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What is adiabaticity? Suggestions from a fluctuating linear potential

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Abstract

We consider a Brownian particle in a well with a dichotomously fluctuating barrier. We show that, for a linear slope, the time to deterministically slide down the barrier is also the relaxation time for the escape rate after the barrier changes shape. © 1998 Published by Elsevier Science B.V.

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The behavior of a Brownian particle located in a potential well is described by a Langevin equation:

$$\beta \dot{x} = -\frac{d}{dx}U(x) + \beta(\sqrt{2D}) \xi(t), \quad (1)$$

where $U(x)$ is the shape of the potential, β is the coefficient of viscous friction and D is the diffusion coefficient which sets the amplitude of the noise. The term $\xi(t)$ describes normalized Gaussian white noise. For a system in equilibrium β and D are connected to each other through the fluctuation–dissipation theorem, $\beta = kT/D$. The system is overdamped so there is no momentum or inertia and the velocity of the particle at any time is determined solely by the force on the particle at that moment. Qualitative explanations frequently employ the notion of “adiabaticity”. When the shape of the well $U(x)$ changes, it takes the prob-

ability density distribution some time to relax back to a Boltzmann function of the energy level. This is the so-called “adiabatic adjustment time”.

When the barrier fluctuates (Fig. 1 inset) another timescale enters the problem. If the barrier fluctuates faster than the adiabatic relaxation, 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 (slow fluctuations) to the nonadiabatic regime (fast fluctuations).

First we use the principle of least action to calculate the most likely path to lead over any (not necessarily linear) barrier and this leads to another characteristic timescale. It appears 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

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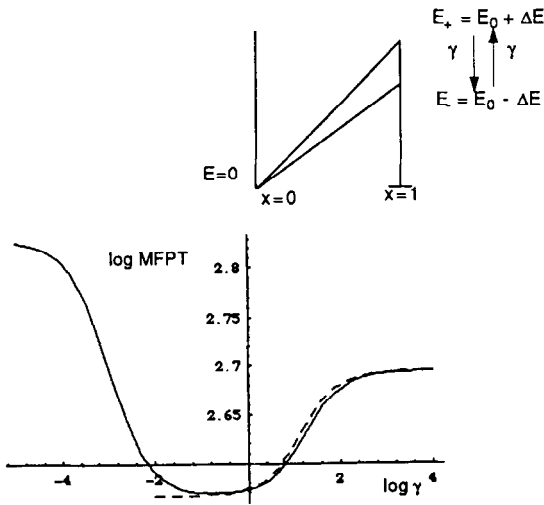


Fig. 1. The inset depicts the piecewise linear setup for our problem. The height of the barrier fluctuates between $E_+ = E_0 + \Delta E$ and $E_- = E_0 - \Delta E$. We study how long it takes before the particle escapes over the barrier and how this changes with the fluctuation rate γ . The graph shows \log_{10} of the mean first passage time (MFPT) 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 (Eq. (3)) for when $1/\gamma \ll \text{MFPT}$.

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.

For a system with noise the application of the principle of least action is only slightly more involved than in the traditional treatment [1]. The function $\xi(t)$ describes white noise with amplitudes that have a Gaussian distribution with a zero average and a standard deviation of 1. The probability that a particular sequence $\xi(t_1), \xi(t_2), \dots, \xi(t_n)$ is realized is proportional to $\prod_{i=1}^n \exp[-\frac{1}{2}\xi^2(t_i)] = \exp[-\frac{1}{2}\sum_{i=1}^n \xi^2(t_i)]$. Going to the limit of a continuous $\xi(t)$ on $t \in [0, T]$, this sum becomes an integral:

$$P[\xi(t)] \propto \exp\left(-\frac{1}{2} \int_{t=0}^T \xi^2(t) dt\right).$$

We view Eq. (1) 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 we have for the probability of a particular path $x(t)$ the following proportionality: $P[x(t)] \propto \exp[-S(x)/D]$, where $S[x(t)] \equiv \frac{1}{4} \int_{t=0}^T [\dot{x} - F(x)]^2 dt$. $S[x(t)]$ is the action that is

associated with a certain path. Notice that this quantity can never be negative. The path with the highest probability $P[x(t)]$ is the one for which $S[x(t)]$ is minimal. Taking the integrand $L(x, \dot{x}) = [\dot{x} - F(x)]/\beta$ as the Lagrangian and 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 called an “instanton”.

