Rates of Activated Processes with Fluctuating Barriers

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We study the ultimate *rate of relaxation* to equilibrium, as defined by the appropriate master equation, in a bistable potential that is *fluctuating* in a stationary manner; we obtain results for both dichotomic and Gaussian barrier fluctuations, as a function of the correlation time characterizing the fluctuations. "Resonant activation," previously observed in specific model problems, is shown to be typical and to have a simple physical interpretation. In the slow fluctuation limit we find that the ultimate rate of relaxation—when it exists—differs from the inverse mean first passage time.

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The discovery [1] of "resonant activation" in the problem of passage over a fluctuating barrier—the discovery that the mean first passage time (MFPT) has a minimum as a function of the correlation time characterizing the fluctuations—has prompted a flurry of literature [2]. The original work, and almost all that followed, dealt with MFPT's for special model problems. In contrast, our contribution here is a study of the ultimate *rate of relaxation* to equilibrium, as defined by the appropriate master equation, in a fluctuating bistable potential; we assume only that the potential barrier is high compared to k_BT and that the fluctuations in it are relatively small, although possibly also large compared to k_BT. We find that resonant activation is typical and that it has a simple physical interpretation. If barrier fluctuations are very fast, the rate of relaxation is determined by the average barrier. If barrier fluctuations are very slow, the ultimate rate of relaxation is determined by the highest barrier. If barrier fluctuations are slow enough that, during a correlation time, we may speak of a rate over the instantaneous barrier, but fast enough that a number of correlation times must pass before substantial relaxation occurs, the rate is the average of the "instantaneous" rates over the various barrier heights. Given the Arrhenius dependence of rate on barrier height, this average rate must be greater than the rate over the average barrier and, of course, greater than the rate over the highest barrier; that is the maximum called resonant activation.

We will support this picture by calculations on both dichotomic and Gaussian barrier fluctuations. The slow fluctuation limit in the Gaussian case is particularly delicate, for there is no "highest" barrier, arbitrarily large fluctuations being permitted by a Gaussian distribution.

First the dichotomic case, which is easier. The potential is $V(x) + yW(x)$, where y is the stationary Markov process with values ± 1, zero mean, and correlation $\langle y(t)y(t')\rangle = \exp(-|t-t'|/\tau_c)$. We might, for example, be concerned with a chemical isomerization whose barrier is modulated by a second isomerization, already at equilibrium; the relaxation rate of the second isomerization sets the time scale τ_c. In the overdamped (Smoluchowski) limit the master equation for the probability densities $\rho_\pm(x,t)$ is

$$\partial_t \begin{pmatrix} \rho_+ \\ \rho_- \end{pmatrix} = \begin{pmatrix} L_+ - \gamma & \gamma \\ \gamma & L_- - \gamma \end{pmatrix} \begin{pmatrix} \rho_+ \\ \rho_- \end{pmatrix}, \qquad (1)$$

where the subscripts $\pm$ refer to the two possible values of y, $\gamma = (2\tau_c)^{-1}$, and $L_\pm$ are the Fokker-Planck operators associated with $V \pm W$: $L_\pm = \partial_x(V' \pm W' + \beta^{-1}\partial_x)$, where $V'(x) \equiv dV/dx$, etc., and $\beta^{-1} = k_BT$. In this equation "time" has dimensions "(length)^2/energy" because we have absorbed a friction constant into it.

In the limit $\gamma = 0$, eigenvectors of the matrix operator in Eq. (1) can be constructed from eigenfunctions of $L_\pm$. Let $\rho_+^e = \exp[-\beta(V+W)]/Z_+$ be the equilibrium density in the potential $V+W$, where $Z_+ = \int dx \exp[-\beta(V+W)]$; then $L_+\rho_+^e = 0$. Let ρ_+^r be the "relaxation" eigenfunction of L_+—the eigenfunction with the least negative eigenvalue, $L_+\rho_+^r = -k_+\rho_+^r$. With respect to the dot product $\langle \rho_{1+}|\rho_{2+}\rangle_+ = \int (dx/\rho_+^e)\rho_{1+}^*\rho_{2+}$, L_+ is Hermitian, ρ_+^e is normalized and orthogonal to ρ_+^r, and both are orthogonal to eigenfunctions of L_+ with more negative eigenvalues. We may assume that ρ_+^r is normalized. Similarly, ρ_-^e and ρ_-^r denote the equilibrium and relaxation eigenfunctions of L_-, orthonormal with respect to the dot product $\langle \rho_{1-}|\rho_{2-}\rangle_- = \int (dx/\rho_-^e)\rho_{1-}^*\rho_{2-}$. We construct four orthonormal eigenvectors of the $\gamma = 0$ matrix in Eq. (1) as follows: $(\rho_+, \rho_-) = (\rho_+^e, \rho_-^e)/\sqrt{2}$, $(\rho_+^e, -\rho_-^e)/\sqrt{2}$, $(\rho_+^r, 0)$, and $(0, \rho_-^r)$. For $\gamma \neq 0$ we calculate the eigenvalues of the 4×4 matrix formed over this basis. The eigenvalues 0 and -2γ are of no interest: One refers to overall equilibrium, the other to relaxation of the stochastic process y, if it were not already in equilibrium. The eigenvalue of interest, $-k(\gamma)$, is the less negative eigenvalue of the 2×2 matrix,

