Intrawell relaxation of overdamped Brownian particles

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(Received 12 November 1998)

We consider an overdamped Brownian particle in a well. When the particle escapes, it does so as an instanton, i.e., in one run and without dwelling anywhere on the way from the bottom of the well to the top of the barrier. For a sufficiently steep slope the instanton time equals the time it takes the particle to deterministically slide *down* the same slope. We show that the instanton time is also the relaxation time for the escape rate after the barrier changes shape. [S1063-651X(99)04906-5]

PACS number(s): 05.40.−a, 02.50.Ey, 82.20.−w

INTRODUCTION

Suppose we have overdamped particles executing Brownian motion in a smooth potential well (Fig. 1). The Kramers formula

$$k_{\rm esc}=\frac{1}{\beta 2\pi}\sqrt{U''(a)|U''(b)|}e^{[U(a)-U(b)]/kT} \qquad (1)$$

expresses the escape rate from the well in terms of the structure of the well, the temperature T, the Boltzmann constant k and the coefficient of viscous friction β of the medium. At $x=a$ there is a minimum and at $x=b$ there is a maximum. $U''(a)$ and $U''(b)$ represent the second derivatives at these extrema. The formula applies when $U(b)-U(a)$ is significantly larger than kT and when the Brownian particles in the well obey the stationary Boltzmann distribution, i.e.,

$$P(x)=\frac{1}{Z}e^{-U(x)/kT}, \qquad (2)$$

where Z is a normalization factor.

Now suppose that the distribution of particles in the well is not a Boltzmann distribution. In that case the distribution will relax to a Boltzmann distribution. At the same time the escape rate from the well will relax to the one expressed by the above Kramers formula (1).

The main result of this paper is that *the relaxation time of the majority of the probability around the bottom of the well and the time for the transition rate to relax to the Kramers rate are different quantities that scale differently with barrier height and temperature*. The two rates have often been taken to be identical. But this can lead to serious misunderstanding. Generally the escape rate will have a longer relaxation time than the majority of the probability in the well. Furthermore, the relaxation rate of the escape time does not depend on temperature, whereas the relaxation time of the majority of the probability does.

We will present analytic as well as numerical results. Even though the mathematics we will present will be tricky, the final physical picture is an attractive and easy to understand one. We will find the relaxation time to the Kramers escape rate to be equal to the time it takes to deterministically slide down the barrier. Our results apply for barriers that are more than a few kT high. But this essentially encompasses all activated processes, including chemical reactions, nucleation phenomena, etc.

The relaxation of the escape rate is also the key factor in the escape behavior of an overdamped Brownian particle in a well with a fluctuating barrier. There are a great many problems in physics, chemistry, and biology that involve imposing an external fluctuation or oscillation on a system that takes time to equilibrate to the stationary distribution. Take, for instance, the situation that arises when a protein that is embedded in a cell membrane is subjected to a fluctuating electric field (e.g., the 60 Hz electromagnetic field from a power line) [1]. Proteins are very polar molecules and the different conformational states that a protein cycles through when it is catalyzing a chemical reaction generally have different values for the electric dipole moment. Imposing a fluctuating electromagnetic field on such a protein amounts to fluctuating the energy levels of the states in the catalysis. In such systems the relaxation time to stationarity within the well is an important quantity.

The theoretical study of overdamped particles in a well with a fluctuating barrier has led to the discovery of the

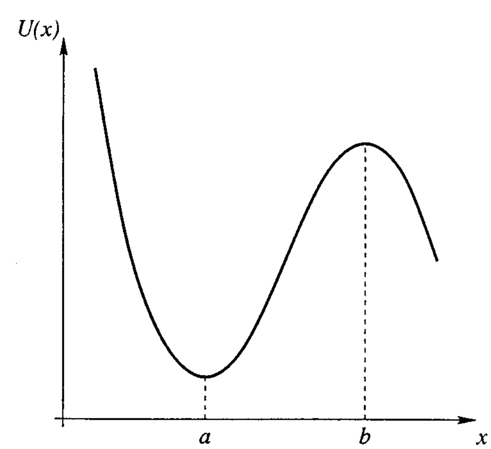

FIG. 1. A smooth potential with a well and a barrier. With a height of several kT units and with a Boltzmann distribution in the well the escape rate for overdamped Brownian particles is given by the Kramers formula (1).

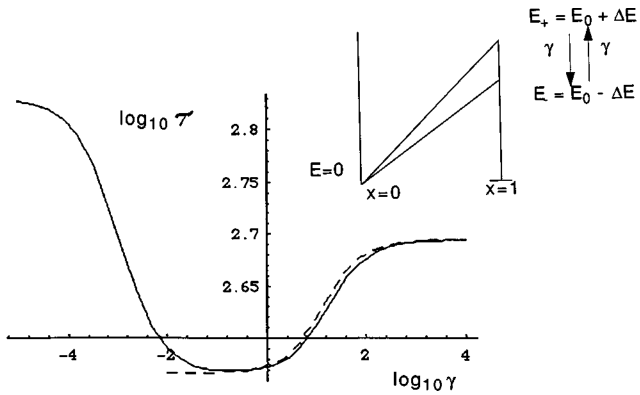

FIG. 2. The inset depicts the piecewise linear setup for our problem. The height of the barrier fluctuates between $E_+ = E_0 + \Delta E$ and $E_- = E_0 - \Delta E$. We study how long it takes before the particle escapes over the barrier and how this changes with the fluctuation rate γ. The graph shows $\log_{10}$ of the mean first passage time ($\mathcal{T}$) versus $\log_{10}(\gamma)$ with $E_0 = 11$ and $\Delta E = 1$. The solid line represents an exact evaluation. The dashed line is the prediction of the instanton mechanism (27) for $1/\gamma \ll \mathcal{T}$.

''resonant activation'' phenomenon [2–4]. Take, for instance, the system depicted in the inset in Fig. 2. The linear barrier is flipping between $(E_0 + \Delta E)$ and $(E_0 - \Delta E)$ with a rate γ for both transitions. At $t = 0$ we have for the probability density a δ function at $x = 0$ and probability 1/2 to be in $(E_0 + \Delta E)$ and probability 1/2 to be in $(E_0 - \Delta E)$. If, in the high frequency regime, the barrier fluctuations are very fast, the particle ''can never adjust'' to the instantaneous slope and the mean first passage time (MFPT) over the barrier is the one corresponding to the average barrier E_0. If, in the low frequency regime, the barrier fluctuations are slower than the actual escape rate the particle will escape before any barrier flip will occur. In that case the MFPT over the fluctuating barrier is the average of $\mathcal{T}_{E_0 + \Delta E}$ (the MFPT over a stationary $E_0 + \Delta E$) and $\mathcal{T}_{E_0 - \Delta E}$ (the MFPT over a stationary $E_0 - \Delta E$). The MFPT $\mathcal{T}_E$ over a stationary barrier of height E increases exponentially with E. So the low frequency MFPT, $\frac{1}{2}(\mathcal{T}_+ + \mathcal{T}_-)$, will be higher than the $\mathcal{T}_{E_0}$ of the high frequency limit. In the middle frequency regime the fluctuations are faster than the MFPT, but still slow enough that a stationary escape rate can be established each time we are in E_+ or E_-. We then get a situation where the effective escape rate over the fluctuating barrier is the average $\frac{1}{2}(k_+ + k_-)$, where $k_+ = 1/\mathcal{T}_+$ and $k_- = 1/\mathcal{T}_-$ represent the escape rates over the individual stationary barriers. The rate k_- is much larger than k_+ and, again because of the exponential dependence, the MFPT in the middle frequency regime will be smaller than $\mathcal{T}_{E_0}$. Figure 2 shows $\log_{10}(\mathcal{T})$ as a function of $\log_{10}(\gamma)$ and all the frequency regimes are present in this graph. The enhanced escape in the middle frequency regime has been called ''resonant activation'' [2]. With smooth wells and barriers and with other than dichotomous Markovian barrier flips the phenomenon also occurs [3].