In order to get manageable mathematics we analyze a 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 timescale and expressing the energy in kT units. Because of the fluctuation-dissipation theorem this also leads to the disappearance of D from Eq. (1). 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 $\exp(-\frac{1}{2}\sum \xi_i^2)$ that a “small kick” that is subsequently compensated for by a “big kick” is less likely than two kicks of the average magnitude.

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

$$\begin{aligned} \partial_t P_+ &= (E_0 + \Delta E) \partial_x P_+ + \partial_{xx} P_+ - \gamma(P_+ - P_-), \\ \partial_t P_- &= (E_0 - \Delta E) \partial_x P_- + \partial_{xx} P_- + \gamma(P_+ - P_-), \end{aligned} \quad (2)$$

can be evaluated to yield the MFPT [2,3]. The MFPT over a stationary barrier of height E for a particle at $x = 0$ when $t = 0$ is $T_E = (e^E - 1 - E)/E^2$. When we let the barrier fluctuate between $E_0 + \Delta E$ and $E_0 - \Delta E$

(see Fig. 1), all the characteristic timescales for the Brownian particle in the well will show up in the $\log(\text{MFPT})$ versus $\log \gamma$ graph (Fig. 1, solid curve), where γ represents the fluctuation rate. 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. $P_+(0) = \frac{1}{2}$ and $P_-(0) = \frac{1}{2}$. The problem of escape over a fluctuating barrier has been analyzed and understood in ever greater generality (see Refs. [2,4–7] and references in Ref. [7]). A curve like Fig. 1, with two inflection points and the minimum plateau in the middle, occurs also for non-piecewise linear wells [7]. 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 $T_{E_0+\Delta E}$ and $T_{E_0-\Delta E}$. In the middle frequency regime the flipping time of the barrier (i.e. the average time between two transitions) is much shorter than $T_{E_0+\Delta E}$, what happens as a result is that escape will only take place over the lower barrier. Since half the time is spent on the lower barrier the MFPT is $2T_{E_0-\Delta E}$. In the high frequency regime the MFPT is the passage time over the average barrier, i.e. T_{E_0} . The standard view of this is that in the high frequency regime the probability density distribution of the particle never gets an opportunity for intrawell relaxation and effectively “feels” the average potential. Below we will show that in this escape problem the timescale for intrawell relaxation is actually the timescale 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 our linear slope this will turn out to be easy and straightforward. Suppose that the flipping is infinitely fast, i.e. $\gamma \rightarrow \infty$. This means that a particle that is ascending to mount the barrier moves half the time against a slope $E_0 + \Delta E$ and half the time against a slope $E_0 - \Delta E$. The most efficient way to move up this slope is again one where the Brownian kicks all do have the same magnitude. If this magnitude is the one corresponding to the ascent of the average slope E_0 , then we are moving half the time with a speed of $E_0 - \Delta E$ (when the slope is $E_0 + \Delta E$) and half the time with a speed of $E_0 + \Delta E$ (when the slope is $E_0 - \Delta E$). In the end this means that it takes the instanton $t_0 = 1/E_0$ to reach the top of the barrier, i.e. the same time it would take the instanton to move up the average slope if it were stationary. For a finite value of γ the ascending

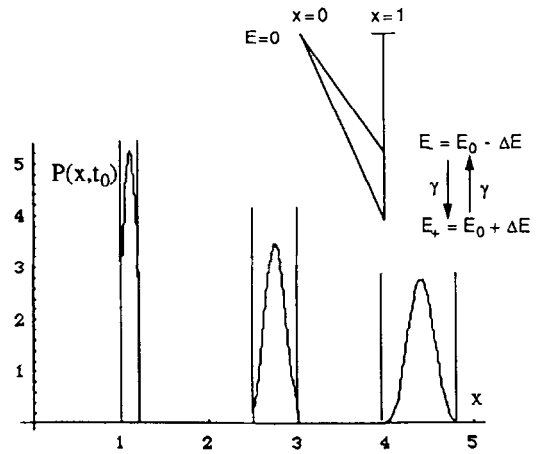


Fig. 2. In order to find the distribution of instanton times for the system of Fig. 1 we solve the equations for the evolution of the probability density distribution when a particle slides down a fluctuating slope (see inset) with $P_+(x, t = 0) = P_-(x, t = 0) = \frac{1}{2}\delta(x)$. In the graph the evolution of the probability density distribution $(P_+ + P_-)(x, t)$ for $\gamma = 200$, $E_0 = 11$ and $\Delta E = 1$ is depicted at $t = 0.01$, $t = 0.025$ and $t = 0.04$. Two delta functions grow smaller and move apart, while between them a Gaussian develops.

