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Peter Talkner, Hans-Benjamin Braun

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Peter Talkner and Hans-Benjamin Braun

Transition rates of a non-Markovian Brownian particle in a double well potential

Peter Talkner
Institut für Physik, Universität Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland
Hans-Benjamin Braun
Theoretische Physik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

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The transition rate of a non-Markovian Brownian particle in a double well potential is determined analytically by means of asymptotic methods and compared with both current theories and numerical simulations by Straub, Borkovec, and Berne [J. Chem. Phys. **83**, 3172 (1985)]. We obtain good agreement with these simulations. The ranges of validity for the different current theories which we find do, however, not exhaust the complete parameter range. In particular, for large static friction we identify a region of bath correlation times in which the rate differs grossly from the value predicted by either Grote–Hynes theory or non-Markovian energy diffusion. Additionally, corrections to the Grote–Hynes rate are determined and an analytical expression for the non-Markovian energy diffusion rate is obtained.

I. INTRODUCTION

The movement of a Brownian particle in a potential with different locally stable states is frequently employed as a model for chemical reactions. The reaction rates are then identified with the rates at which the Brownian particle moves from one locally stable state to another one. This model has been established by Kramers[1] and during the past decade has witnessed a renaissance.[2]

As already pointed out by Kramers,[1] two regimes of different rate limiting mechanisms must be distinguished: In one regime the particle experiences weak frictional forces. Consequently, the energy of the particle is slowly varying and energy diffusion becomes the relevant rate limiting process. In the second regime, for intermediate and strong friction, the rate is determined by a diffusion process in phase space. In both cases the rate can be represented as a product of the rate predicted by the transition state theory, k_{TST}, and a correction factor f,

$$k = f k_{\mathrm{TST}}. \tag{1.1}$$

In the second regime the correction factor depends solely on the dynamics in the linear vicinity of the saddle point which lies on the most probable trajectory joining two adjacent wells. According to current theories for a non-Markovian process the correction factor f should still solely be determined by the linear dynamics at the saddle point.[3,4]

This simple picture was spoiled by numerical simulations of a non-Markovian Brownian motion in a double well potential by Straub, Borkovec, and Berne[5] (SBB). Whereas for small and intermediate damping theory and simulation agree, for large values of the damping constant the correction factor f depends strongly on the well dynamics leading to discrepancies up to orders of magnitude between current theories and simulations. Several facts indicate an energy-like-diffusion mechanism to be rate limiting for large values of the damping constant γ:

(i) the energy diffusion rate depends on the well dynamics, indeed.

(ii) In the particular model of SBB for large γ the energy dissipation rate is inversely proportional to γ consequently leading to small energy dissipation.

(iii) A properly defined memory-renormalized damping constant becomes arbitrarily small for large γ indicating the failure of the Grote–Hynes theory.[2]

Nevertheless, non-Markovian energy diffusion may still give rates grossly deviating from the simulated data. It has been claimed that spatial diffusion should lead to the observed decrease of the rate.[6] However, the trajectories one would expect in the case of spatial diffusion would have a rather different appearance than those found by SBB.

Zwanzig[7] and one of the present authors[8] have pointed out, that for infinite damping in the absence of noise the particle undergoes a conservative Hamiltonian dynamics with a modified energy e and an additional conserved quantity u.

In this paper we will argue that this is a main clue to the understanding of the rates at large γ.

The paper is organized as follows: In Sec. II the model is described and the conventional rate theories are sketched. An explicit expression for the non-Markovian energy diffusion rate is obtained. In Sec. III the saddle point approximation implicit in the Grote–Hynes theory is discussed and corrections are calculated. We show that for large values of γ the abovementioned modified energy e and the additional quantity u undergo a two-dimensional Markov process. This process is qualitatively different depending on whether the bath correlation time τ_C of the underlying non-Markovian process is above or below a certain threshold. In both cases the crossing of particular curves in the e–u plane indicates a transition from one well to the other. The corresponding mean first passage time yields the rate. For τ_C above the threshold the rate is inversely proportional to temperature like an energy diffusion rate. It agrees very well with the simulated data of SBB. Below the threshold the Grote–Hynes rate is recovered being in reasonable agreement with the simulated data. Section IV provides a summary.

II. THE MODEL AND THE CONVENTIONAL THEORIES

A. The model

Following SBB we consider a Brownian particle with coordinate x and velocity v, moving in a potential $U(x)$ with two symmetric wells separated by a high barrier:

$$\dot{x} = v, \tag{2.1a}$$

$$\dot{v} = -U'(x) + z, \tag{2.1b}$$

$$\dot{z} = -\frac{1}{\alpha} v - \frac{1}{\alpha\gamma} z + \frac{1}{\alpha\sqrt{\beta\gamma}} \xi(t), \tag{2.1c}$$

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

$$\langle \xi(t) \rangle = 0, \tag{2.2a}$$

$$\langle \xi(t)\xi(s) \rangle = 2\delta(t-s), \tag{2.2b}$$

and where β is the inverse temperature of the heat bath, coupled to the particle. The meaning of the variable z and the positive constants α and γ becomes evident if the third equation (2.1c) is integrated to yield together with Eqs. (2.1a) and (2.1b) a two-dimensional non-Markovian process, rather than the three-dimensional Markovian process (2.1a)–(2.1c):

$$\dot{x} = v, \tag{2.3a}$$

$$\dot{v} = -U'(x) - \int_{-\infty}^{t} \zeta(t-s)v(s)ds + R(t), \tag{2.3b}$$

where the Gaussian random force $R(t)$ satisfies the fluctuation dissipation theorem

$$\langle R(t)R(s) \rangle = \beta^{-1}\zeta(t-s) \tag{2.4}$$

and where the memory kernel $\zeta(t)$ reads

$$\zeta(t) = \alpha^{-1}e^{-t/\tau_C}. \tag{2.5}$$

Hence, $\tau_C = \alpha\gamma$ is the correlation time of the noise and γ is the static friction:

$$\gamma = \int_0^\infty \zeta(t)dt. \tag{2.6}$$

For the sake of simplicity we consider a piecewise parabolic potential $U(x)$:

$$U(x) = \begin{cases} -\frac{1}{2}\omega_B^2 x^2, & |x| < l \\ \frac{1}{2}\omega_0^2 \left\{ x \mp l \left[1 + \left(\frac{\omega_B}{\omega_0} \right)^2 \right] \right\}^2 - Q, & x \gtrless \pm l \end{cases}, \tag{2.7}$$

where Q is the barrier height:

$$Q = \frac{1}{2}\omega_B^2 \left[1 + \left(\frac{\omega_B}{\omega_0} \right)^2 \right] l^2 \tag{2.8}$$

and where ω_0 and ω_B are the well and barrier frequencies, respectively. The points $x = \pm l$ separate the barrier from the well regions.

To the Markovian Langevin equations (2.1) Fokker–Planck equation belongs governing the time evolution of the probability density $p(x,v,z;t)$ in the enlarged phase space spanned by x, v, and z:

$$\dot{p}(x,v,z;t) = Lp(x,v,z;t), \tag{2.9}$$

where

$$L = -\frac{\partial}{\partial x} v + \frac{\partial}{\partial v} [U'(x) - z] + \frac{\partial}{\partial z} \left(\frac{1}{\alpha} v + \frac{1}{\alpha\gamma} z \right) + \frac{1}{\alpha^2\beta\gamma} \frac{\partial^2}{\partial z^2}. \tag{2.10}$$

The stationary probability density w satisfying

$$Lw = 0 \tag{2.11}$$

reads

$$w(x,v,z) = Z^{-1}e^{-\beta\Phi(x,v,z)}, \tag{2.12}$$

where Φ is a generalized potential in the extended phase space:

$$\Phi(x,v,z) = \frac{1}{2} v^2 + U(x) + \frac{\alpha}{2} z^2. \tag{2.13}$$

With Eq. (2.7), the deterministic motion following from Eq. (2.1) in the limit $\beta^{-1} \to 0$ reads

$$\begin{pmatrix} \dot{x} \\ \dot{v} \\ \dot{z} \end{pmatrix} = \begin{cases} B_B \begin{pmatrix} x \\ v \\ z \end{pmatrix}, & |x| < l \\ B_0 \begin{pmatrix} x \\ v \\ z \end{pmatrix} \pm \begin{pmatrix} \omega_0^2 \left[1 + \left(\frac{\omega_B}{\omega_0} \right)^2 l \right] \\ 0 \\ 0 \end{pmatrix}, & x \gtrless \pm l \end{cases}, \tag{2.14}$$

where B_B and B_0 are the dynamical matrices in the barrier and the well region, respectively,

$$B_B = \begin{pmatrix} 0 & 1 & 0 \\ \omega_B^2 & 0 & 1 \\ 0 & -1/\alpha & -1/\alpha\gamma \end{pmatrix}, \tag{2.15}$$

$$B_0 = \begin{pmatrix} 0 & 1 & 0 \\ -\omega_0^2 & 0 & 1 \\ 0 & -\frac{1}{\alpha} & -\frac{1}{\alpha\gamma} \end{pmatrix}. \tag{2.16}$$