In the first section we will see how for a sufficiently high barrier (or, equivalently, for sufficiently small noise) the escape rate relaxes like the probability density near the top of the barrier. The bulk of the probability is at the bottom of the well and relaxes faster. We will furthermore see how the relaxation time of the escape rate is identical to the instanton time, i.e., the time it takes to slide down from the top of the barrier to the bottom of the well.

In the second section we will analyze the aforementioned fluctuating linear barrier problem in detail and we will show how the identification of the instanton time with the relaxation time for the escape rate can quantitatively account for the transition from the middle frequency regime to the high frequency regime in the $\log_{10}(\mathcal{T})$ vs $\log_{10}(\gamma)$ graph (Fig. 2). In this section we will focus on the piecewise linear case which allows for many quantities to be analytically derivable.

I. INTRAWELL RELAXATION TIMES

The motion of an overdamped Brownian particle in a potential well is described by the Langevin equation

$$\beta \dot{x} = F(x) + \beta(\sqrt{2D})\xi(t), \tag{3}$$

where $F(x) = -(d/dx)U(x)$ is the force due to a potential $U(x)$, β is the coefficient of viscous friction, and D is the diffusion coefficient. The term $\xi(t)$ represents the Gaussian white noise with zero average and autocorrelation function $\langle \xi(t)\xi(t') \rangle = \delta(t - t')$. The system is overdamped, so there is no inertia and at any time the velocity of the particle is determined solely by the force on the particle at that moment. For a system in equilibrium β and D are connected to each other through the fluctuation-dissipation theorem, $\beta = kT/D$.

In a mathematical analysis the $\xi(t)$ is hard to handle. Because of $\xi(t)$, Eq. (3) is an ordinary differential equation that describes an evolution in time that is not deterministic. It is possible to derive an equivalent partial differential equation, the Fokker-Planck equation, to deterministically describe the evolution of the particle's probability density $P(x,t)$:

$$\beta \partial_t P(x,t) = -\partial_x [F(x)P(x,t)] + kT\partial_{xx}P(x,t). \tag{4}$$

A Brownian particle in a well (Fig. 1) will eventually escape. Given that the particle escapes it is possible to calculate the most likely escape path. The following derivation is due to Onsager and Machlup [5]. The derivation employs the principle of least action and shows that when the Brownian particle escapes, it most likely does so in one run, i.e., it does not dwell anywhere on the slope for any considerable time on the way to the top. Furthermore, the time it takes to do this ''run up the barrier'' is identical to the time that it would take to slide down the barrier in the absence of noise (see Fig. 3).

For a system with noise the application of the principle of least action is only slightly more involved than in the traditional treatment. For discretized time, i.e., $t_j = t_0 + j\Delta t$ with $j = 1,2,3, \ldots$, the $\xi(t_j)$'s are independent and have a Gaussian distribution with a zero average and a standard deviation of $1/\sqrt{\Delta t}$. The probability that a particular sequence of ''Brownian kicks'' $\xi(t_1), \xi(t_2), \ldots, \xi(t_n)$ is realized is proportional to $\Pi_{j=1}^{n} \exp[-\frac{1}{2}\xi^2(t_j)\Delta t] = \exp[-\frac{1}{2}\Sigma_{j=1}^{n}\xi^2(t_j)\Delta t]$. Going to the limit of a continuous time that runs from an initial time $t = t_i$ to a final time $t = t_f$ the sum becomes an integral:

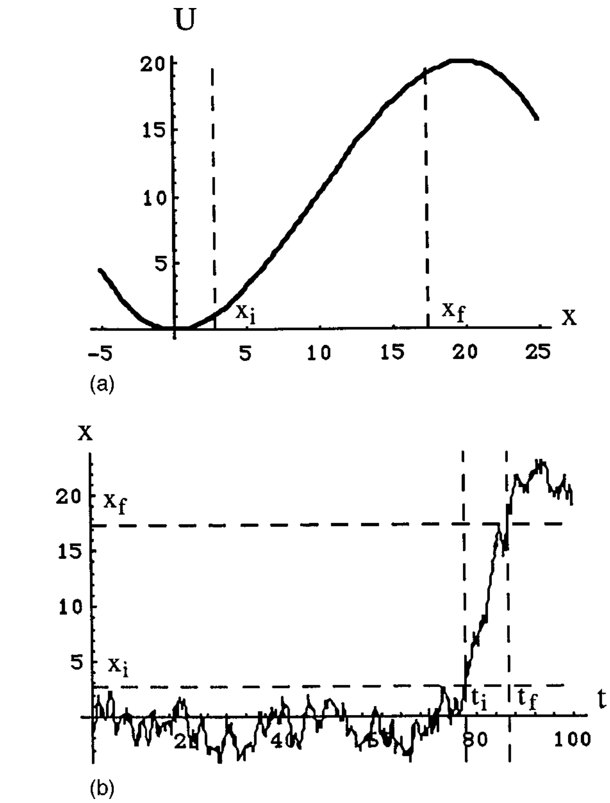

FIG. 3. An escape over the barrier requires a sequence of Brownian kicks that brings the particle against the strong deterministic force from x_i to x_f. In the text it is derived that the most likely such trajectory (between the last touch at x_i and the first touch at x_f) is an upslide that is the exact reverse of the deterministic downslide.

$$P[\xi(t)]\propto \exp\left(-\frac{1}{2}\int_{t_i}^{t_f}\xi^2(t)dt\right). \tag{5}$$

When we view the Langevin equation (3) as a mapping from ξ space to x space, $\xi(t)$ can be expressed as $[\dot{x}-F(x)/\beta]/\sqrt{2D}$. This means that the exponent of the above expression becomes $-S[x(t)]/D$, where

$$S[x(t)]\equiv\frac{1}{4}\int_{t_i}^{t_f}\left(\dot{x}-\frac{F(x)}{\beta}\right)^2 dt \tag{6}$$

is the action associated with a path $x(t)$. Notice that this quantity can never be negative.

When we change variables from $\xi(t)$ to $x(t)$ the probability densities must obey

$$\int_{\mathcal{S}}P[x(t)]dx(t)=\int_{\mathcal{S}}P[\xi(t)]d\xi(t), \tag{7}$$

where $\mathcal{S}$ represents a set of trajectories. For this equation to hold for all possible sets of trajectories we must have $P[x(t)]=\|d\xi/dx\|P[\xi(t)]$. So we have to evaluate the Jacobian $\|d\xi/dx\|$. After discretization this Jacobian becomes the determinant of a matrix. Because the matrix is triangular the determinant is the product of the trace elements $\Pi_{j=1}^{n}\|d\xi_j/dx_j\|$. The Jacobian compensates for the stretching and shrinking involved in the transformation from trajectories in noise space to trajectories in x space. The exact form of the Jacobian depends on the way the Langevin equation (3) is discretized. With the discretization

$$\frac{x_j-x_{j-1}}{\Delta t}=-\frac{U'(x_j)+U'(x_{j-1})}{2\beta}+\sqrt{2D}\xi_j \tag{8}$$

we derive

$$\prod_{j=1}^{n}\left\|\frac{d\xi_j}{dx_j}\right\|=\prod_{j=1}^{n}\frac{1}{\sqrt{2D}\Delta t}\left(1+\frac{1}{2}\frac{U''(x_j)}{\beta}\Delta t\right)$$
$$\approx\left(\frac{1}{\sqrt{2D}\Delta t}\right)^n\exp\left[\frac{1}{2\beta}\sum_{j=1}^{n}U''(x_j)\right]. \tag{9}$$

Eventually, in the continuum limit, this Jacobian takes the form

$$J[x(t)]=\exp\left\{\frac{1}{2\beta}\int_{t_i}^{t_f}U''[x(t)]dt\right\}. \tag{10}$$

This form for the Jacobian is also obtained when the noise is first assumed to have a nonzero correlation time, and when at the end of the calculation the limit is taken in which the correlation time goes to zero [6].