particle will generally spend a fraction φ_+ of the total time on the steep $E_0 + \Delta E$ slope and a fraction φ_- on the $E_0 - \Delta E$ slope. It is a trivial exercise to prove that the most probable way to move up the barrier is with the identical Brownian kicks corresponding to the instanton going up the time averaged slope $E^0 = \varphi_+(E_0 + \Delta E) + \varphi_-(E_0 - \Delta E)$ in a time $t^0 = 1/E^0$.

The fluctuation of the linear slope is stochastic: in both the + state and the - state there is an exponentially distributed dwelling time around an average of $1/\gamma$. This means that there is a distribution of instanton times. To derive this distribution we solve the differential equations describing the evolution of the probability density distribution during the “fluctuating downslope” (see Fig. 2):

$$\begin{aligned} \partial_t P_+ &= -(E_0 + \Delta E)\partial_x P_+ - \gamma(P_+ - P_-), \\ \partial_t P_- &= -(E_0 - \Delta E)\partial_x P_- + \gamma(P_+ - P_-). \end{aligned} \quad (3)$$

As the $t = 0$ condition we have the particle at $x = 0$ and equal probability for the barrier being up or down, i.e. $P_+(x, t = 0) = P_-(x, t = 0) = \frac{1}{2}\delta(x)$. Eqs. (3) are identical to the Fokker–Planck equations (2) 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. sec-

ond derivative). It is the stochastic fluctuations of the slope that are responsible for the delta functions turning into a distribution during the descent from $x = 0$ to $x = 1$. We will thus find a distribution of instanton times (see Fig. 2). 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 Refs. [8,9]. We let $\zeta(x, t) = \sqrt{(\Delta Et)^2 - (E_0 t - x)^2}$ and find

$$(P_+ + P_-)(x, t) = \frac{\gamma e^{-\gamma t}}{2\Delta E} I_0\left(\frac{\gamma}{\Delta E} \zeta(x, t)\right) + \frac{\gamma t e^{-\gamma t}}{2\zeta(x, t)} I_1\left(\frac{\gamma}{\Delta E} \zeta(x, t)\right) + \frac{e^{-\gamma t}}{2\Delta E} \left(\frac{\delta(t/\Delta E - x/\Delta E(E_0 + \Delta E))}{E_0 + \Delta E} + \frac{\delta(t/\Delta E - x/\Delta E(E_0 - \Delta E))}{E_0 - \Delta E} \right),$$

on $x/(E_0 + \Delta E) \leq t \leq x/(E_0 - \Delta E)$ and zero elsewhere. The functions I_0 and I_1 represent the modified Bessel functions of the zeroth and first kind [8]. The third part of this expression describes delta functions that slide down the $-(E_0 + \Delta E)$ slope with $x/t = (E_0 + \Delta E)$ and the $-(E_0 - \Delta E)$ slope with $x/t = (E_0 - \Delta E)$. Because of the exponential flipping time distribution these delta functions carry an $\exp[-\gamma t]$ in front. For large enough t many flips occur. Then the central limit theorem becomes applicable and $(P_+ + P_-)$ becomes a Gaussian around $x = E_0 t$ (see Fig. 2). Using the same canonical forms for the inverse Laplace transformation, we also obtain

$$(P_+ - P_-)(x, t) = \frac{(E_0 t - x) \gamma t e^{-\gamma t}}{2\Delta E \zeta(x, t)} I_1\left(\frac{\gamma}{\Delta E} \zeta(x, t)\right) + \frac{e^{-\gamma t}}{2\Delta E} \left(\frac{\delta(t/\Delta E - x/\Delta E(E_0 + \Delta E))}{E_0 + \Delta E} + \frac{\delta(t/\Delta E - x/\Delta E(E_0 - \Delta E))}{E_0 - \Delta E} \right),$$

again on $x/(E_0 + \Delta E) \leq t \leq x/(E_0 - \Delta E)$ and zero elsewhere.