$$\begin{pmatrix} -k_+ - \gamma & \gamma\langle \rho_+^r|\rho_-^r\rangle_+ \\ \gamma\langle \rho_-^r|\rho_+^r\rangle_- & -k_- - \gamma \end{pmatrix}.$$

The barrier separating the left and right wells in the potential $V+W$ is high compared to k_BT, so *in each well* ρ_+^r is to good approximation proportional to ρ_+^e. The proportionality constants are easily determined by $\langle \rho_+^e|\rho_+^r\rangle_+ = 0$, $\langle \rho_+^r|\rho_+^r\rangle_+ = 1$: In the left well $\rho_+^r \cong \rho_+^e(p_+^{\text{right}}/p_+^{\text{left}})^{1/2}$; in the right well

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$\rho_+^r \cong -\rho_+^e(p_+^{\rm left}/p_+^{\rm right})^{1/2}$, where the p's are equilibrium occupation probabilities (i.e., $p_+^{\rm left} = \rho_+^e$ integrated over the left well). Similarly, ρ_-^r is well approximated by analogous formulas for the potential $V - W$. Then

$$\langle\rho_+^r|\rho_-^r\rangle_+ \cong (p_-^{\rm right}p_-^{\rm left}/p_+^{\rm right}p_+^{\rm left})^{1/2} \cong 1/\langle\rho_-^r|\rho_+^r\rangle_- .$$

The relaxation rate $k(\gamma)$ is therefore independent of the occupation probabilities p and is given by (if $k_- > k_+$ and $\Delta k = k_- - k_+$)

$$k(\gamma) = k_+ + \gamma - (\Delta k/2)\{[1 + (2\gamma/\Delta k)^2]^{1/2} - 1\}. \quad (2)$$

This approximation is accurate as long as γ is small in magnitude compared not with $k_\pm$ but with the other nonzero eigenvalues of $L_\pm$, that is, as long as the correlation time τ_c is long compared with the characteristic times of relaxation *within the wells* of the bistable potential. If the barriers are high, intrawell relaxation is much faster than barrier passage, and Eq. (2) therefore accurately describes the range from $\gamma = 0$ to $\gamma \gg \Delta k$ (but still small compared to intrawell rates). In this range $k(\gamma)$ increases monotonically from k_+—the rate over the higher barrier, when $\gamma = 0$—to $(k_+ + k_-)/2$—the average rate—when $\gamma \gg \Delta k$.

It is worth emphasizing the basic point that in the "static" limit of very small γ the ultimate rate of relaxation is that over the higher barrier, for in this limit the mean first passage time turns out to be the arithmetic average of the MFPT's for each of the *two* barriers $V \pm W$ [1,2]. In this limit the usual equivalence between calculation of a rate and calculation of a mean first passage time T_{rp} (from reactant to product) *breaks down,* i.e., $k(\gamma) \neq T_{rp}^{-1}$ [3].

In the opposite limit $\gamma \to \infty$, i.e., τ_c, short compared with intrawell relaxation times, we expect the relaxation eigenvector to be close to a zero-eigenvalue vector of the operator obtained by setting $L_\pm = 0$. We therefore write $\rho_\pm(x,\gamma) = \phi(x,\gamma) \pm \delta\phi(x,\gamma)$, where $\delta\phi$ is a small correction, and try an expansion in γ^{-1}:

$$\phi(\gamma) = \phi_0 + \gamma^{-1}\phi_1 + \cdots ,$$
$$k(\gamma) = k_0 + \gamma^{-1}k_1 + \cdots ,$$
$$\delta\phi(\gamma) = \gamma^{-1}\delta\phi_0 + \cdots .$$

We find $L_V\phi_0 = -k_0\phi_0$, where $L_V = (L_+ + L_-)/2$ is the Fokker-Planck operator for the average potential, which is just V. Therefore $\phi_0 = \phi_V$ and $k_0 = k_V$, the relaxation eigenfunction and the rate in the average potential V.

The rate in the limit $\gamma \to \infty$, i.e., k_V, is smaller than the average rate $(k_+ + k_-)/2$, for $(k_+ + k_-)/2 \cong k_V[\exp(-\beta\Delta) + \exp(\beta\Delta)]/2$, where Δ denotes the shift in barrier height due to W.