All in all, for the probability that a certain path $x(t)$ is realized we have

$$P[x(t)]\propto\exp\left\{-\frac{S(x)}{D}+\frac{1}{2\beta}\int_{t_i}^{t_f}U''[x(t)]dt\right\}. \tag{11}$$

Notice that in the low noise limit ($D\rightarrow 0$) the contribution of the $U''[x(t)]$ becomes negligible in comparison to the contribution of the action term. In that case the trajectory with the highest probability $P[x(t)]$ is simply the one for which the action $S[x(t)]$ is minimal.

Next we go to the low noise limit. We neglect the Jacobian contribution in Eq. (11) and take the integrand $L(x,\dot{x})=[\dot{x}-F(x)/\beta]^2$ as the Lagrangian. Using the Euler-Lagrange theorem, $[\partial/\partial x-(d/dt)(\partial/\partial\dot{x})]L(x,\dot{x})=0$, we derive the equation of motion $\beta^2\ddot{x}=F(x)(d/dx)F(x)$. A first integral is easily derived: $(\beta\dot{x})^2-F(x)^2=C$, where C is the constant of integration. It is obvious from the formula for $S[x(t)]$ that the most likely way to slide down is $\beta\dot{x}=F(x)$, i.e., the particle behaving as if there were no noise. This is not a surprising result. But from the integral we also infer that the most likely path up the barrier from a small diffusion dominated zone around the bottom of the well [where $F(x)\approx 0$ for smooth potentials and the noise thus dominates] to the small diffusion dominated zone around the top is $\beta\dot{x}=-F(x)$, i.e., the particle following the reverse path from the deterministic downslide. Such an upslide is what we call the ''instanton.''

The intuitive picture with this derivation is as follows. There are many ''attempts'' during which the particle goes quite a way up the barrier and then falls back. But the final ''successful attempt'' is most likely one during which the particle did not dwell anywhere on the slope for any time. The ''successful attempt'' was one during which the particle went up in one smooth ''instanton'' upslide that is the exact reverse of the deterministic downslide.

The instanton is the most likely trajectory, i.e., it is the maximum of a distribution and not the average. However, for smaller noise (i.e., higher barriers) the distribution of trajectories is more sharply peaked around this most likely trajectory and the exact instanton becomes an ever more likely escape route. Analog electrical circuits have been employed to observe such instantons [7]. For barriers of several kT the actual escape trajectories appear ''hairy'' because of the noise, but they are indeed very close to the instanton path (Fig. 3).

Next consider a well and a barrier as in Fig. 3. Equation (11) tells us that the most likely escape trajectory, i.e., the path between the ''last touch'' at the initial position x_i and the ''first touch'' at the final position x_f (Fig. 3) is the reverse of the deterministic downslide. But Eq. (11) gives even more information. The expression for the action can be rewritten as follows:

$$\frac{S[x(t)]}{D}=\frac{1}{2}\frac{\Delta U}{kT}+\frac{1}{4D}\int_{t_i}^{t_f}\left[\dot{x}(t)^2+\left(\frac{U'[x(t)]}{\beta}\right)^2\right]dt, \tag{12}$$

where ΔU is the energy difference between the end point x_f and the initial point x_i. The arguments $\dot{x}^2$ and $U'(x)^2$ are insensitive to whether you run your trajectory forward or backward. Also the $U''(x)$ in the Jacobian is unaffected by time reversal. So whether you run from (t_i,x_i) to (t_f,x_f) or from (t_i,x_f) to (t_f,x_i) via the time reversed path is only reflected in the prefactor, which is $e^{-\Delta U/2kT}$ for the upward path and $e^{\Delta U/2kT}$ for the downward path. This means that a sequence of Brownian kicks leading to an upward path $\chi(t)_{\mathrm{up}}$ is less likely than the sequence leading to the downward path $\chi(t)_{\mathrm{down}}$ by a factor $e^{-\Delta U/kT}$, i.e.,

$$P[\chi_{\mathrm{up}}(t)]=P[\chi_{\mathrm{down}}(t)]e^{-\Delta U/kT}. \tag{13}$$

This result makes sense. Suppose we have a reaction coordinate $U(x)$ and $U(x_f)$ is ΔU higher than $U(x_i)$. Then at a Boltzmann distribution the probability to be between x_i and $x_i+\Delta x$ is a factor $e^{\Delta U/kT}$ larger than the probability to be between x_f and $x_f+\Delta x$. So for the system as a whole there are just as many $(x_i,x_i+\Delta x)\rightarrow(x_f,x_f+\Delta x)$ transitions as there are $(x_f,x_f+\Delta x)\rightarrow(x_i,x_i+\Delta x)$ transitions. This is, in its most general form, the microscopic reversibility that we are supposed to have at equilibrium.

We take a slope that is part of a continuous potential $U(x)$ (Fig. 4). The point $x=0$ is at the left of a diffusion dominated basin around the minimum. We define the diffusion dominated basin as the interval where the energy is less than a kT higher than the energy at the minimum. The point $x=L$ is to the right of the diffusion dominated basin around the maximum (i.e., the interval where the energy is less than a kT lower than at the maximum). For a particle to make a full escape from the well it has to reach $x=L$. An escape thus also involves a crossing of the diffusion dominated basins. In these basins the instanton theory no longer applies and mere diffusion in an almost flat region has to do the job. The textbook by Gardiner [8] gives a derivation from the Fokker-Planck equation (Sec. 5.2.7) of the mean first passage time from any point along any potential to any other point. This MFPT is expressed in terms of a double integral of a function involving $U(x)$. Using this result we have for the MFPT, $\mathcal{T}_0(x\rightarrow L)$, from any point $x(0\leqslant x\leqslant L)$ to L,

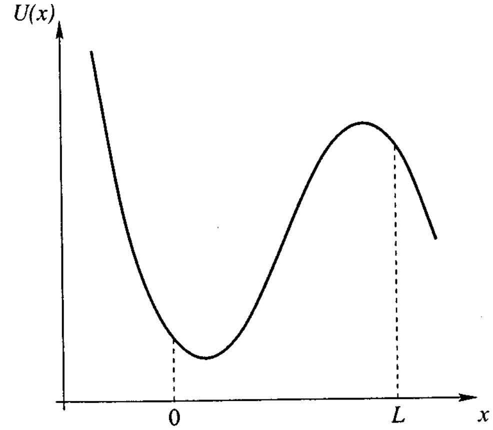

FIG. 4. A passage from the well over the barrier also involves diffusion across the flatter basins around the minimum and maximum. If this diffusion time is negligible in comparison to the instanton time to ''climb the barrier,'' then an escape trajectory from $x=0$ to $x=L$ can be identified with an instanton trajectory from $x=x_i$ to $x=x_f$ in the previous figure. In the text we relate mean first passage times between $x=0$ and $x=L$ to instanton times and intrawell relaxation times.

$$\mathcal{T}_0(x\rightarrow L)=\frac{1}{D}\int_x^L\int_0^y e^{[U(y)-U(z)]/kT}dz\,dy. \tag{14}$$

Technically this result is only valid when there is a reflecting barrier at $x=0$ (hence the ''0'' subscript), but when the potential is sufficiently steep at $x<0$ this formula is a good approximation for the potential in Fig. 4. From any point x $(0\leqslant x\leqslant L)$ to 0 we have

$$\mathcal{T}_L(x\rightarrow 0)=\frac{1}{D}\int_0^x\int_y^L e^{[U(y)-U(z)]/kT}dz\,dy. \tag{15}$$