The flow of probability over $x = 1$ at time t equals $J_{x=1}(t) = -\int_0^1 \partial_t(P_+ + P_-) dx$, i.e. the rate at which

the total probability to be on the unit interval decreases. $J_{x=1}(t)$ can also be thought of as the distribution of passage times at $x = 1$ for sliding down the fluctuating ramp. Adding up the evolution equations (3) we derive $\partial_t(P_+ + P_-) = -E_0 \partial_x(P_+ + P_-) - \Delta E \partial_x(P_+ - P_-)$. Integrating this equation we find that for $t > 0$ we have

$$J_{x=1}(t) = E_0(P_+ + P_-)(1, t) + \Delta E(P_+ - P_-)(1, t).$$

With the formulae we derived in the previous paragraph we can express $J_{x=1}(t)$ in terms of the system parameters γ , ΔE and E_0 .

When $\gamma \rightarrow \infty$ the deterministic particle on the fluctuating downslide spends as much time on the “+” slope with speed $E_0 + \Delta E$ as it spends on the “-” slope with speed $E_0 - \Delta E$. So eventually the particle behaves as if it is sliding down the average E_0 slope and it will arrive at $x = 1$ at time $t_0 = 1/E_0$. This is identical to the time it takes the Brownian instanton to go up the fluctuating slope. But no longer do the Brownian instanton and the deterministic downslide follow paths that are each others time reverse as in the case of the stationary slope; the Brownian instanton has its lower speed on the steep slope, whereas the deterministic downslide has its higher speed on the steep slope. For a finite value of γ the descending particle will generally spend a fraction φ_+ of the total time on the steep slope $E_0 + \Delta E$ and a fraction φ_- on the $E_0 - \Delta E$ slope. It is easy to derive that, as with the ascending instanton, the particle will reach $x = 1$ at time $t^0 = 1/E^0$, where E^0 is the averaged slope $E^0 = \varphi_+(E_0 + \Delta E) + \varphi_-(E_0 - \Delta E)$. But again the time reversibility is broken.

We now imagine the particle in Fig. 1 as “sitting” at $x = 0$ for the duration of the passage time. Next it takes a run over the barrier that takes the same time as it would take to slide down that barrier deterministically and, by the result of the previous paragraph, also the same time it would take to slide down the average slope E . For $O(\gamma) \gtrsim O(E_0 + \Delta E)$ the particle faces a distribution of barrier heights, because of stochastic flipping during the instanton time. The escape rate k depends on the barrier height E as $k(E) = E^2[\exp(E) - 1 - E]^{-1}$. When ΔE is small relative to E_0 the MFPT can be well approximated as $T_{\text{avg}} = [\int_{E_-}^{E_+} k(E) p(E) dE]^{-1}$, where $p(E)$ is the probability density distribution of the barrier heights. With $E =$

$1/t$, where t is the instanton time (i.e. sliding down time) for a barrier of average height E , we can formulate the integral for T_{avg} in terms of the instanton time

$$T_{\text{avg}} = \left\{ \int_{1/E_+}^{1/E_-} \frac{1}{t^2} \left[\exp\left(\frac{1}{t}\right) - 1 - \frac{1}{t} \right]^{-1} J_{x=1}(t) dt \right\}^{-1} \tag{4}$$

The expression $t^{-2}[\exp(1/t) - 1 - 1/t]^{-1}$ puts the passage rate in terms of the instanton time and this is integrated over $J_{x=1}(t)$, which is the distribution of instanton times. The integration runs from the minimum instanton time $1/E_+$ to the maximum instanton time $1/E_-$. $J_{x=1}(t)$ is a complicated function, but the modified Bessel functions are a standard feature of *Mathematica* and the integral is readily calculated with this package.

Fig. 1 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 (4) for T_{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. 1 from the lowest plateau to the $\gamma \rightarrow \infty$ plateau is the transition from the regime where the probability density distribution can follow the fluctuation all the time (i.e. the adiabatic regime) to the regime where the probability density distribution is no longer able to do so (i.e. the nonadiabatic regime). It is remarkable that the adiabatic-to-nonadiabatic transition can be quantitatively accounted for by the instanton mechanism. The physics of the instantons, namely, does not appear to have anything whatsoever to do with the physics of intrawell equilibration or adiabatic adjustment.