Clearly, this deterministic motion has two stable points $P_\pm = \{x = \pm\omega_0^2[1 + (\omega_B/\omega_0)^2]l, v = 0, z = 0\}$ and one saddle point $S = (0,0,0)$. To each stable point there belongs a domain of attraction $\Omega_\pm$ with a separatrix $\partial\Omega$ as a common boundary. In the barrier region the separatrix is a plane:

$$R \equiv bx + cv + dz = 0, \tag{2.17}$$

where (b,c,d) is the eigenvector of the transposed dynamical matrix B_B^T belonging to the unique positive eigenvalue λ_+. From Eq. (2.15) we find

$$V = \begin{pmatrix} b \\ c \\ d \end{pmatrix} = \begin{pmatrix} 1 \\ \mu/\omega_B \\ \alpha(1-\mu^2) \end{pmatrix}, \tag{2.18}$$

where

$$\mu = \lambda_+/\omega_B \tag{2.19}$$

is the positive solution of the characteristic equation, $\det(\omega_B\mu - B_B) = 0$,

$$\mu^3 + \frac{1}{\alpha^*\gamma^*}\mu^2 - \left(1 - \frac{1}{\alpha^*}\right)\mu - \frac{1}{\alpha^*\gamma^*} = 0. \tag{2.20}$$

Here we have introduced dimensionless parameters

$$\alpha^* = \alpha\omega_B^2, \tag{2.21}$$

$$\gamma^* = \gamma/\omega_B, \tag{2.22}$$

Eq. (2.20) may be transformed into

$$\frac{\mu}{1-\mu^2} = \alpha^*\mu + \frac{1}{\gamma^*}. \tag{2.23}$$

Figure 1 showing Eq. (2.23) clearly demonstrates the uniqueness of the positive solution. For later use we note as another consequence of Eq. (2.23), that this positive solution obeys the inequality

$$0 < \alpha^*(1-\mu^2) < 1. \tag{2.24}$$

B. Mean first passage time of the separatrix and the Grote–Hynes formula

The transition rate, say, from x_+ to x_- is given by the inverse mean time after which a stochastic trajectory starting in x_+ reaches x_- for the first time. In general, it would be difficult to calculate this time. Fortunately, one can often replace the condition to reach the final state by the condition to reach the separatrix for the first time. This, however, is only possible if the probability for a recrossing of the separatrix decreases rapidly as a function of the distance from the separatrix, i.e., the backscattering of a trajectory from points beyond the separatrix must be negligible.[1,2,9] If this condition is met the mean first crossing time T of the separatrix yields the rate[10]

$$k = \frac{1}{2T}. \tag{2.25}$$

T can be expressed in terms of the stationary solution w and a function a on the separatrix[9,11]:

$$T = -\frac{1}{2}\sqrt{\frac{\pi}{\beta}}\frac{\int_{\Omega_+} dx\, dv\, dz\, w}{\int_{\partial\Omega} dS_n\, wD_{nn}a}, \tag{2.26}$$

where dS_n and D_{nn} are the components transversal to the separatrix of the oriented surface element dS and of the diffusion matrix D, respectively. The function a determines the gradient of the mean first passage time at the separatrix. It satisfies there a partial differential equation

$$ga + K_\alpha\frac{\partial a}{\partial y_\alpha} - 2\beta D_{nn}a^3 = 0, \tag{2.27}$$

where y_α $(\alpha = 1,2)$ are coordinates on the separatrix, where K_α denotes the drift in the y_α direction, and where g is the normal derivative of the normal drift at the separatrix

$$g = \left.\frac{\partial K_n}{\partial n}\right|_{\text{separatrix}}. \tag{2.28}$$

For small noise, i.e., large β, the integral over Ω_+ in the numerator of Eq. (2.26) is dominated by the strong peak of w at P_+. Hence, the Gaussian approximation yields an excellent result.[12] Because on the separatrix the stationary probability has its absolute maximum at the saddle point (0,0,0) it is tempting to perform the integral in the denominator in Gaussian approximation, too. This yields for the rate[9,13]

$$k_{\mathrm{GH}} = \mu k_{\mathrm{TST}}, \tag{2.29}$$

where μ is the positive solution of Eq. (2.20) and where k_{TST} denotes the rate predicted by transition state theory

$$k_{\mathrm{TST}} = \frac{\omega_0}{2\pi}e^{-\beta Q}. \tag{2.30}$$

The rate (2.29) coincides with the result of the non-Markovian theories of Grote and Hynes[3] and Hänggi and Mojtabai.[4] It represents the asymptotic value of the rate for $\beta Q \to \infty$ while the remaining parameters ω_B/ω_0, α^* and γ^* must be kept finite. Of course, a large value of βQ alone does not yet guarantee the validity of this asymptotic result.

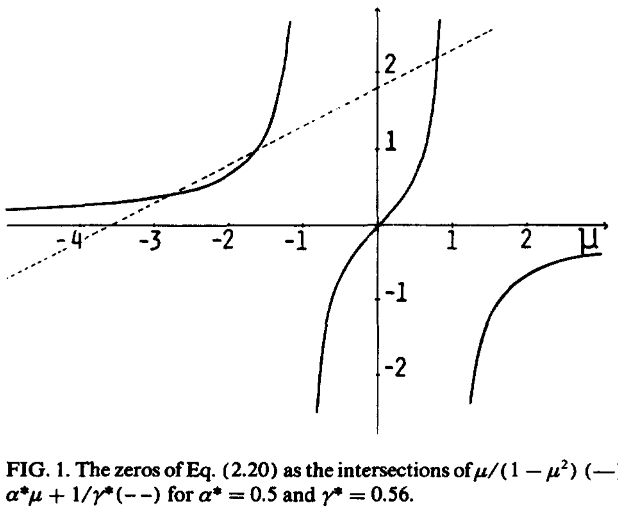

FIG. 1. The zeros of Eq. (2.20) as the intersections of $\mu/(1-\mu^2)$ (—) and $\alpha^*\mu + 1/\gamma^*$(– –) for $\alpha^* = 0.5$ and $\gamma^* = 0.56$.

C. Energy diffusion

We assume now that in the deterministic system (2.14) the dissipation of energy of the particle becomes slow, i.e., we consider the limit $\gamma \to 0$. Then, once the Brownian particle has reached the top of the barrier it will revolve many times around both stable points and will frequently cross the separatrix until it eventually thermalizes in one of the wells. Clearly, the mean first crossing time of the separatrix largely overestimates the rate. It is then more adequate to ask for the mean first time, the Brownian particle needs to acquire the energy necessary to reach the top of the barrier.

For the rate this yields[14]

$$k_{\rm ED} = \frac{\beta\omega_0}{2} e^{-\beta Q}\left[\int_{-Q}^{0} dE \frac{\omega(E)}{D(E)} e^{\beta E}\right]^{-1}, \tag{2.31}$$

where $\omega(E)$ is the frequency of the undamped deterministic system at energy E and where $D(E)$ is the diffusion constant of the energy at E. $D(E)$ can be expressed in terms of the memory function $\zeta(t)$ and the microcanonical velocity correlation function $\langle v(t)v(0)\rangle_E$ of the undamped system at energy E,

$$D(E) = \frac{1}{2\beta}\int_{-\infty}^{\infty} dt\, \zeta(t)\langle v(0)v(t)\rangle_E, \tag{2.32}$$

where we have symmetrically continued $\zeta(t)$ (2.5) for negative times

$$\zeta(-t) = \zeta(t). \tag{2.33}$$

The microcanonical correlation function can be obtained as a time average over one period of the deterministic motion at the energy E:

$$\langle v(0)v(t)\rangle_E = \frac{\omega(E)}{2\pi}\int_{-\pi/\omega(E)}^{\pi/\omega(E)} ds\, v(s)v(t+s). \tag{2.34}$$

The velocity follows from the conservation of energy

$$\tfrac{1}{2}v^2 + U(x) = E. \tag{2.35}$$

With Eq. (2.34) the factor $\omega(E)$ of the integrand in Eq. (2.31) cancels. For small negative values of the energy the factor $\omega(E)/D(E)$ of integrand in Eq. (2.31) depends only little on E. Hence, for large β the integration in Eq. (2.28) can be performed approximately to yield

$$k_{\rm ED} = \frac{\beta\omega_0}{8\pi} e^{-\beta Q}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} ds\, \zeta(t-s)v(t)v(s), \tag{2.36}$$

where the second integral extends to infinity, too, because the frequency $\omega(E)$ vanishes for $E = 0$.

From Eqs. (2.7) and (2.35) we find a trajectory with $E = 0$, that starts at $t = -\infty$ at $x = v = 0$ leaving the top of the barrier infinitely slowly, reaches its most remote point at $t = 0$ and returns to $x = 0$ after another infinite amount of time. This trajectory reads

$$x(t) = \begin{cases} l e^{\omega_B(t+t_a)}, & t \leqslant -t_a \\ l\left[1+\left(\frac{\omega_B}{\omega_0}\right)^2\right] + \frac{\sqrt{2Q}}{\omega_0}\cos\omega_0 t, & t < |t_a| \\ l e^{-\omega_B(t-t_a)}, & t \geqslant t_a \end{cases}, \tag{2.37}$$

where $-t_a$ is the time at which the particle enters the well at $x = l$ and t_a at which it leaves the well:

$$\cos\omega_0 t_a = -\frac{\omega_B}{\omega_0}\left[1+\left(\frac{\omega_B}{\omega_0}\right)^2\right]^{-1/2}. \tag{2.38}$$