Again this result is valid when there is a reflecting barrier at $x=L$. When we want to find the MFPTs of a ''Boltzmann distributed particle'' we have to integrate this double integral over a Boltzmann distribution. So to reach $x=L$ from a Boltzmann distribution on $[0,L]$ takes on the average

$$\mathcal{T}_0(B\rightarrow L)=\frac{1}{DZ}\int_0^L\int_x^L\int_0^y e^{[-U(x)+U(y)-U(z)]/kT}dz\,dy\,dx, \tag{16}$$

where $Z=\int_0^L\exp[-U(x)/kT]dx$ is again the normalization factor [cf. Eq. (2)]. Changing the order of integration we rewrite $\mathcal{T}_0(0\rightarrow L)$ in the following way:

$$\mathcal{T}_0(0\to L)=\frac{1}{D}\int_0^L\int_0^y e^{[U(y)-U(x)]/kT}dx\,dy$$
$$=\frac{1}{D}\int_0^L\int_x^L e^{[U(y)-U(x)]/kT}dy\,dx$$
$$=\frac{1}{DZ}\int_0^L\int_x^L\int_0^L e^{[-U(x)+U(y)-U(z)]/kT}dz\,dy\,dx. \tag{17}$$

From the above two formulas we derive

$$\mathcal{T}_0(0\to L)-\mathcal{T}_0(B\to L)$$
$$=\frac{1}{DZ}\int_0^L\int_x^L\int_y^L e^{[-U(x)+U(y)-U(z)]/kT}dz\,dy\,dx. \tag{18}$$

We rewrite this expression in two steps:

$$\frac{1}{DZ}\int_0^L\int_0^L\int_y^L e^{[-U(x)+U(y)-U(z)]/kT}dz\,dy\,dx$$
$$-\frac{1}{DZ}\int_0^L\int_0^x\int_y^L e^{[-U(x)+U(y)-U(z)]/kT}dz\,dy\,dx$$
$$=\frac{1}{D}\int_0^L\int_y^L e^{[U(y)-U(z)]/kT}dz\,dy$$
$$-\frac{1}{Z}\int_0^L e^{-U(x)/kT}\left[\frac{1}{D}\int_0^x\int_y^L e^{[U(y)-U(z)]/kT}dz\,dy\right]dx \tag{19}$$

and find it to be equal to $\mathcal{T}_L(L\to 0)-\mathcal{T}_L(B\to 0)$.

All in all, we have derived the following equality:

$$\mathcal{T}_0(0\to L)-\mathcal{T}_0(B\to L)=\mathcal{T}_L(L\to 0)-\mathcal{T}_L(B\to 0). \tag{20}$$

It is important to realize that this equation is not an approximation and that it is valid between any two points $x=0$ and $x=L$ on any potential $U(x)$ [9]. If the time to diffuse across the diffusion dominated basin around the minimum $\mathcal{T}_L(B\to 0)$ is negligible in comparison to the time $\mathcal{T}_L(L\to 0)$, i.e., the time to diffuse across the diffusion dominated basin near the maximum plus the time to slide down, we have

$$\mathcal{T}_0(0\to L)-\mathcal{T}_0(B\to L)\approx\mathcal{T}_L(L\to 0). \tag{21}$$

This equation has an interesting interpretation. $\mathcal{T}_0(B\to L)$ is the escape time from a stationary distribution, i.e., the inverse of the Kramers rate. $\mathcal{T}_0(0\to L)$ is the escape time when we start from a Dirac δ distribution at $x=0$. The difference of these two times can be interpreted as the time $\tau=\mathcal{T}_0(0\to L)-\mathcal{T}_0(B\to L)$ it takes for the probability density to change to a distribution where the Kramers rate applies. If the times to diffuse across the diffusion dominated basins are negligible in comparison to the time to deterministically slide down the barrier, then formula (21) tells us that the relaxation time τ of the MFPT is identical to the instanton time.

So the relaxation time of the MFPT equals the instanton time to deterministically slide down the barrier. It is worth noticing that the instanton time is independent of temperature. This is a counterintuitive result: the relaxation is diffusion driven and one would expect a faster relaxation for higher temperature. At the end of Sec. II we will come back to this point.

For Fig. 5 we took $U(x)=-E(2x^3/20^3-3x^2/20^2)$, where the energy is in kT units. This is a smooth and differentiable function for all values of x. The bottom of the well is at $x=0$, where we have $U(0)=0$, and the top of the barrier is at $x=20$ for which $U(20)=E$. The time is scaled such that $\beta=D=1$. Figure 5 is the result of a simulation of the Fokker-Planck equation (4). We start with a Dirac δ function at $x=0$ and we depict the flux, $J(x,t)=-[U'(x)+\partial_x]P(x,t)$, as a function of time for $x_1=10$. It is clear from the graph that the appropriate amount of probability at $x_1=10$ arrives in a ''package.'' We can calculate the time T_{det} it takes a particle to deterministically slide down from $x_1=10$ to an x_0 at the edge of the diffusion dominated basin on the bottom. From $\dot{x}=-dU(x)/dx$ it is straightforwardly derived that

$$T_{\mathrm{det}}=-\int_{x_1}^{x_0}\left[\frac{dU(x)}{dx}\right]^{-1}dx=\frac{200}{3E}\ln\left[\frac{(20-x_0)x_1}{(20-x_1)x_0}\right]. \tag{22}$$

When we take for x_0 the value of x for which $U(x)=1$, we find $x_0=1.9$ for $E=40$ and $x_0=2.7$ for $E=20$. Substituting these values in the above expression for T_{det} we find $T_{\mathrm{det}}=3.8$ for $E=40$ and $T_{\mathrm{det}}=6.2$ for $E=20$. These estimates for T_{det} correspond very well with the location of the peaks of the instantons in Fig. 5.

It is reasonable to associate the relaxation time at any x_1 with the peak of the instanton. The trajectory of this peak is the reverse of the deterministic downslide. When a distribution in a well like Fig. 1 relaxes to a Boltzmann distribution it is the little bit of probability near the top of the barrier that matters for the escape rate over the barrier. The relaxation takes place last near the top of the barrier. The escape rate therefore relaxes slower than the ''rest of the distribution.'' It would be a definite mistake to identify the relaxation of the escape rate with the relaxation of the majority of the probability in the bottom of the well. The latter is generally much faster.

II. PIECEWISE LINEAR CASE

In this section we will take the example of a linear slope with a reflecting barrier at $x=0$ and an absorbing barrier at $x=1$. The slope, and thus the barrier height, equals E (Fig. 6). In a linear setup like this it is often possible to formulate analytic solutions. The results we will obtain below illustrate the general points made in the broader context of the preceding section. In problems with diffusion it usually does not make for qualitatively different results when ''corners'' are introduced. Diffusion tends to ''smooth things out.'' The solutions for the piecewise linear potential are therefore expected not to differ qualitatively from those for smooth differentiable potentials (as is borne out by numerical calculations).

