\{ \left[\left[\frac{\bar{\gamma}}{2}\right]^2 + \bar{\omega}_B^2\right]^{1/2} - \frac{\bar{\gamma}}{2} \right\} \exp(-E_B/k_B T) \tag{B32}$$

to arrive at Eq. (3.20).

APPENDIX C

Define $\bar{\Gamma}(t)$ as the solution of the quadratic equation

$$\frac{\omega_B^2}{\bar{\Gamma}(t)} = \bar{\gamma}(t) + \bar{\Gamma}(t)\frac{\bar{\omega}_B^2(t)}{\omega_B^2} , \tag{C1}$$

namely,

$$\bar{\Gamma}(t) = -\frac{\omega_B^2}{\bar{\omega}_B^2(t)} \left\{ \frac{\bar{\gamma}(t)}{2} \pm \left[\left[\frac{\bar{\gamma}(t)}{2}\right]^2 + \bar{\omega}_B^2(t)\right]^{1/2} \right\} . \tag{C2}$$

These two roots may be written in the forms

$$\bar{\Gamma}_1 = \frac{\omega_B}{\dfrac{\bar{\gamma}}{2} - \left[\left[\dfrac{\bar{\gamma}}{2}\right]^2 + \bar{\omega}_B^2\right]^{1/2}} , \tag{C3}$$

$$\bar{\Gamma}_2 = \frac{\omega_B}{\dfrac{\bar{\gamma}}{2} + \left[\left[\dfrac{\bar{\gamma}}{2}\right]^2 + \bar{\omega}_B^2\right]^{1/2}} . \tag{C4}$$

The condition (3.6) is equivalent to the requirement

$$\Gamma = \lim_{t\to\infty} \bar{\Gamma}(t) . \tag{C5}$$

If this limit exists then Eq. (3.4) admits a steady-state solution which satisfies the equation

$$\frac{k_B T}{M}\frac{d^2F}{du^2} + \bar{\alpha}u\frac{dF}{du} = 0 \tag{C6}$$

with

$$\bar{\alpha} = \frac{\omega_B^2}{\Gamma^2 - \omega_B^2} . \tag{C7}$$

The existence of a limit is insured for Γ_1 (see Appendix A). Note that $\bar{\Gamma}_1$ is also the root which in the Markovian limit ($\bar{\omega}_B^2 \to \omega_B^2, \bar{\gamma} \to \gamma$) becomes Γ of Eq. (2.9) and which in this limit yields $\bar{\alpha} \to \alpha$. In contrast to the Markovian case we could neither prove generally that $\omega_B^2/(\bar{\Gamma}_1^2 - \omega_B^2) > 0$ nor that $\omega_B^2/(\bar{\Gamma}_2^2 - \omega_B^2) > 0$. Thus, there is no absolute insurance that only one of the roots obtained here or that any of them corresponds to a physically relevant solution. The same problem exists in the formations of Grote and Hynes[3] and of Hanggi and Mojtabai.[4] Here we follow these authors in choosing Γ_1 as the only relevant root and in assuming that the corresponding $\bar{\alpha}$ is positive.

APPENDIX D

Here we provide some details concerning the numerical evaluation of the function $\epsilon(J)$ given by [cf. Eq. (1.22)]

$$\epsilon(J) = 2M \sum_{n=1}^{\infty} n^2 |X_n(J)|^2 \mathrm{Re}\{\hat{Z}_n[\omega(J)]\} . \tag{D1}$$

Taking the derivative of Eq. (1.23) with respect to time [using $d\varphi/dt = \omega(J)$] we get

$$v = \dot{x} = i\omega(J) \sum_{n=-\infty}^{\infty} n x_n(J) \exp(in\varphi) \tag{D2}$$

and hence,

$$v(0)v(t) = -\omega^2(J) \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} nm x_n(J) x_m(J) \times \exp[i(n+m)\varphi_0 + in\omega(J)t] , \tag{D3}$$

where $\varphi_0=\varphi(t=0)$. Averaging (D3) over the initial phases, using

$$\int_0^{2\pi} d\varphi_0 \exp[i(n+m)\varphi_0]=2\pi\delta_{n,-m} ,$$

we get

$$\langle v(0)v(t)\rangle=\omega^2(J)\sum_{n=-\infty}^{\infty} n^2|x_n(J)|^2\exp[in\omega(J)t] . \quad \text{(D4)}$$

Comparing Eqs. (D1) and (D4) we have

$$\epsilon(J)=\frac{M}{\omega^2(J)}\int_0^\infty dt\, Z(t)\langle v(0)v(t)\rangle . \quad \text{(D5)}$$

This result was originally obtained by Grote and Hynes.[6] Since $Z(t)$ is usually a rapidly decaying function of time, this provides a convenient way to evaluate $\epsilon(J)$. This is done by solving for the isolated system trajectory for the energy $E(J)$ [using Eq. (1.7) without the Z and R terms], evaluating $\langle v(0)v(t)\rangle$ as

$$\frac{\omega(J)}{2\pi}\oint d\tau\, v(\tau)v(t+\tau)$$

($\oint$ denotes integration over a period) and then performing the second integral in Eq. (D5) to obtain $\epsilon(J)$.

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[17]Note that the average (1.25) which should be formally taken has no consequence for the escape rate from deep wells. The reason is that $\tau(J_B,J_0)$ is a very weak function of J_0 for such J_0 for which the population in the well is appreciable [see comment (b) in Sec. IV].
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