With the velocity following from Eq. (2.37) and with Eqs. (2.5), (2.30), and (2.33) the integrals in Eq. (2.36) can exactly be performed to yield for the rate

$$\frac{k_{\rm ED}}{k_{\rm TST}} = \frac{\beta Q\gamma^*}{1+(\omega_B/\omega_0)^2}\left(\frac{1}{1+\tau_C^*}\left(1-\frac{\tau_C^*}{1+\tau_C^*}e^{-2\omega_B t_a/\tau_C^*}\right) + \frac{(\omega_B/\omega_0)^2}{(\omega_B/\omega_0)^2+\tau_C^{*2}}\left\{\left[1+\left(\frac{\omega_B}{\omega_0}\right)^2\right]\omega_B t_a + \left(\frac{\omega_B}{\omega_0}\right)^2 + \left(\frac{\omega_B}{\omega_0}\right)^2\frac{\tau_C^*}{(\omega_B/\omega_0)^2+\tau_C^{*2}}\left[(1-\tau_C^{*2})e^{-2\omega_B t_a/\tau_C^*} + (1+\tau_C^*)^2\right] + 2\tau_C^*\left(1+e^{-2\omega_B t_a/\tau_C^*}\frac{1-\tau_C^*}{1+\tau_C^*}\right)\right\}\right), \tag{2.39}$$

where τ_C^* is the dimensionless correlation time of the non-Markovian noise:

$$\tau_C^* = \alpha^*\gamma^* = \tau_C\omega_B. \tag{2.40}$$

In the Markovian limit $\tau_C \to 0$ we find from Eq. (2.36),

$$\left.\frac{k_{\rm ED}}{k_{\rm TST}}\right|_{\tau_C=0} = \beta Q\gamma^*(1+\omega_B t_a). \tag{2.41}$$

For a sharp barrier, $\omega_B/\omega_0 \to \infty$, Eq. (2.39) simplifies further to the well known result[1]:

$$\left.\frac{k_{\rm ED}}{k_{\rm TST}}\right|_{\substack{\omega_B\to\infty \\ \tau_C=0}} = \pi\beta Q\frac{\gamma}{\omega_0}, \tag{2.42}$$

where we have used $\omega_0 t_a|_{\omega_B/\omega_0\to\infty} = \pi$ [see Eq. (2.38)]. In the non-Markovian case we find for a sharp barrier

$$\left.\frac{k_{\rm ED}}{k_{\rm TST}}\right|_{\omega_B/\omega_0\to\infty} = \frac{\gamma}{\omega_0}\frac{\beta Q}{1+(\omega_0\tau_C)^2} \times\left[\pi + \frac{(\omega_0\tau_C)^3}{1+(\omega_0\tau_C)^2}\left(1-e^{-2\pi/\omega_0\tau_C}\right)\right]. \tag{2.43}$$

Another limit in which the expression (2.39) simplifies considerably is $\tau_C \to \infty$:

$$\left.\frac{k_{\rm ED}}{k_{\rm TST}}\right|_{\tau_C\to\infty} = \beta Q\frac{\gamma^*}{\tau_C^{*2}}\left\{\frac{\omega_B}{\omega_0}\left[3\left(\frac{\omega_B}{\omega_0}\right)^2+2\right]\omega_0 t_a + 3\left(\frac{\omega_B}{\omega_0}\right)^2+1\right\}. \tag{2.44}$$

To conclude this section we given a simple necessary condition for the validity of Eq. (2.39). If the energy diffusion is rate limiting, the energy loss for a round trip of a determinisitic trajectory starting with $E = 0$ at the barrier must be less than β^{-1}. From the deterministic part of the non-Markovian Langevin equation (2.3) we obtain for the time rate of change of the energy

$$\dot{E}(t) = -v(t)\int_{-\infty}^{t} ds\, \zeta(t-s)v(s) \tag{2.45}$$

and, hence, for the energy loss

$$\Delta E = -\int_{-\infty}^{\tau} dt \int_{-\infty}^{t} ds\, \zeta(t-s)v(t)v(s), \tag{2.46}$$

where τ is the time at which the trajectory comes closest to the barrier. For small dissipation we may replace the actual velocity $v(t)$ by the velocity of the undampened system in which case τ is infinite:

$$\Delta E \simeq -\frac{1}{2}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} ds\, \zeta(t-s)v(t)v(s). \quad (2.47)$$

Combining

$$\beta|\Delta E| < 1 \quad (2.48)$$

with Eqs. (2.30), (2.36), and (2.47) we obtain as a condition for the validity of energy diffusion

$$k_{\mathrm{ED}}/k_{\mathrm{TST}} < 1. \quad (2.49)$$

With Eqs. (2.40) and (2.44) we find that this condition is not only met for sufficiently small values of γ^* but for large γ^* and τ_C^*, too (see the broken line in Fig. 2). However, SBB have found large deviations from energy diffusion for particular values of γ^* and τ_C^* although for these values Eq. (2.49) is fulfilled. In the next section we will show that other slowly changing quantities than the energy yield the correct rates in accordance with the simulations.

Finally we note that energy diffusion gives the correct asymptotic result for the rate at least in the limit $\beta Q \to \infty$, $\gamma^* \beta Q \to 0$.

III. IMPROVEMENTS

A. Corrections to the Grote–Hynes formula

Provided that the crossing of the separatrix is a proper criterion for the determination of the rate, the most delicate assumption of the Grote–Hynes theory consists of the steepest descent approximation of the denominator in Eq. (2.26). This approximation requires[15] (i) that the exponent $\beta\Phi$ restricted to the plane $R=0$ [see Eqs. (2.12) and (2.17)] strongly increases in any direction away from its minimum at the saddle (ii) that $D^{nn}a$ is a slowly varying function on the plane $R=0$.

First, we comment on (ii). Because in our case the dynamics in the barrier region is strictly linear, it follows from Eq. (2.22) that $D^{nn}a$ is constant there (see Appendix A) and, hence, that (ii) is met.

Now to (i). With Eqs. (2.7), (2.13), (2.17), and (2.18) we find for the restriction of to the plane $R=0$ as a function of x and v:

$$\Phi|_{R=0} = \frac{1}{2}\frac{\mu^2+\alpha^*(1-\mu^2)^2}{\alpha^*(1-\mu^2)^2} \times\left[v+\frac{\mu\omega_B}{\mu^2+\alpha^*(1-\mu^2)^2}x\right]^2 + \frac{Q}{1+(\omega_B/\omega_0)^2} \times\frac{(1-\mu^2)[1-\alpha^*(1-\mu^2)]}{\mu^2+\alpha^*(1-\mu^2)^2}\left(\frac{x}{l}\right)^2. \quad (3.1)$$

Because of Eq. (2.24) on the plane $R=0$ the generalized potential $\Phi|_{R=0}$ is an elliptic paraboloid with minimum at $x=v=0$. On the boundary of the saddle region $x=\pm l\Phi|_{R=0}$ takes its minimal value at

$$v = \mp\frac{\mu\omega_B}{\mu^2+\alpha^*(1-\mu^2)^2}\, l,$$

$$\Phi_{\min} = \frac{Q}{1+(\omega_B/\omega_0)^2}\frac{1-F}{F}, \quad (3.2)$$

where F denotes

$$F = \mu^2+\alpha^*(1-\mu^2)^2. \quad (3.3)$$

We note that Eq. (2.24) implies

$$0 < F < 1. \quad (3.4)$$

According to (i), $\Phi_{\min}$ must at least be larger than β^{-1}, hence,

$$\beta\Phi_{\min} > 1. \quad (3.3)$$

The curves in the τ^*–γ^* plane for which $\beta\Phi_{\min}$ is constant are determined by Eqs. (2.20), (3.2), and (3.3) yielding the parameter representation

$$\tau^* = \frac{q(1-\mu^2)-\mu^2}{\mu}, \quad (3.4a)$$

$$\gamma^* = \frac{(1-\mu^2)^2}{\mu}(1+q), \quad (3.4b)$$

where

$$q = \frac{\beta Q}{\beta\Phi_{\min}[1+(\omega_B/\omega_0)^2]} \quad (3.5)$$

and where the parameter μ varies in the interval $[0,(q/1+q)^{1/2}]$. Figure 3 shows these curves for different q values. Figure 2 contains the curves $\beta\Phi_{\min} = 1,5,10$ for $\beta Q = 20$ and $\omega_B/\omega_0 = 2$. Qualitatively these curves agree with the lower boundary of the region where SBB have found the strongest deviations from Grote–Hynes theory. In fact there are no rates simulated with parameter values with $\beta\Phi_{\min} > 5$ which disagree with Grote–Hynes.

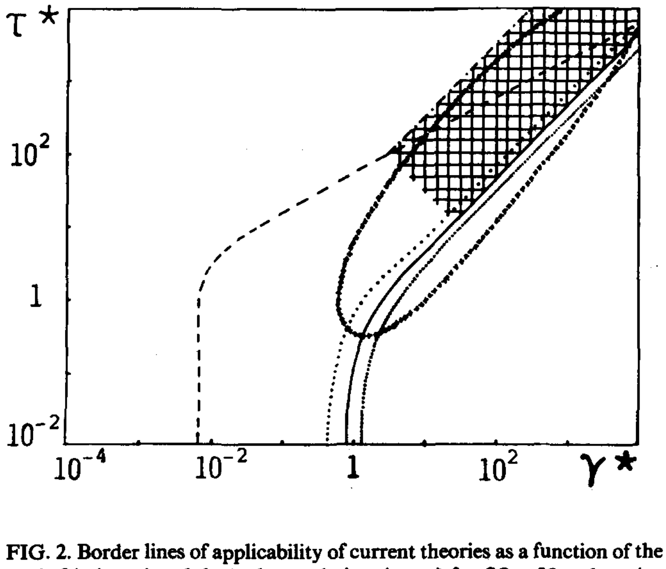

FIG. 2. Border lines of applicability of current theories as a function of the static friction γ^* and the bath correlation time τ_C^* for $\beta Q = 20$ and $\omega_B/\omega_0 = 2$. Above both lines representing $\beta|\Delta E| = 1$, Eqs. (2.48) and (2.29), (– –) and $(k_{\eta u} - k_{\mathrm{ED}})/k_{\mathrm{ED}} = 0.5$, Eq. (3.40), (–·–·) non-Markovian energy diffusion yields correct rates. The lines ···,—,···, represent curves of constant $\beta\Phi_{\min} = 1, 5, 10$, Eq. (3.3), respectively. Below the solid line Grote–Hynes theory may savely be applied. The line (××) represents the border of the region where SBB conjectured largest deviations from current theories. Within the hatched region the η–u diffusion rate $k_{\eta u}$ applies and deviates most strongly from current theories.