When the barrier fluctuates (Fig. 2, inset) the time scale of

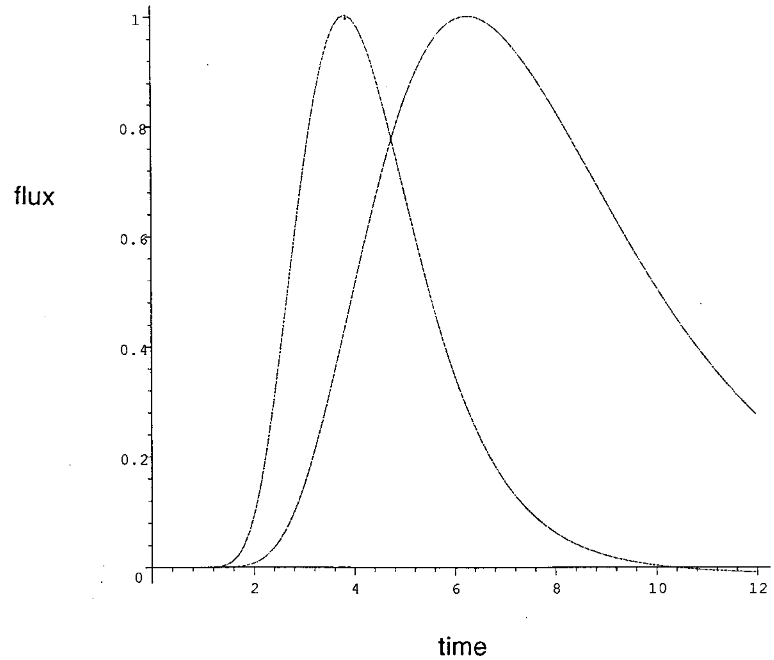

FIG. 5. The differentiable potential $U(x) = -E(2x^3/20^3 - 3x^2/20^2)$ has the shape depicted in Figs. 1, 3(a), and 4 with a $U=0$ minimum at $x=0$ and a $U=E$ maximum at $x=20$. We start with a Dirac δ function at $x=0$ at $t=0$ and follow how the probability density develops as a function of time. The graph shows the flux through $x=10$ (halfway the barrier) as a function of time for $E=20$ (right curve) and for $E=40$ (left curve). The fluxes have been normalized by factors 9.7×10^{-7} for $E=20$ and 6.7×10^{-11} for $E=40$. Instantons appear to be traveling up at the sliding down speed (see text).

the fluctuation enters the problem. If the barrier fluctuates faster than the relaxation of the escape rate, the particle effectively ''sees'' the average barrier height and the escape time over the barrier is indeed observed to be identical to the one over the average barrier if it were stationary. Below we will study the transition from the adiabatic regime (where the fluctuations are slow and the probability distribution can follow the flipping slope and be Boltzmann most of the time) to the nonadiabatic regime (where fluctuations are too fast and the probability distribution never gets adjusted to the slope).

As we explained in the preceding section, when the Brownian particle escapes, it most likely does so in one smooth run without dwelling anywhere on the slope for any considerable time. The time it takes to execute this ''run up the barrier'' is identical to the time that it would take to slide down the barrier in the absence of noise. This instanton time is a characteristic time scale in the fluctuating barrier setup and through analytic results we will see in this section how this time scale is responsible for the adiabatic-to-nonadiabatic transition.

We analyze the linear slope with a reflecting barrier at $x=0$ and an absorbing barrier at $x=1$. We, furthermore, dedimensionalize the variables by absorbing β in the time scale and expressing the energy in kT units. Because of the fluctuation-dissipation theorem ($D=kT/\beta$) this also leads to the disappearance of D from the Langevin equation (3) and the equivalent Fokker-Planck equation (4). When, in this setup, a stationary barrier height is E_0, the instanton lasts $t_0=1/E_0$. It is, furthermore, worth noticing that with the stationary linear slope the most likely upward path is one where the ''Brownian kicks'' do all have the same strength. It is because of the upward concavity (positive second derivative) of the quadratic in $\exp[-\Sigma\xi_i^2/2]$ that a ''small kick'' that is subsequently compensated for by a ''big kick'' is less likely than two kicks of the average magnitude ($\exp[-2\xi^2] > \exp[-(\xi+\Delta\xi)^2-(\xi-\Delta\xi)^2]$).

We consider a Brownian particle in a well and we are interested in the mean first passage time over a barrier. Even when the barrier is fluctuating at a rate γ the associated Fokker-Planck equations

$$\begin{aligned}\partial_t P_+ &= (E_0+\Delta E)\partial_x P_+ + \partial_{xx}P_+ - \gamma(P_+ - P_-),\\ \partial_t P_- &= (E_0-\Delta E)\partial_x P_- + \partial_{xx}P_- + \gamma(P_+ - P_-)\end{aligned} \tag{23}$$

can be evaluated to yield an analytic expression for the MFPT [8,4], even though the algebra involved in such an evaluation requires the power of a symbolic manipulation package like MATHEMATICA. The MFPT over a stationary barrier of height E (Fig. 6) for a particle at $x=0$ when $t=0$ is $\mathcal{T}_E = (e^E - 1 - E)/E^2$. When we let the barrier fluctuate between $E_0+\Delta E$ and $E_0-\Delta E$ (see Fig. 2), all the characteristic time scales for the Brownian particle in the well

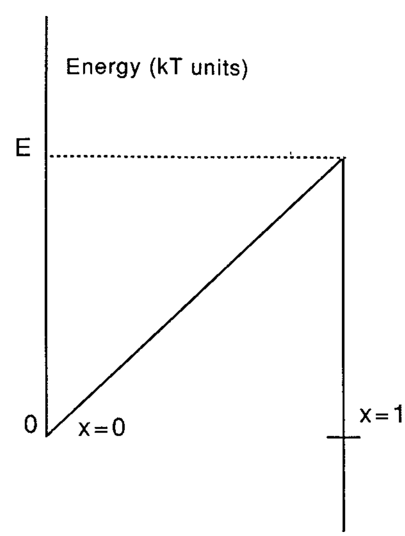

FIG. 6. A stationary linear well of width 1 and height E. There is a reflecting barrier at $x=0$ and an absorbing barrier at $x=1$. With the energy in kT units and diffusion coefficient $D=1$ it can be derived that the mean first passage time for a particle that is located at $x=0$ at $t=0$ equals $(e^E-1-E)/E^2$.

will show up in the $\log_{10}(\mathcal{T})$ vs $\log_{10}(\gamma)$ graph (Fig. 2,solid curve). As the initial condition we take the particle to be at $x=0$ and the barrier to be equally likely in the $+$ as in the $-$ state, i.e., $P_+(0)=1/2$ and $P_-(0)=1/2$. The problem of escape over a fluctuating barrier has been analyzed and understood in ever greater generality (see [2,4,3,10,11], and references in [3]). A curve like Fig. 2, with two inflection points and the minimum plateau in the middle, occurs also for nonpiecewise linear wells [3]. For small γ, i.e., the low frequency regime, the particle escapes before the barrier can ever change and the MFPT is the average of $\mathcal{T}_{E_0+\Delta E}$ and $\mathcal{T}_{E_0-\Delta E}$. For sufficiently large ΔE this average is well approximated by $\frac{1}{2}\mathcal{T}_{E_0+\Delta E}$. In the middle frequency regime the flipping time of the barrier (i.e., the average time between two transitions) is much shorter than $\mathcal{T}_{E_0+\Delta E}$. What happens as a result is that escape will most likely take place over the lower barrier. Since half the time is spent on the lower barrier the MFPT can be well approximated by $2\mathcal{T}_{E_0-\Delta E}$. In the high frequency regime the MFPT is the passage time over the average barrier, i.e., $\mathcal{T}_{E_0}$. The standard view of this is that in the high frequency regime the probability distribution of the particle never gets an opportunity for intrawell relaxation and effectively ''feels'' the average potential. Below we will apply the ideas of the preceding section and we will see how in this escape problem the time scale for intrawell relaxation is actually the time scale for the ascending instanton.

Next we must extend the principle of least action to a nonstationary system and derive the time it takes the instanton to run up the fluctuating slope. For that purpose we should consider a deterministic particle on a fluctuating downslide (Fig. 7). The evolution of the probability distribution during the fluctuating downslide is described by

$$\begin{aligned} \partial_t P_+ &= -(E_0+\Delta E)\partial_x P_+ - \gamma(P_+-P_-), \\ \partial_t P_- &= -(E_0-\Delta E)\partial_x P_- + \gamma(P_+-P_-). \end{aligned} \tag{24}$$

As the $t=0$ condition we have the particle at $x=0$ and equal probability for the barrier being up or down, i.e., $P_+(x,t=0)=P_-(x,t=0)=\delta(x)/2$. Equations (24) are identical to the Fokker Planck equations (23) that describe the problem of escape over a barrier, except for the sign of $(E_0+\Delta E)$ and $(E_0-\Delta E)$ and the fact that there is no diffusion term (i.e., second derivative). It is the stochastic fluctuations of the slope that are responsible for the δ functions turning into a continuous distribution during the descent from $x=0$ to $x=1$. We will thus find a distribution of instanton times [see Fig. 7(b)] from which a distribution of MFPTs and an average MFPT can be derived. This approximate average MFPT can then be compared to the exact solution of Fig. 2. In [12] we perform this calculation. Below we show a derivation with a few shortcuts that also leads to a good approximation.