When the shape of a potential well changes, the probability density distribution for a Brownian particle in that well follows in the course of time. Suppose we have a barrier as in Fig. 1, but with a nonfluctuating height E . When we start with a Dirac delta function at $x = 0$ as the initial condition, we can solve the Fokker–Planck equation by separation of variables (cf. Ref. [3, Section 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 distribution as a whole. 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. 1 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 ($1/E$ versus $2/E^2$). To understand this in another way take again a barrier as in Fig. 1, but with a stationary height E . For a particle at position x , $0 \leq x \leq 1$, at $t = 0$ the MFPT is $T(x) = [e^E - e^{Ex} - E(1-x)]/E^2$. When the particle is at $x = 0$ at $t = 0$ this means $T(0) = (e^E - 1 - E)/E^2$. For an “equilibrated particle” we have a Boltzmann distribution $P(x) = Ee^{-Ex}/(1 - e^{-E})$. For such a particle the MFPT is $T^* = \int_0^1 T(x) P(x) dx$, which works out to $T^* = (e^E - 2E - e^{-E})/E^2(1 - e^{-E})$. T^* is smaller than $T(0)$ and we can take $\tau = T(0) - T^*$ to be the time it takes for the probability density to go from a delta function at $x = 0$ to an equilibrated Boltzmann distribution. As such it is a good measure for the intrawell equilibration time. We find $\tau = 1/E - 2/E^2 + 2e^{-E}/E(1 - e^{-E})$. 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 approach of the last paragraph actually generalizes beyond the piecewise linear case. Take any two points along a continuous potential $U(x)$. Next define $T(x_1 \rightarrow x_2)$ as the average time it takes for a particle at $x = x_1$ at $t = 0$ to first reach $x = x_2$. Using a well-known formula for such a time (Ref. [3, Section 5.2.7]) and taking $T(P_B\langle x_1, x_2 \rangle \rightarrow x_i)$ as the time it takes to first reach x_i ($i = 1, 2$) from a Boltzmann distribution on $\langle x_1, x_2 \rangle$, the following equality can be derived,

$$\begin{aligned} T(x_1 \rightarrow x_2) - T(P_B\langle x_1, x_2 \rangle \rightarrow x_2) \\ = T(x_2 \rightarrow x_1) - T(P_B\langle x_1, x_2 \rangle \rightarrow x_1). \end{aligned}$$

In the case of our piecewise linear slope (or generally for any monotonically increasing segment that is sufficiently steep) $T(P_B\langle 0, 1 \rangle \rightarrow 0)$ is negligibly small in comparison to $T(1 \rightarrow 0)$ and the main result of this paper is again obtained.

When we take the instanton/equilibration time of $1/E$ back to dimensionalized variables with a well of any width L , we get $L^2/E\beta$. 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, but 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. There is slower diffusion at low temperature, but less material has to diffuse. Hence the independence of temperature. The $2/E^2$ equilibration time of the distribution in the bottom of the well unscales like $2kTL^2/\beta E^2$ and does depend on temperature.

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. If this result extends beyond the piecewise linear, it means that the relaxation of the probability density distribution cannot be identified with the relaxation of the Kramers rate and that the latter in fact relaxes slower.

A great many problems in physics, chemistry and biology involve imposing an external fluctuation or oscillation on a system that takes time to equilibrate. An example is the influence of an oscillating or fluctuating electromagnetic field on an enzyme that is embedded in a cell membrane. In enzyme-driven catalysis the involved protein goes from one potential well to the next as it changes conformational state. Different conformational states generally have different values of the dipole moment and imposing a fluctuating electromagnetic field has the effect of fluctuating the activation barriers. The timescale for adiabatic adjust-

ment is important in such systems.

A well in an energy profile has two characteristic timescales: the adiabatic adjustment time and the MFPT. Both these times say something about the structure of the well. When the barrier fluctuation is imposed these characteristic timescales become visible as inflection points in a $\log(\text{MFPT})$ versus fluctuation rate graph like Fig. 1 [10–12]. In an experimental application graphs like Fig. 1 could thus be used to obtain information about energy profiles of actual systems like ion pumps or ion channels.

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