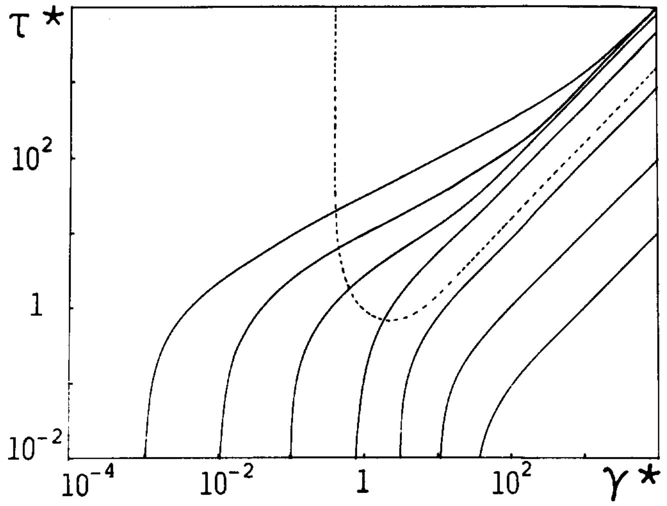

FIG. 3. Lines of constant q, Eqs. (3.4) and (3.5) (—) in the α^*-γ^* plane. From left to right $q = 10^3, 10^2, 10, 1, 10^{-1}, 10^{-2}, 10^{-3}$. To the right of each line the Grote–Hynes theory applies for all processes with respective q. Above the broken line the Grote–Hynes theory differs from the Markovian Kramers rate by more than 20%.

Our next aim is to improve the Grote–Hynes formula for parameter values in the vicinity of $\beta\Phi_{\min} \approx 1$. For this purpose we have to calculate the integral in the denominator of Eq. (2.23) more accurately by allowing for the contributions of the well regions

$$J = \int_{\partial\Omega} dS_n\, wD_{nn}a. \tag{3.6}$$

We recall that the separatrix $\partial\Omega$ is a two-dimensional surface which is infinitely many times wrapped around the two stable points $P_\pm$. Its innermost part consists of the plane $R = 0$ (2.17) in the barrier region and of a smoothly matching curved surface in the well regions. If $\Phi_{\min}$ is not much smaller than one most of the contributions to the integral (3.6) from the well regions come from those parts of the separatrix which can still be approximated by the plane $R = 0$. Moreover, there we approximate the factor $D^{nn}a$ by the constant value it takes in the barrier region. Under these assumptions we find for the integral $J = J_B + J_0$ the contributions (for calculational details see Appendix B)

$$J_B = \frac{2\pi D_{nn} a}{[\alpha(1-F)]^{1/2}\beta Z}\,\mathrm{erf}(\beta\Phi_{\min})^{1/2} \tag{3.7}$$

from the barrier, and

$$J_0 = \frac{2\pi D_{nn} a(\omega_B/\omega_0)}{\{\alpha[(\omega_B/\omega_0)^2 + F]\}^{1/2}\beta Z}\, e^{-B}(1 - \mathrm{erf}\, A^{1/2}) \tag{3.8}$$

from the well where erf denotes the error function and where A and B are defined by

$$A = \frac{\beta Q}{1 + (\omega_B/\omega_0)^2}\left(\frac{\omega_B}{\omega_0}\right)^2 \frac{(1-F)^2}{F[(\omega_B/\omega_0)^2 + F]}, \tag{3.9}$$

$$B = \beta Q\left\{\frac{1 + (\omega_B/\omega_0)^2}{(\omega_B/\omega_0)^2 + F} - 1\right\}, \tag{3.10}$$

respectively. $\Phi_{\min}$ is defined in Eq. (3.2), F in Eq. (3.3). With Eq. (3.4) we find $0 < A < \phi_{\min}$ and $B > 0$.

The standard steepest descent approximation corresponds to $\Phi_{\min} = A = B = \infty$ yielding

$$J_{\mathrm{SD}} = \frac{2\pi D_{nn} a}{[\alpha(1-F)]^{1/2}\beta Z}. \tag{3.11}$$

With Eq. (2.26) the ratio of J and J_{SD} determines that of the rate k_{IA} in the improved approximation and the Grote–Hynes rate

$$\frac{k_{\mathrm{IA}}}{k_{\mathrm{GH}}} = \frac{J}{J_{\mathrm{SD}}}. \tag{3.12}$$

With Eqs. (3.6) and (3.7) we find

$$k_{\mathrm{IA}} = \left\{\left[\frac{1-F}{(\omega_B/\omega_0)^2 + F}\right]^{1/2} \frac{\omega_B}{\omega_0}\, e^{-B}(1 - \mathrm{erf}\, A^{1/2}) + \mathrm{erf}(\beta\Phi_{\min})^{1/2}\right\} k_{\mathrm{GH}}. \tag{3.13}$$

If we compare Eq. (3.13) with the simulated data by SBB we find qualitative agreement for $\omega_B/\omega_0 = 0.2$ and 2 [see Figs. 4(a) and 4(b)]. The rate (3.13) coincides with the Grote–Hynes theory in an intermediate range of γ values and deviates for small and large γ's, however, much weaker than the simulated data do. One reason is, that we have neglected the curvature of the separatrix and the variation of $D^{nn}a$ outside of the barrier region. Another reason is that at least for small γ's because of energy diffusion the mean first crossing time of the separatrix fails to determine the rate. In the next section we will show that an energy-diffusion-like mechanism determines the rate for large γ's, too.

For $\omega_B/\omega_0 = 20$ and $\alpha^* = 4/3$ the maximal value of $\beta\Phi_{\min}$ is about 10^{-2} and, hence, Grote–Hynes theory should fail for all values of γ. Nevertheless, the simulated data seemingly agree with Grote–Hynes theory for γ^*'s ranging from 10^{-2} to 10^{-1} [see Fig. 4(c)]. In Appendix D we show that the rate for a potential with a cusp at the barrier ($\omega_B/\omega_0 \to \infty$) coincides with that of the transition state theory, provided energy diffusion is irrelevant.[16] For $\omega_B/\omega_0 = 20$ a cusp is fairly well approximated and so the simulated data agree with the transition state theory for $10^{-2} < \gamma < 10^{-1}$.

B. Two-dimensional diffusion

In the sequel we shall consider the limiting case of large static friction γ. For infinite γ the deterministic system (2.14) possess two constants of motion.[7,8] The first one follows from the x and z components of Eq. (2.14) as a linear combination of x and z,

$$u = z + \frac{1}{\alpha} x. \tag{3.14}$$

In the v component of Eq. (2.14) z may then be expressed in terms of u and x resulting in the Hamiltonian motion of a particle in a renormalized potential $V(x,u)$,

$$\dot{x} = v, \tag{3.15a}$$

$$\dot{v} = -\frac{\partial}{\partial x} V(x,u), \tag{3.15b}$$

where

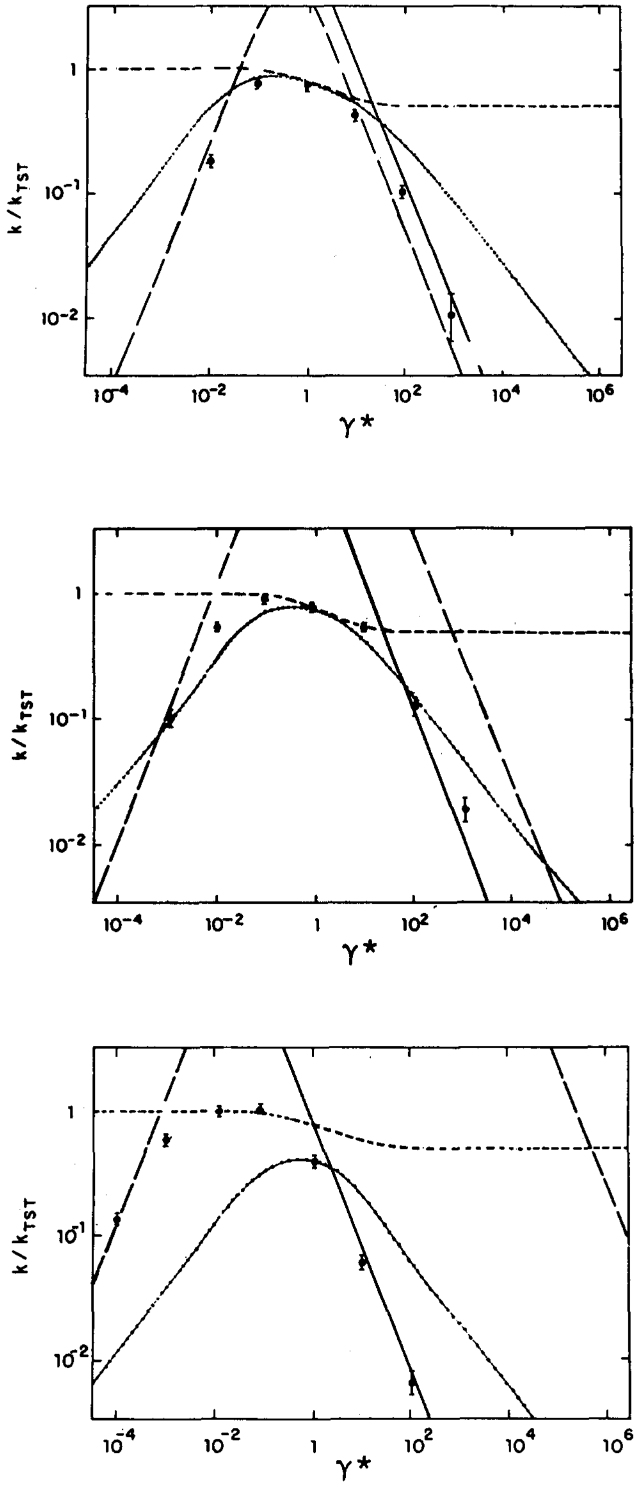

FIG. 4. Rate constants as a function of the static friction γ^* for $\beta Q = 20$ and $\alpha^* = 4/3$ for different frequency ratios (a) $\omega_B/\omega_0 = 0.2$, (b) $\omega_B/\omega_0 = 2$, (c) $\omega_B/\omega_0 = 20$. The dots represent the numerical data by SBB. Theoretical predictions are represented by lines: Energy-diffusion equation (2.39) (– –), Grote–Hynes equation (2.29) (---), corrected Grote–Hynes equation (3.13) (···), two-dimensional η–u diffusion equation (3.38) (—).