We pointed out earlier in this section that when the instanton goes up a static linear slope, the Brownian kicks provide a constant force along the most probable path. In a discretization this means that all the Brownian kicks have an identical magnitude κ. This makes sense because the probability of a sequence of n such kicks is proportional to $\exp[-n\kappa^2/D]$, whereas a sequence with $n-2$ kicks of size κ and one kick of $\kappa+\Delta\kappa$ and one kick of $\kappa-\Delta\kappa$ brings the particle equally fast over the barrier, but has a smaller probability, which is proportional to $\exp[-n\kappa^2/D-2(\Delta\kappa)^2/D]$. Note that this reasoning only applies in the low noise (small D) limit. Only then does the exponential overcome the effect of the extra permutations.

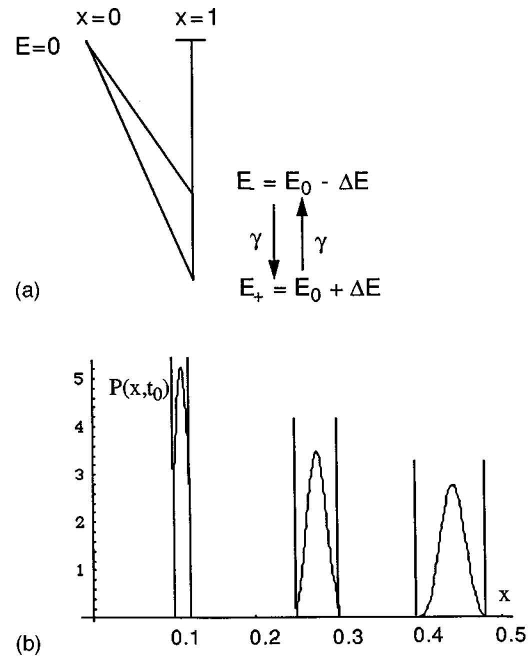

FIG. 7. In order to find the distribution of instanton times for the system of Fig. 2 we solve the equations for the evolution of the probability density when a particle slides down a fluctuating slope (a) with $P_+(x,t=0)=P_-(x,t=0)=\delta(x)/2$. (b) depicts the evolution of the probability density $(P_++P_-)(x,t)$ when a particle is going down the fluctuating slope. The fluctuation rate is $\gamma=20$ and we have $E_0=11$ and $\Delta E=1$. $(P_++P_-)(x,t)$ is depicted at $t=0.01$, $t=0.025$, and $t=0.04$. Two δ functions grow smaller and move apart, while between them a Gaussian develops.

Because the Langevin equation is linear in the force, the above argument holds even if the slope is fluctuating: if we decrease one Brownian kick and increase another one by the same amount, the duration of the particle's escape remains unchanged, but the probability of the sequence of these kicks becomes smaller. This means that the most likely escape trajectory, i.e., the Brownian instanton, has a lower speed when the slope is steeper. For the deterministic downslide, on the other hand, the speed is higher on the steeper slope. Thus, the Brownian instanton and the deterministic downslide no longer follow paths that are each other's time reverse as in the case of the stationary slope. However, if the fluctuation ΔE is small relative to the barrier height E_0, we can well approximate the velocity of the Brownian instanton by E_0 and the instanton time by $t_0=1/E_0$.

The escaping instanton spends part of the time on the $(E_0+\Delta E)$ slope and part of the time on the $(E_0-\Delta E)$ slope. On the steep $(E_0+\Delta E)$ slope it increases its potential energy at a rate $r_+=(E_0+\Delta E)/t_0$. On the $(E_0-\Delta E)$ slope the potential energy increases at a rate $r_-=(E_0-\Delta E)/t_0$. This implies that there is a distribution of the exit energies $p(E)$ when the particle reaches $x=1$. To derive this distribution we solve the continuity equations for the probability distributions $Q_+(E,t)$ and $Q_-(E,t)$.

$$\partial_t Q_+ + r_+ \partial_E Q_+ = \gamma(Q_+ - Q_-),$$
$$\partial_t Q_- + r_- \partial_E Q_- = \gamma(Q_- - Q_+). \tag{25}$$

$Q_\pm(E,t)dE$ is the probability for the ascending instanton to be on the $(E_0 \pm \Delta E)$ slope and have accumulated an amount of energy between E and $E+dE$. At $t=0$ we have $E=0$ and the barrier has equal probability for being up or down. So the initial condition is $Q_+(E,t=0)=Q_-(E,t=0)=\delta(E)/2$. Stochastic fluctuations of the slope turn the δ functions into a distribution during the escape. Equation (25) will thus yield a distribution of exit energies. After a Laplace transform of the time the system can be solved. For the inverse Laplace transformation the required canonical forms are $\exp[-sT]-\exp[-T\sqrt{(s^2+a^2)}]$, $[s/\sqrt{(s^2+a^2)}]\exp[-T\sqrt{(s^2+a^2)}]-\exp[-sT]$ and $\exp[-T/\sqrt{(s^2+a^2)}]/\sqrt{(s^2+a^2)}$. These are listed in [13] and [14]. We let $\zeta(E,t)=\sqrt{(E_0\Delta E t)^2-(E_0^2 t-E)^2}$ and find

$$Q_+(E,t)+Q_-(E,t)=\frac{\gamma e^{-\gamma t}}{2E_0\Delta E}I_0\left[\frac{\gamma}{E_0\Delta E}\zeta(E,t)\right]+\frac{\gamma t e^{-\gamma t}}{2\zeta(x,t)}I_1\left[\frac{\gamma}{E_0\Delta E}\zeta(E,t)\right]$$
$$+e^{-\gamma t}\frac{\delta[tE_0(E_0+\Delta E)-E]+\delta[tE_0(E_0-\Delta E)-E]}{2} \tag{26}$$

on $tE_0(E_0-\Delta E)\leqslant E\leqslant tE_0(E_0-\Delta E)$ and zero elsewhere. The functions I_0 and I_1 represent the modified Bessel functions of the zeroth and first kind [13]. The third term of this expression describes δ functions that advance with velocities r_+ and r_-. Because of the exponential flipping time distribution these δ functions carry an $\exp(-\gamma t)$ in front. For large enough t many flips occur. Then the central limit theorem becomes applicable and $Q_+ + Q_-$ becomes a Gaussian around $E=E_0^2 t$. The final probability distribution of the exit energies can be expressed as $p(E)=Q_+(E,t=t_0)+Q_-(E,t=t_0)$.

We take the escape rate k over the stationary barrier of height E (Fig. 6) as the inverse of the MFPT, i.e., $k(E)=E^2[\exp(E)-1-E]^{-1}$. Since ΔE is small relative to E_0 this formula can be used even if the slope fluctuates, and the MFPT can be well approximated as

$$\mathcal{T}_{\text{avg}}=\left[\int_{E_- -0}^{E_+ +0}k(E)p(E)dE\right]^{-1} \tag{27}$$

for $\gamma \gg k(E_0)$. $p(E)$ is a complicated function, but the modified Bessel functions are a standard feature of MATHEMATICA and the integral is readily calculated with this package.

Figure 2 shows how in the middle and high frequency regime there is good correspondence between the exact solution (solid line) and the curve predicted by the above formula (27) for $\mathcal{T}_{\text{avg}}$ (dashed line). We checked for many values of E_0 and ΔE and the deviation between the curves is always small.

The transition of the solid line in Fig. 2 from the lowest plateau to the $\gamma\to\infty$ plateau is the transition from the regime where the probability distribution can follow the fluctuation all the time (i.e., the adiabatic regime) to the regime where the probability distribution is no longer able to do so (i.e., the nonadiabatic regime). In Fig. 2 we are looking at MFPTs, i.e., the escape behavior, so it is the probability density near the top of the barrier that is important. The adiabatic-to-nonadiabatic transition in Fig. 2 can therefore be quantitatively accounted for by the instanton mechanism. The relaxation time of the escape rate appears to be the time it takes the instanton to ascend.

When the shape of a potential well changes, the probability distribution for a Brownian particle in that well follows in the course of time. Suppose we have a barrier as in Fig. 6 with a nonfluctuating height E. When we start with a Dirac δ function at $x=0$ as the initial condition, we can solve the Fokker-Planck equation by separation of variables (cf. [8], Sec. 5.2.5). This leads to a sequence of eigenfunctions, each of which exponentially relaxes to zero. The relaxation times can be derived to be the positive solutions for τ of $\tan(\frac{1}{2}\sqrt{4/\tau-E^2})=-\sqrt{4/\tau-E^2}/E$. The largest relaxation time, τ_1, is the one corresponding to the first eigenfunction and this time can be taken to be the intrawell relaxation time of the bulk of the distribution. In the small noise limit (large E) τ_1 approaches $2/E^2$.

The eigenfunction expansion emphasizes the bottom of the well, near $x=0$, where most of the probability is concentrated. But in the setup of Fig. 2 it is the relaxation of the escape rate that is of importance. For the escape over the barrier it is the little bit of probability near the top, i.e., $x=1$, that is relevant and in that region the equilibration takes longer ($1/E$ vs $2/E^2$). To understand this in another way take again the barrier as in Fig. 6 with a stationary height E. For a particle at position x, $0\leqslant x\leqslant 1$, at $t=0$ the MFPT is $\mathcal{T}(x)=\{e^E-e^{Ex}-E(1-x)\}/E^2$. When the particle is at $x=0$ at $t=0$ this means $\mathcal{T}(0)=(e^E-1-E)/E^2$. For an "equilibrated particle" we have a Boltzmann distribution $P(x)=Ee^{-Ex}/(1-e^{-E})$. For such a particle the MFPT is $\mathcal{T}^*=\int_0^1\mathcal{T}(x)P(x)dx$, which works out to $\mathcal{T}^*=(e^E-2E-e^{-E})/[E^2(1-e^{-E})]$. $\mathcal{T}^*$ is smaller than $\mathcal{T}(0)$ and we can take $\tau=\mathcal{T}(0)-\mathcal{T}^*$ to be the time it takes for the probability density to go from a δ function at $x=0$ to a an equilibrated Boltzmann distribution. As such it is a good measure for the intrawell equilibration time. We find $\tau=(1/E)-(2/E^2)$

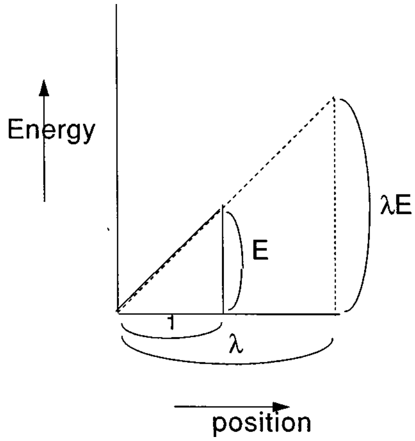

FIG. 8. We create a bigger and wider well with the same slope by taking the well depicted in Fig. 6 and extend the height and length by the same factor λ. The instanton time and the relaxation time of the Kramers rate increase by the same factor λ, whereas the intrawell relaxation time for the majority of the probability remains unaffected.

$+2e^{-E}/(E(1-e^{-E}))$. So at leading order in $1/E$ (taking the large E limit is equivalent to taking the low noise limit) the adiabatic adjustment time τ equals the instanton time.

The result of the preceding paragraph is a special case of Eq. (20) as derived in Sec. I. But for the piecewise linear slope there is no curvature at the top and no curvature at the bottom. So there are no flat basins that are to be crossed by mere diffusion.

When we take the instanton (equilibration) time of $1/E$ back to dimensionalized variables with a well of any width L, we get $\beta L^2/E$. It is worth noticing that this time does not depend on the temperature. This may seem paradoxical since the equilibration is a diffusion driven process. However, the slower diffusion at lower temperature is apparently balanced out by the fact that the Boltzmann distribution prescribes a smaller probability density near the top of the barrier at lower temperatures. The slower diffusion at lower temperature is compensated for exactly by the smaller fraction that has to diffuse and the equilibration time comes out independent of temperature. On the other hand, the $2/E^2$ equilibration time of the distribution in the bottom of the well unscales as $2kT\beta L^2/E^2$ and does depend on temperature.

Take a sufficiently high linear barrier of height E at width 1 (Fig. 8). If both the height and the width are multiplied with the same factor λ a linear well with the same slope is obtained. The instanton time, and thus the relaxation time of the escape rate, increases with the same magnification factor λ. When the relaxation is from a δ function to a Boltzmann distribution, for E larger than about 4, the vast majority of the probability is and stays near the bottom of the well and does not ''sense'' anything of what happens to the right of $x=1$. Indeed the $2kT\beta L^2/E^2$ equilibration time of the distribution in the bottom of the well is insensitive to the magnification as the λ's in E^2 and L^2 cancel each other out.

There is no obvious quantitative definition for the relaxation time of a distribution in a well. This relaxation is not a simple exponential one and proceeds differently at different points in the well. Taking as the criterion the behavior of the majority of the probability in the bottom of the well leads to different characteristic times than taking the relaxation time of the escape rate as the criterion. Generally, the relaxation of the probability distribution cannot be identified with the relaxation of the escape rate to the Kramers rate [Eq. (1)]. The escape rate has a slower relaxation.

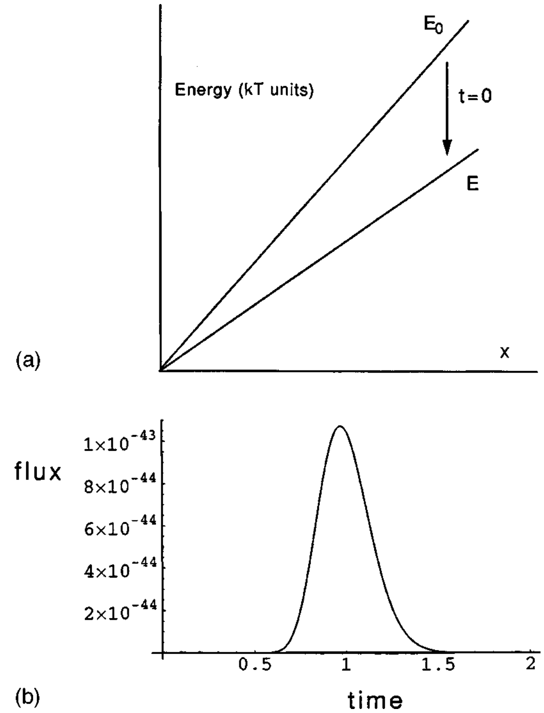

FIG. 9. (a) We have a reflecting barrier at $x=0$ and a positive slope that extends to $x\to\infty$. At $t=0$ the slope is changed from a value E_0 to E. For this linear setup it is possible to analytically follow how the probability density for an overdamped Brownian particle relaxes to a new Boltzmann distribution. In the text we find the simplest mathematics for the case that $E_0\to\infty$, i.e., at $t=0$ we start out with a Dirac δ function. (b) A plot of the flux, $\partial_t P(x_0,t)$, through $x_0=10$ for $E=10$. Apparently the appropriate amount of probability arrives in an ''instanton package'' after a time x_0/E.

Finally, in the same way as we did at the end of Sec. I we can ''see'' the instanton by following the relaxation of the probability density in a stationary potential through the Fokker-Planck equation. Again we start with a delta function at the bottom and look at the flux at a point sufficiently far away from the bottom. This time we do not need numerics. For the linear case an easy analytic expression for the flux can be derived.