$$V(x,u) = U(x) + \frac{1}{2\alpha} x^2 - ux. \tag{3.16}$$

Note that in the barrier region the renormalized potential $V(x)$ is repulsive only for $\alpha^* > 1$ but attractive for $\alpha^* < 1$. In any case

$$e = \tfrac{1}{2}v^2 + V(x,u) \tag{3.17}$$

is the other conserved quantity.

For large but finite γ, e, and u will change much slower than the original variables x, v, and z.

The additional temperature fluctuations then lead to a slow diffusional motion of e and u which is approximately Markovian. If we can identify a curve in the e–u plane the crossing of which indicates a transition from one well into the other we can express the rate in terms of the mean first passage time of that curve.

The different qualitative behavior of $V(x,u)$, for $\alpha^* > 1$ and $\alpha^* < 1$ makes it necessary to consider these cases separately.

1. $\alpha^* > 1$

According to Eqs. (2.7), (3.16), and (3.17) in the barrier region the deterministic trajectories for $\gamma = \infty$ are hyperbolas with center at $(X_B, v = 0)$

$$e - \frac{1}{2\Omega_B^2} u^2 = \frac{1}{2} v^2 - \frac{1}{2} \Omega_B^2 (x - X_B)^2, \tag{3.18}$$

$$X_B = -\frac{u}{\Omega_B^2}, \tag{3.19}$$

where Ω_B denotes the renormalized barrier frequency

$$\Omega_B = \left(\frac{\alpha^* - 1}{\alpha^*}\right)^{1/2} \omega_B. \tag{3.20}$$

For $e - u^2/2\Omega_B^2 < 0$ each trajectory starting in one well either stays in this well or returns to it after a short excursion. For $e - u^2/2\Omega_B^2 > 0$ the trajectories join both wells. Starting in one well for $e - u^2/2\Omega_B^2 = 0$ the particle moves on a straight line towards the center of the hyperbola which is approached infinitely slowly. In the vicinity of the center the trajectory is extremely sensitive to the influence of the random force which either may turn the particle back to the well it is coming from or, equally likely, may push it to the other well. Hence, for $\gamma^* \to \infty$ and $\alpha^* > 1$ the transition rate is determined by the mean time T that the Markov process of u and e takes to cross $e - u^2/2\Omega_B^2 = 0$ for the first time:

$$k_{\eta,u} = \frac{1}{2T}. \tag{3.21}$$

For convenience we introduce the variable

$$\eta = e - \frac{1}{2\Omega_B^2} u^2. \tag{3.22}$$

The mean first passage time is then given by[17] (for a short derivation see Appendix C)

$$T = -\lim_{\epsilon \to 0^-} \frac{\int_{\eta<0} d\eta \, du \, \rho(\eta,u)}{\int du \, K_\eta(\eta = \epsilon,u)\rho(\eta = \epsilon,u)}, \tag{3.23}$$

where K_η denotes the drift in η direction, i.e., transversal to the boundary line $\eta = 0$, and where $\rho(\eta,u)$ denotes the stationary probability density for η and u. It will become clear, soon, why we have shifted the boundary line to a negative value of η. The probability density $\rho(\eta,u)$ is obtained from Eqs. (2.12) and (2.13) with Eqs. (3.14), (3.17), (3.18), and (3.22),

$$\rho(\eta,u) = \int dx\,dv\,dz\,\delta\Big(\eta - \frac{1}{2}v^2 - U(x) - \frac{1}{2\alpha}x^2 + ux + \frac{1}{2\Omega_B^2}u^2\Big) \times\delta\left(u - z - \frac{1}{\alpha}x\right) Z^{-1}\exp\Big[-\beta\Big(\frac{1}{2}v^2 + U(x) + \frac{\alpha}{2}z^2\Big)\Big] = \frac{2\pi}{\omega(\eta,u)Z}\exp\Big[-\beta\Big(\eta + \frac{\alpha^*}{2\Omega_B^2}u^2\Big)\Big], \tag{3.24}$$

where $\omega(\eta,u)$ denotes the frequency of the reversible motion [Eqs. (3.15) and (3.16)] at constant parameters η and u:

$$\omega(\eta,u) = 2\pi\left\{\oint dx\left[2\Big(\eta + \frac{u^2}{2\Omega_B^2} - V(x,u)\Big)\right]^{-1/2}\right\}^{-1}. \tag{3.25}$$

The period $2\pi/\omega(\eta,u)$ consists in the time spent in the barrier region, and in the well region, t_B and t_0, respectively. In the limit $\eta\to 0$ t_B diverges and, hence, $\rho(\eta,u)$, too. With Eq. (3.24) the integral in the numerator yields in leading order in $(\beta Q)^{-1}$,

$$\int_{\eta<0} d\eta\,du\,\rho(\eta,u) = \frac{e^{\beta Q}}{\omega_0\alpha^{1/2}Z}\left(\frac{2\pi}{\beta}\right)^{3/2}. \tag{3.26}$$

In leading order for large γ the drift $K_\eta(\eta,u)$ is given by the average of the time rate of change of η along the conservative dynamics (3.15) and (3.16) at fixed η and u over one period:

$$K_\eta(\eta,u) = \frac{\omega(\eta,u)}{2\pi}\int_{-\pi/\omega(\eta,u)}^{\pi/\omega(\eta,u)} dt\,\dot\eta[x(t),v(t)]. \tag{3.27}$$

Hence, the diverging factors in the denominator of Eq. (3.23) cancel and the limit $\epsilon\to 0^-$ can easily be performed:

$$T = \frac{e^{\beta Q}}{\omega_0\alpha^{1/2}}\left(\frac{2\pi}{\beta}\right)^{3/2} \times\left\{\int_{-\infty}^{+\infty} du\,\exp\Big(-\beta\frac{\alpha^* u^2}{2\Omega_B^2}\Big) \times\int_{-\infty}^{+\infty} dt\,\dot\eta[x(t),v(t)]\right\}^{-1}. \tag{3.28}$$

With the deterministic equations (2.14), (3.17), and (3.22) $\dot\eta$ can be expressed in terms of x and u:

$$\dot\eta = -\frac{\omega_B^3}{\alpha^{*2}\gamma^*}(x - X_B)^2 + \frac{\omega_B}{\gamma^*(\alpha^* - 1)}u(x - X_B). \tag{3.29}$$

In the limit $\eta\to 0^-$ the periodic solution of the conservative system (2.7) and (3.15)–(3.17) reads

$$x(t) = \begin{cases} X_B + (l - X_B)e^{\Omega_B(t+t_0)}, & t\leqslant -t_0 \\ X_0 + A\cos\Omega_0 t, & |t|\leqslant t_0 \\ X_B + (l - X_B)e^{-\Omega_B(t-t_0)}, & t\geqslant t_0 \end{cases}, \tag{3.30}$$

where

$$X_0 = l + \left(\frac{\Omega_B}{\Omega_0}\right)^2\left(l + \frac{u}{\Omega_B^2}\right), \tag{3.31}$$

$$A = \frac{\Omega_B}{\Omega_0}\left[1 + \left(\frac{\Omega_B}{\Omega_0}\right)^2\right]^{1/2}\left(l + \frac{u}{\Omega_B^2}\right), \tag{3.32}$$

where Ω_0 denotes the renormalized well frequency

$$\Omega_0^2 = \omega_0^2 + \frac{1}{\alpha} \tag{3.33}$$

and where t_0 is the shortest time to reach the vertex $X_0 + A$ from $x = l$,

$$\cos\Omega_0 t_0 = \frac{l - X_0}{A} = -\frac{\Omega_B}{\Omega_0}\left[1 + \left(\frac{\Omega_B}{\Omega_0}\right)^2\right]^{-1/2}. \tag{3.34}$$