Take a linear slope that has a reflecting barrier at $x=0$. At $x=1$ the potential energy is E. The slope extends to infinity, so for all x, E is also the value of the slope and therefore of the deterministic force driving a particle to $x=0$. Before $t=0$ the slope is $E_0\to\infty$. At $t=0$ the value of the slope switches to a finite value E [Fig. 9(a)]. The Fokker-Planck equation that describes the time evolution of the probability density when $t>0$ is $\partial_t P(x,t)=(E+\partial_x)\partial_x P(x,t)$. The boundary condition is obtained from the fact that the flux at the reflecting barrier at $x=0$ equals zero at all times, i.e., $(E+\partial_x)P(0,t)=0$. The initial condition is constituted by the Boltzmann distribution on E_0, i.e., $P(x,0)=E_0 e^{-E_0 x}$. Laplace transforming the time $[\pi(x,s)=\int_0^\infty e^{-st}P(x,t)dt]$ leads to the following ordinary differential equation in x:

$$\partial_{xx}\pi(x,s)+E\partial_x\pi(x,s)-s\pi(x,s)=-E_0e^{-E_0x}. \quad (28)$$

This equation is easily solved and yields for $\pi(x,s)$

$$\pi(x,s)=Ce^{\lambda x}-\frac{E_0}{E_0^2-E_0E-s}e^{-E_0x}, \quad (29)$$

where λ is the only negative eigenvalue,

$$\lambda=-\frac{1}{2}(E+\sqrt{E^2+4s}). \quad (30)$$

The exponential with the positive eigenvalue is not a legitimate part of the solution since it would let $\pi(x,s)$ blow up at $x\rightarrow\infty$. Demanding the solution to be normalizable is equivalent to allowing only the negative eigenvalue. The value of the constant C is to be determined from the boundary condition and we find

$$C=\frac{2E_0(E_0-E)}{(E+\sqrt{E^2+4s})[s-E_0(E_0-E)]}. \quad (31)$$

Taking the $E_0\rightarrow\infty$ limit effectively means that we start with a δ function at $x=0$. In Laplace space the $t\rightarrow 0$ limit corresponds to $s\rightarrow\infty$. For infinite E_0 and finite s the second part of the solution (29) (the particular part) cancels out and the numerator of C cancels against the $s-E_0(E_0-E)$ part in the denominator. The inverse Laplace transformation can now easily be performed and gives as the solution

$$P(x,t)=Ee^{-Ex}\left[\frac{1}{2}+\frac{e^{-(-Et+x)^2/4t}}{E\sqrt{\pi t}}+\frac{1}{2}\mathrm{erf}\left(\frac{-Et+x}{2\sqrt{t}}\right)\right]. \quad (32)$$

Using the $z\rightarrow\infty$ expansion for the erf function [13] we take $\mathrm{erf}(z)\approx 1-(1/z\sqrt{\pi})e^{-z^2}$ and find at $x=0$

$$P(0,t\rightarrow\infty)=E\left[1+\frac{4}{E^3t\sqrt{\pi t}}e^{(-E^2/4)t}\right]. \quad (33)$$

So we see a relaxation time for the probability density at $x=0$ that is proportional to E^{-2}. We get a different picture for $x_0>1/E$, i.e., when x_0 is outside the diffusion dominated domain. For the $t\rightarrow\infty$ limit the Boltzmann distribution prescribes $P(x_0,t\rightarrow\infty)=Ee^{-Ex_0}$. After $t_0=x_0/E$, i.e., the time it takes the instanton to go from 0 to x_0, the argument of the erf function and of the exponential in Eq. (32) equals zero and we thus have

$$P(x_0,x_0/E)=Ee^{-Ex_0}\left[\frac{1}{2}+\frac{1}{\sqrt{\pi Ex_0}}\right]. \quad (34)$$

For Ex_0 being sufficiently larger than one (i.e., being outside of the diffusion dominated domain), we get $\sqrt{\pi Ex_0}\ll 1/2$. This means that after the instanton time x_0/E the probability density at x_0 has reached 1/2 of its final value Ee^{-Ex_0}. Figure 9(b) shows the flux as a function of time through a point x_0 far outside the diffusion dominated domain. The figure shows how the probability arrives in a ''package'' that is centered around the instanton time $t_0=x_0/E$. The flux is easily evaluated as $J(x,t)=-(E+\partial_x)P(x,t)$ and yields the simple expression

$$J(x,t)=\frac{x}{2t\sqrt{\pi t}}e^{-(Et+x)^2/4t}. \quad (35)$$

For large x and t it is the variations in the exponent that are important when x and t vary. At a location x_0 outside the diffusion dominated domain the flux $J(x_0,t)$ will have a maximum when $(Et+x_0)^2/4t$ has a minimum. One easily finds that this happens when $t=x_0/E$, i.e., the peak of the ''probability package'' follows the instanton path. Figure 9(b) shows the shape of the instanton. We can estimate the width of the instanton by making a Taylor expansion of $f(t)=(Et+x_0)^2/4t$ around $t_0=x_0/E$. Going to second order $[f(t)\approx f(t_0)+1/2f''(t_0)(t-t_0)^2]$ leads to $f(t)\approx Ex_0+(E^3/4x_0)(t-t_0)^2$. The coefficient of the second order Taylor term represents the curvature at the maximum and its square root, i.e., $(E/2)\sqrt{E/x_0}$, is a good approximation for the ''sharpness'' of the instanton [cf. Fig. 9(b)]. So the instanton is more sharply peaked for steeper slopes (or, equivalently, lower temperature/smaller noise). The instanton also gets wider for larger x_0, i.e., as it moves up it flattens out.

The picture that emerges is the following. In the relaxation from a δ function to a Boltzmann distribution along the x axis the appropriate amount of probability in some interval is deposited as a package that arrives after the instanton time. The instanton package moves as the reverse of a downsliding particle, except for the fact that the instanton has a widening probability distribution as time goes on.

DISCUSSION

The theory we presented applies in principle to any activated process. For most chemical reactions the intrawell relaxation time (whether you take it to be the relaxation time of the majority of the distribution or the relaxation time of the Kramers rate) is of the order of femtoseconds and as such not yet within a realm that is experimentally accessible. However, there are other activated processes that take place on more measurable time scales. For nucleation phenomena, for instance, the energy as a function of the size of the nucleation kernel looks like a curve as in Fig. 1. In such setups thermal fluctuations have to increase the size of a kernel against the energy gradient until the critical size (i.e., the maximum in Fig. 1) is reached. Once the critical size is exceeded the kernel rapidly grows and loses energy. In nucleation experiments the relaxation times we have studied in this paper are within limits of measurability. A sudden change of the potential could, for instance, be realized by a sudden change in temperature.

Recently there has been a growing interest in the behavior of Brownian particles in oscillating or fluctuating potentials. These studies have also led to the discovery and explanation of stochastic resonance [15,16] and noise induced transport [17]. In all of the systems that exhibit these phenomena the time scale of intrawell relaxation is important and it greatly matters for the response of the system whether the externally imposed fluctuations or oscillations are slower or faster than this time scale. In Sec. II we have shown in great detail how this is the case in resonant activation.

In the Langevin picture we see the instanton as the most likely escape path. As such it happens to be the reverse of the deterministic (noiseless) downslide. In the Fokker-Planck picture we see the instanton again. There it appears that during the intrawell relaxation of a distribution from a Dirac δ function to a Boltzmann distribution the appropriate amount of probability is delivered in the form of a package whose upward journey is the exact reverse of the deterministic downslide. The relaxation time of the escape rate thus equals the time to deterministically slide down the barrier, i.e., the instanton time. This ''happy coincidence'' constitutes the simple, bottom line result of this paper.

ACKNOWLEDGMENT

We are grateful to the NIH (Grant No. R29ES06620) for funding.

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