After some simple but lengthy algebra we obtain from Eqs. (3.29)–(3.34) the change of η during one period in leading order in γ^{-1},

$$\Delta\eta = \int_{-\infty}^{\infty} dt\,\dot\eta[x(t)] = \Delta\eta_B + \Delta\eta_0, \tag{3.35}$$

where $\Delta\eta_B$ and $\Delta\eta_0$ are the contributions from the barrier region and the well, respectively,

$$\Delta\eta_B = -\frac{\omega_B^3 l^2}{\alpha^{*2}\gamma^*\Omega_B}\left[1 - 2(\alpha^* - 1)\frac{u}{l\Omega_B^2} - (2\alpha^* - 1)\left(\frac{u}{l\Omega_B^2}\right)^2\right], \tag{3.36}$$

$$\begin{aligned}\Delta\eta_0 = -\frac{2\omega_B^2 l^2}{\alpha^{*2}\gamma^*\Omega_0}\Bigg[&\left[1 + \left(\frac{\Omega_B}{\Omega_0}\right)^2\right]\left[\frac{3}{2}\left(\frac{\Omega_B}{\Omega_0}\right)^2 + 1\right]\Omega_0 t_0 + \frac{3}{2}\left(\frac{\Omega_B}{\Omega_0}\right)^3 + 2\frac{\Omega_B}{\Omega_0} \\ &+ \left\{\left[1 + \left(\frac{\Omega_B}{\Omega_0}\right)^2\right]\left[3\left(\frac{\Omega_B}{\Omega_0}\right)^2 - \alpha^* + 2\right]\Omega_0 t_0 + \frac{\Omega_B}{\Omega_0}\left[3\left(\frac{\Omega_B}{\Omega_0}\right)^2 - \alpha^* + 4\right]\right\}\frac{u}{l\Omega_B^2} \\ &+ \left(\left\{\frac{3}{2}\left(\frac{\Omega_B}{\Omega_0}\right)^4 + \frac{5}{2}\left(\frac{\Omega_B}{\Omega_0}\right)^2 - \left[\left(\frac{\Omega_B}{\Omega_0}\right)^2 + 1\right]\alpha^* + 1\right\}\Omega_0 t_0 + \frac{5}{2}\left(\frac{\Omega_B}{\Omega_0}\right)^2 - (\alpha^* - 2)\frac{\Omega_B}{\Omega_0}\right)\left(\frac{u}{l\Omega_B^2}\right)^2\Bigg]. \end{aligned} \tag{3.37}$$

With Eqs. (3.36) and (3.37) the remaining u integral in Eq. (3.28) is readily performed to yield with Eq. (3.21) the rate

$$\frac{k_{\eta u}}{k_{\rm TST}} = \frac{\beta Q}{[1+(\omega_B/\omega_0)^2]\alpha^{*2}\gamma^*}\left[1+\frac{\Omega_B}{\Omega_0}\left[1+\left(\frac{\Omega_B}{\Omega_0}\right)^2\right]\left[3\left(\frac{\Omega_B}{\Omega_0}\right)^2+2\right]\Omega_0 t_0+3\left(\frac{\Omega_B}{\Omega_0}\right)^4+4\left(\frac{\Omega_B}{\Omega_0}\right)^2\right.$$
$$+\frac{1+(\omega_B/\omega_0)^2}{2\beta Q(\alpha^*-1)}\left(1-2\alpha^*+\frac{\Omega_B}{\Omega_0}\left\{3\left(\frac{\Omega_B}{\Omega_0}\right)^4+5\left(\frac{\Omega_B}{\Omega_0}\right)^2\right.\right.$$
$$\left.\left.\left.-\left[\left(\frac{\Omega_B}{\Omega_0}\right)^2+1\right]\alpha+1\right\}\Omega_0 t_0+\left(\frac{\Omega_B}{\Omega_0}\right)^2\left[5\left(\frac{\Omega_B}{\Omega_0}\right)^2-2(\alpha^*-2)\right]\right)\right]. \quad (3.38)$$

The first two terms in the large square brackets are due to the u-independent contributions to $\Delta\eta$ while the correction term proportional to $(\beta Q)^{-1}$ coming from the u^2 terms in $\Delta\eta$ is only important for sharp barriers and temperatures not too low. Figure 4 shows good agreement of Eq. (3.38) with the simulated rates for large γ. We note that for large α^* the renormalized frequencies Ω_0 ands Ω_B approach the bare ones ω_0 and ω_B, respectively. In this limit t_0 approaches the time t_a [Eq. (2.38)] entering in the energy diffusion rate (2.39) and, moreover, the rate (3.38) simplifies to the energy diffusion rate for large correlation times (2.44) as expected from physical grounds[2,5]

$$k_{\eta u}|_{\alpha^*\to\infty} = k_{\rm ED}|_{\tau_c^*\to\infty}. \quad (3.39)$$

Disregarding temperature dependent corrections the leading order deviation is found to be

$$\frac{k_{\eta u}-k_{\rm ED}}{k_{\rm ED}} = -\frac{\omega_B}{\omega_0}\frac{1}{2\alpha^*}\frac{[1+25(\omega_B/\omega_0)^2+27(\omega_B/\omega_0)^4]\omega_0 t_a+9(\omega_B/\omega_0)[2+3(\omega_B/\omega_0)^2]}{(\omega_B/\omega_0)[3(\omega_B/\omega_0)^2+2]\omega_0 t_a+3(\omega_B/\omega_0)^2+1}. \quad (3.40)$$

Note that for large α^* and γ^* energy diffusion overestimates the rate. The deviations are stronger for sharp barriers compared with flat ones. For particular values of ω_B/ω_0 and βQ Fig. 2 shows the curve below which energy diffusion overestimates the rate by more than 50%. For large γ^* it lies considerably above the self-consistently determined boundary of energy diffusion.

For the validity of the η–u diffusion rate (3.38) we can give a self-consistent condition by requiring

$$\beta\Delta\eta \lesssim 1. \quad (3.41)$$

Considering only the most probable value $u=0$ we find from Eqs. (3.35)–(3.37),

$$\beta\Delta\eta = \frac{2\beta Q}{1+(\omega_B/\omega_0)^2}\frac{1}{\alpha^{*3/2}(\alpha^*-1)^{1/2}\gamma^*}$$
$$\times\left\{1+\frac{\Omega_B}{\Omega_0}\left[1+\left(\frac{\Omega_B}{\Omega_0}\right)^2\right]\left[3\left(\frac{\Omega_B}{\Omega_0}\right)^2+2\right]\right.$$
$$\left.\times\Omega_0 t_0+3\left(\frac{\Omega_B}{\Omega_0}\right)^4+4\left(\frac{\Omega_B}{\Omega_0}\right)^2\right\}. \quad (3.42)$$

Neglecting high temperature corrections we find from Eqs. (3.41) and (3.42) with Eq. (3.38) the required self-consistent condition

$$\frac{k_{\eta u}}{k_{\rm TST}} \lesssim \left(\frac{\alpha^*-1}{\alpha^*}\right)^{1/2}. \quad (3.43)$$

For large values of γ^* Eq. (3.43) reduces to the obvious condition $\alpha^*>1$. It is worth noting that Eqs. (3.41) and (3.42) implies for very weak noise, i.e., for βQ very large, that the two-dimensional diffusion mechanism is no longer rate limiting. Physically speaking then the noise cannot compensate for the energy loss during one round trip of the particle. This coincides with the findings of SBB.

Another self-consistency condition follows from the change Δu during a round trip. At the first sight this condition seems render the two-dimensional diffusion mechanism impossible because for $\eta=0$ Δu diverges for any choice of parameters. However, the divergence is only logarithmic in $|\eta|$ and disappears completely by averaging over u for all finite η. The resulting Δu contains nothing new compared with Eq. (3.41) and, hence, we shall not go into further details.

2. $\alpha^*<1$

We recall that according to Eqs. (2.7), (3.16) and (3.17) for $\gamma=\infty$ the particle moves in ordinary phase space, whereas the extra variable z is following the motion of the coordinate rigidly and without backaction. For $\alpha^*<1$ the trajectories in the barrier region consist of ellipses or parts of ellipses depending on the values of the conserved quantities e and u,

$$e+\frac{u^2}{2\bar\Omega_B^2} = \frac{1}{2}v^2+\frac{1}{2}\bar\Omega_B^2(x-\bar X_B)^2, \quad |x|<l, \quad (3.44)$$

where

$$\bar X_B = \frac{u}{\bar\Omega_B^2}, \quad (3.45)$$

$$\bar\Omega_B = \left(\frac{1-\alpha^*}{\alpha^*}\right)^{1/2}\omega_B. \quad (3.46)$$

Clearly, one must have

$$e+\frac{1}{2}\frac{u^2}{\bar\Omega_B^2}>0. \quad (3.47)$$

Moreover, one finds from Eq. (3.44) for the region of complete ellipses in the barrier region a condition on e and u (see Fig. 5),

$$e \leqslant -l|u|+\frac{\bar\Omega_B^2 a^2}{2}. \quad (3.48)$$

By considering only these complete ellipses we average the time rate of change of the slow quantities e and u over the fast conservative motion

$$x(t) = \bar X_B+\frac{(2e+u^2/\bar\Omega_B^2)^{1/2}}{\bar\Omega_B}\cos\bar\Omega_B t. \quad (3.49)$$

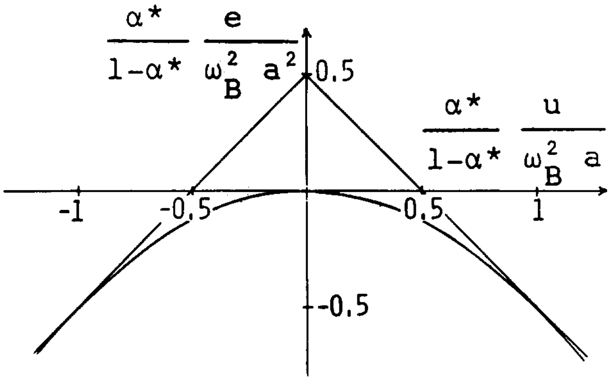

FIG. 5. The curvilinear triangle defined by Eqs. (3.47) and (3.48) represents that region in the suitably scaled e–u plane, where the corresponding conservative motion (3.44) consists in complete ellipses in the barrier region.

With Eqs. (2.14), (3.14), and (3.18) this yields the equations of motion of e and u valid for large γ,

$$\dot{u}(t) = \frac{1}{\gamma^*}\frac{\omega_B}{1-\alpha^*}u(t), \tag{3.50}$$

$$\dot{e}(t) = -\frac{\omega_B}{\alpha^*\gamma^*}\frac{1}{1-\alpha^*}e(t) - \frac{1+2\alpha^*}{2\gamma^*(1-\alpha^*)^2\omega_B}u(t)^2. \tag{3.51}$$

Obviously, $u=0$ is a separatrix of Eqs. (3.50) and (3.51). Its significance for the fast motion of x and v is evident from Eqs. (3.44) and (3.45): for $u>0$ the center of the ellipses is located right of the barrier and for $u<0$ left of it. Clearly, for $u>0$ the particle is more likely to thermalize in the right well and vice versa for $u<0$. Hence, the crossing of $u=0$ due to thermal fluctuations characterizes transitions from one well to the other.

Consequently, the mean first passage time of $u=0$ for $e\geqslant 0$ determines the rate (2.23), which is given by Eq. (2.27) where for μ one has to put $\gamma^{*-1}(1+\alpha^*)^{-1}$, i.e., the positive eigenvalue of the equations of motion (3.50) and (3.51) linearized about the saddle $e=u=0$:

$$\frac{k_{eu}}{k_{\rm TST}} = \frac{1}{\gamma^*}\frac{1}{1-\alpha^*}. \tag{3.52}$$

For a more thorough deviation of this result we refer to Appendix E. Actually, for large γ the Grote–Hynes rate is the same as Eq. (3.52). This coincidence is partly due to the fact that in the derivation of Eq. (3.52) the influence of the well dynamics has been neglected completely. We will come back to this point below. Another reason is that $u=0$ looked as a plane in the extended phase space coincides with the separatrix $R=0$ [Eqs.(2.17) and (2.18)] up to order γ^{-1}. This entails that the respective motions of u and R are governed by the same positive eigenvalue and, moreover, that the system is found in the neighborhood of the respective saddles with the same probability:

$$\int_{\substack{R<0\\ \beta|\Phi|<1}} w(x,v,z)dx\,dv\,dz = \int_{\substack{u<0\\ \beta|\Phi|<1}} \rho(e,u)de\,du. \tag{3.53}$$

The coincidence of the two rates is reminiscent to the Markovian case where for large γ the full Kramers equation yields the same rate as the reduced Smoluchowky equation, the only difference being that in the Markovian case the eliminated quantity is rapidly decreasing rather than rapidly oscillating as in the non-Markovian case.

Finally we give a rough estimate under which condition the well dynamics can safely be neglected. Clearly, the particle experiences both the saddle and one or both well regions if condition (3.48) is violated. For the rate those trajectories with $u=0$ and $e<\beta^{-1}$ are decisive. Hence, we find from Eqs. (3.48) and (3.46) with Eq. (2.8) that for

$$\frac{\beta Q}{1+(\omega_B/\omega_0)^2} > \frac{\alpha^*}{1-\alpha^*} \tag{3.54}$$

the well region has no influence on the rate.

All data simulated by SBB with $\alpha^*<1$, γ^* large fall into the parameter range where Eq. (3.54) is fulfilled. Nevertheless, the data with α^* close to one ($\alpha^*=0.5,0.7$) agree with Eq. (3.52) within a factor of 2, only (see Table I). We have no explanation for this discrepancy, except that the numerical error of the simulated data might be larger than stated by SBB.

A discussion of the rate for parameters where Eq. (3.54) is violated will be given elsewhere.

IV. CONCLUSIONS

We have dealt with one of the simplest non-Markovian models showing bistable behavior in the deterministic limit. Before summarizing the results we describe the methods we have used to determine the transition rates.

Starting from a Markovian description in an extended phase space, the first goal is to identify slowly varying quantities of the corresponding deterministic drift motion and, if there are any, to eliminate the remaining fast variables. In the presence of fluctuating forces the slow variables constitute a Markov process, at least approximately. In the next step a criterion has to be found telling in terms of the slow variables whether the system belongs to one or the other stable state. This criterion defines a boundary in the space of the slow variables. Its crossing indicates a transition and the corresponding mean first passage time determines the rate. In the present model one encounters two different situations

TABLE I. Comparison of the rates according to SBB, $k_{\rm SBB}$, and that of Grote–Hynes, $k_{\rm GH}$, for $\beta Q=20$ and different values of ω_B/ω_0, γ^*, and $\alpha^*<1$.

ω_b/ω_0	γ^*	α^*	$k_{\rm SBB}/k_{\rm TST}$	$k_{\rm GH}/k_{\rm TST}$
2	1	0.001	0.609 ± 0.035	0.618
2	10	0.001	0.106 ± 0.015	0.099
20	10	0.01	0.036 ± 0.009	0.100
				0.037[a]
20	0.1	0.01	0.929 ± 0.043	0.951
0.2	100	0.1	0.014 ± 0.010	0.011
0.2	100	0.5	0.053 ± 0.020	0.020
2	300	0.5	0.014 ± 0.010	0.007
0.2	100	0.7	0.107 ± 0.028	0.033

[a] Rate for spatial diffusion over a sharp barrier (Ref. 4).

reminiscent of spatial diffusion and energy diffusion in the original Kramers model. In the first case in which Eq. (2.26) yields the mean first passage time the probability density of the slow variables consists of a constant density of states and a Boltzmann factor with a minimum at the boundary. In the second case in which Eq. (C10) yields the mean first passage time, the density of states diverges and the Boltzmann factor changes monotonically if the boundary is crossed. In any case, the rate is determined by the drift in the direction transverse to the boundary and by the stationary probability density of the slow variables. Hence, it is sufficient to perform the adiabatic elimination (or averaging) of the fast variables in the deterministic equations. The stationary probability of the slow variables is simply obtained from the one in the extended phase space by means of coarse graining.

For the particular model considered in this paper various asymptotic regimes may be distinguished. At a fixed temperature and for a particular ratio of the well and barrier frequencies these regimes are depicted in the γ^*–τ_C^* plane in Fig. 2. Left of the broken line and above the dash–dotted line the rate is given by non-Markovian energy diffusion [Eq. (2.39)]. Below the solid line Grote–Hynes theory applies and in the shaded region a two-dimensional energy diffusion mechanism determines the rate. In the vicinity of the solid line the agreement with the corrected Grote–Hynes theory (3.13) is fairly good. In the remaining part of the γ^*–τ_C^* plane below the broken and above the solid line the interpolation[18]

$$k^{-1} = k_{\rm GH}^{-1} + k_{\rm ED}^{-1} \tag{4.1}$$

yields good results[5] although a satisfactory theory is missing. If the temperature decreases the broken line moves rigidly to the left in the γ^*, τ_C^* plane [see Eqs. (2.39) and (2.49)]. Qualitatively the same happens with the solid line (see Fig. 2). In contrast, the dash–dotted line is temperature independent. Because this line is only significant above the broken line for decreasing temperature the shaded region moves towards higher τ_C^* and γ^* values. Hence, as it is expected the regimes of energy diffusion and the two-dimensional η–u diffusion shrink, whereas the regime of the Grote–Hynes rate grows with decreasing temperature. For an increasing ratio of barrier and well frequencies, ω_B/ω_0 the solid line moves in the γ^*–τ_C^* plane to the right (see Fig. 3), whereas the broken and dash–dotted lines move to the left (see Fig. 5). Hence, both regimes of Grote–Hynes and energy diffusion rate shrink, whereas that of the two-dimensional η–u diffusion grows.

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APPENDIX A: SOLUTION OF EQ. (2.27) ON THE PLANE $R=0$

First we transform Eq. (2.25) into a linear equation

$$gf - \frac{1}{2} K_\alpha \frac{\partial f}{\partial x_\alpha} - \frac{\beta}{2} D_{nn} = 0, \tag{A1}$$

where

$$f = a^{-2}. \tag{A2}$$

Next we have to determine g, K_α, and D_{nn}. In the saddle region the drift vector reads [Eq. (2.14)]

$$K = B_B \begin{pmatrix} x \\ v \\ z \end{pmatrix}. \tag{A3}$$

Its component transverse to the separatrix is given by

$$K_n = (V,K) = \lambda_+ R, \tag{A4}$$

where we have used Eqs. (2.17) and (2.18) and the fact that V is the eigenvector of B_B^T with the positive eigenvalue λ_+ [Eqs. (2.19) and (2.20)]. Combining Eq. (2.28) with Eq. (A4) yields

$$g = \lambda_+ = \mu\omega_B. \tag{A5}$$

The normal component D^{nn} on $R=0$ is simply given by the $V-V$ matrix element of the diffusion matrix D which can be read off from the Fokker–Planck equation (2.10),

$$D = \frac{1}{\alpha^2\beta\gamma} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{A6}$$

Hence,

$$D_{nn} = (V, DV) = \frac{(1-\mu^2)^2}{\beta\gamma}. \tag{A5}$$

As coordinate system x^α, $\alpha = 1,2$, on the separatrix ($R=0$) we may choose x and z. Then we obtain for the components of the drift vector on the plane $R=0$,

$$K_1 = K_x|_{R=0} = -\frac{\omega_B}{\mu} x - \frac{\alpha\omega_B}{\mu}(1-\mu^2)z, \tag{A6}$$

$$K_2 = K_z|_{R=0} = +\frac{\omega_B}{\alpha\mu} x + \left(\frac{\omega_B}{\mu}(1-\mu^2) - \frac{1}{\alpha\gamma}\right) z. \tag{A7}$$

Now we look for the general solution of Eq. (A1).

First we observe that the constant

$$f_p = \frac{\beta D_{nn}}{g} = \frac{(1-\mu^2)^2}{\gamma\omega_B\mu} \tag{A8}$$

solves Eq. (A2). Hence, the general solution reads

$$f = f_p + h, \tag{A9}$$

where h obeys the homogeneous equation

$$hf - \frac{1}{2} K_\alpha \frac{\partial h}{\partial x_\alpha} = 0. \tag{A10}$$

Because $h = x = z = 0$ is a common point of all characteristics of Eq. (A10) there is only the trivial solution $h \equiv 0$.[19] This proves that Eq. (2.25) has a unique solution in the barrier region which reads

$$a = \left(\frac{\lambda_+}{2\beta D_{nn}}\right)^{1/2}. \tag{A11}$$

APPENDIX B: THE SURFACE INTEGRAL $\int_{R=0} dS_n\, w$

By introducing a δ function we transform the surface integral $\int_{R=0} dS_n\, w$ into a volume integral

$$\int_{R=0} dS_n\, w = \int dx\, dv\, dz\, \delta(R) w(x,v,z), \tag{B1}$$

where [see Eqs. (2.14) and (2.16)]

$$R = x + \frac{\mu}{\omega_B} v + \alpha(1-\mu^2) z \tag{B2}$$

and where w is given by Eqs. (2.12) and (2.13),

$$w = Z^{-1} \exp\left\{ -\beta \left[\frac{1}{2} v^2 + U(x) + \frac{\alpha}{2} z^2 \right] \right\}. \tag{B3}$$

Using the Fourier representation of the δ function we obtain

$$\int_{R=0} dS_n\, w = (2\pi Z)^{-1} \int dx\, dv\, dz\, dk\, e^{ikR} \times \exp\left\{ -\beta \left[\frac{1}{2} v^2 + U(x) + \frac{\alpha}{2} z^2 \right] \right\}. \tag{B4}$$

The v, z, and k integrals are Gaussian and, hence, readily performed to yield

$$\int_{R=0} dS_n\, w = \frac{\omega_B}{Z} \left(\frac{2\pi}{\alpha\beta F} \right)^{1/2} \times \int_{-\infty}^{+\infty} dx \exp\left\{ -\beta \left[U(x) + \frac{\omega_B^2 x^2}{2F} \right] \right\}, \tag{B5}$$

where F is defined in Eq. (3.3). With the piecewise parabolic potential (2.8) the remaining integration in Eq. (B5) can be done exactly yielding $J/(D^{nn}a)$ [Eqs. (3.7) and (3.8)].

APPENDIX C: A MEAN FIRST PASSAGE TIME TO CROSS A HYPERPLANE

We consider a d-dimensional[20] Markovian Fokker–Planck process. Further, we assume that there is exactly one stable fixed point of the drift in the half-space with $x_1 \geqslant 0$ and that on the hyperplane $x_1 = 0$ the component K_1 of the drift in x_1 direction is everywhere positive

$$K_1(x_1 = 0, x_2, \ldots, x_d) > 0. \tag{C1}$$

Further we assume that for large positive x_1 K_1 grows negative at least proportional to x_1.[21] The mean first time $t(x)$ the process needs to cross the hyperplane $x_1 = 0$ when starting at x with $x_1 > 0$ is the solution of the Dynkin equation

$$k_i \frac{\partial t}{\partial x_i} + \frac{\epsilon}{2} D_{ij} \frac{\partial^2 t}{\partial x_i \partial x_j} = -1 \quad \text{for all } x \text{ with } x_1 > 0, \qquad t(x_1 = 0, x_2, \ldots, x_d) = 0, \tag{C2}$$

where K_i and ϵD_{ij} denote the drift and diffusion, respectively. The diffusion is assumed to be uniformly small. ϵ is needed for bookkeeping only. Under the stated assumptions on the drift $t(x)$ assumes an almost constant value T for most x with $x_1 > 0$ and drops to zero on a small boundary layer at $x_1 = 0$. One sets

$$t(x) = Tf(x) \tag{C3}$$

and finds from Eq. (C2) by multiplying with a stationary solution $w(x)$ of the Fokker–Planck equation and by integrating over all x with $x_1 > 0$,

$$T = -\frac{2\int_{x_1>0} d^d x\, w}{\epsilon \int_{x_1=0} dS_1\, D_{11} (\partial f/\partial x_1) w}, \tag{C4}$$

where dS_1 is the x_1 component of oriented surface element on the hyperplane $x_1 = 0$. w is assumed to be known. From Eqs. (C2) and (C3) we find

$$K_i \frac{\partial f}{\partial x_i} + \frac{\epsilon}{2} D_{ij} \frac{\partial^2 f}{\partial x_i \partial x_j} = 0, \tag{C5}$$

where we have neglected the small inhomogeneity T^{-1}. With the ansatz

$$f(x) = 1 - e^{-\rho(x)/\epsilon} \tag{C6}$$

we obtain for the thickness $\rho(x)$ of the boundary layer in leading order in ϵ,

$$K_i \frac{\partial \rho}{\partial x_i} - \frac{1}{2} D_{ij} \frac{\partial \rho}{\partial x_i} \frac{\partial \rho}{\partial x_j} = 0. \tag{C7}$$

Because $\rho(x)$ must vanish at $x_1 = 0$ we immediately obtain

$$\left. \frac{\partial \rho}{\partial x_1} \right|_{x_1=0} = \frac{2K_1(x_1=0)}{D_{11}(x_1=0)}. \tag{C8}$$

With Eqs. (C4) and (C6) this yields for the mean first passage time T,

$$T = -\frac{\int_{x_1>0} d^d x\, w}{\int_{x_1=0} dS_1\, K_1 w}. \tag{C9}$$

We stress that a stationary probability density w and the component of the drift $K_1(x_1 = 0)$ transversal to the boundary ($x_1 = 0$) already determine the time T. All other details of the process are irrelevant. Finally we note that Eq. (C9) is readily generalized for arbitrary domains Ω out of which the exit takes place:

$$T = -\frac{\int_\Omega d^d x\, w}{\int_{\partial\Omega} dS_n\, K_n w}, \tag{C10}$$

where dS_n and K_n denote the transversal component of the oriented surface element on $\partial\Omega$ and that of the drift, respectively. Equation (C10) holds under similar conditions as Eq. (C9), namely, that there is exactly one attractor of the drift (not necessarily a point) in Ω, and that on $\partial\Omega$ the drift points inside Ω, i.e., that $dS_n\, K_n < 0$.

APPENDIX D: A CUSP SHAPED BARRIER

In the limit $\omega_B/\omega_0 \to \infty$, $a \to 0$, Q fixed, the potential (2.7) shows a sharp cusp at the barrier. For finite γ (not too small and not too large) and sufficiently large βQ every particle approaching the barrier from the right with negative velocity will almost surely leave the right potential well and will eventually thermalize in the left one. Hence, the rate is simply determined by the reciprocal mean first time to cross the plane $x = 0$ with $v < 0$. With Eq. (C9) we find

$$k_{\rm SB} = \frac{1}{T} = -\frac{\int_{-\infty}^{0} dv \int_{-\infty}^{\infty} dz K_x(x=0,v,z) w(x=0,v,z)}{\int_0^\infty dx \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dz\, w(x,v,z)}. \tag{D1}$$

With $K_x = v$ [Eqs. (2.1) and (2.12)] we find

$$k_{\rm SB} = \frac{\omega_0}{2\pi} e^{-\beta Q}. \tag{D2}$$

Hence, the escape rate over a sharp barrier coincides with that of transition state theory.

APPENDIX E: MEAN FIRST PASSAGE TIME FOR $\gamma^* \to \infty$, $\alpha^* < 1$

We calculate the mean first passage time over the line $u = 0$ at $e > 0$ for the Markovian process obtained from Eq. (2.1) by averaging over the fast motion in ordinary phase space. The drift of this process in the barrier region (see Fig. 5) is given by Eqs. (3.50) and (3.51). The stationary distribution follows immediately from Eqs. (2.12), (2.13), and (3.14), and (3.17):

$$\rho(e,u) = \frac{2\pi}{\bar{\Omega}_B Z} \exp\left[-\beta\left(e + \frac{\alpha}{2} u^2 \right) \right]. \tag{E1}$$

At $e = u = 0$ the drift has a stable point which is attractive in the e direction and repulsive in the u direction. At this point $\rho(e,u)$ has a saddle (recall $e > -u^2/2\bar{\Omega}_B^2$). Consequently the mean first passage time reads [compare Eq. (2.26)]

$$T = \frac{1}{2}\left(\frac{\pi}{\beta}\right)^{1/2} \frac{\int_{u>0} de\, du\, \rho(e,u)}{\int_0^\infty de\, \rho(e,u=0) D_{uu} a}, \tag{E2}$$

where

$$D_{uu} = \frac{1}{\alpha^2 \beta \gamma} \tag{E3}$$

is the u–u matrix element of the diffusion, and where a is given by (see Appendix A)

$$a = \frac{\alpha^*}{\omega_B [2(1-\alpha^*)]^{1/2}}. \tag{E4}$$

Clearly, we have for large βQ,

$$\int_{u>0} de\, du\, \rho(e,u) = \int_{x>0} dx\, dv\, dz\, w(x,vz) \approx \frac{(2\pi)^{3/2} e^{\beta Q}}{\beta^{3/2} \omega_0 \alpha^{1/2} Z}. \tag{E5}$$

By putting everything together we obtain Eq. (3.52).

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