The first-order correction to the rate is readily calculated from the first-order eigenfunction equation

$$(L_V + k_V)\phi_1 = -k_1\phi_V - (L_+ - L_-)^2\phi_V/8$$

by multiplying through with $\exp(\beta V)\phi_V$, integrating over x, and using the fact that $L_V^*\exp(\beta V) = \exp(\beta V)L_V$, L_V^* being the adjoint of L_V. One finds

$$k_1\int dx\exp(\beta V)\phi_V^2 = -\int dx\exp(\beta V)\phi_V(L_+ - L_-)^2\phi_V/8 = -\int dx\exp(\beta V)\phi_V\{\partial_x[W'\partial_x(W'\phi_V)]\}/2$$
$$= \int dx\{\partial_x[\exp(\beta V)\phi_V]\}W'[\partial_x(W'\phi_V)]/2.$$

The function $\exp(\beta V)\phi_V$ is essentially constant except in the immediate vicinity of the barrier maximum, where ϕ_V changes sign; in this region $\exp(\beta V)$ is essentially constant and ϕ_V is near zero, so the integrand is approximately $\exp(\beta V)(\phi_V')^2(W')^2/2$. k_1 is therefore positive and proportional to the square of the fluctuation W, i.e., $k_1 = O(\Delta^2)$.

These calculations on the dichotomic case therefore confirm the physical picture outlined in the first paragraph: $k(\gamma)$ has a single maximum whose value is the average of the rates over the higher and the lower barriers, and from this maximum k falls monotonically to the limiting values k_V at $\gamma = \infty$ and k_+ at $\gamma = 0$.

For the case that the barrier fluctuations are Gaussian, the instantaneous potential is $V + yW$, where y is the Gaussian Markov process (Ornstein-Uhlenbeck) with mean zero and correlation $\langle y(t)y(t')\rangle = \exp(-|t - t'|/\tau_c)$. We shall first do a transition state theory estimate of the rate [3] by finding the equilibrium distribution of x and y, $\rho^{\rm eq}(x,y)$, and calculating an effective barrier to reaction along x by integrating $\rho^{\rm eq}$ over y.

The Fokker-Planck equation for $\rho^{\rm eq}$ is

$$\partial_x[(V' + yW' + \beta^{-1}\partial_x)\rho^{\rm eq}] + \gamma\partial_y[(y + \partial_y)\rho^{\rm eq}] = 0, \quad (3)$$

where now $\gamma = 1/\tau_c$. We introduce an auxiliary function u, to be determined, and split the Fokker-Planck equation into two first-order pieces,

$$(V' + yW' + \beta^{-1}\partial_x)\rho^{\rm eq} = \partial_y u, \quad (4a)$$
$$\gamma(y + \partial_y)\rho^{\rm eq} = -\partial_x u. \quad (4b)$$

For large γ we try an expansion in γ^{-1}: $\rho^{\rm eq} = \rho_0 + \gamma^{-1}\rho_1 + \cdots$; $u = \gamma u_{-1} + u_0 + \gamma^{-1}u_1 + \cdots$. From (4a) we find $\partial_y u_{-1} = 0$, i.e., $u_{-1} \equiv u_{-1}(x)$. From (4b) we find $\rho_0(x,y) = \exp(-y^2/2)[\rho_0(x,0) - \int_0^y dy' \times \exp(y'^2/2)\partial_x u_{-1}(x)]$; since ρ_0 must be everywhere non-negative we conclude that $\partial_x u_{-1}(x) = 0$ and that $\rho_0(x,y) = \exp(-y^2/2)\rho_0(x,0)$.

Integrating (4a) over y, we find $(V' + \beta^{-1}\partial_x)\rho_0(x,0) = 0$ or $\rho_0(x,0) = \exp[-\beta V(x)]$ (we ignore normalization constants, which are of no interest). In the limit $\gamma \to \infty$ the effective potential along x is therefore the average potential $V(x)$, as in the dichotomic case.

Similar calculations determine the first-order correction ρ_1: Given ρ_0, solve (4a) for u_0, up to a function of x; then solve (4b) for ρ_1; then use (4a), integrated over y, to determine the function of x. We find that $\rho_1(x,y) = \rho_0(x,y)[y(W'' - \beta V'W') - \beta\int_0^x dx'\, W'(W'' - \beta V'W') + c]$, where c is a constant to be fixed by normalization. Integrating $\rho_0 + \gamma^{-1}\rho_1$ over y, we conclude that to order γ^{-1} the effective potential along x is $V(x) + \gamma^{-1}\int_0^x dx\, W'(W'' - \beta V'W')$. Specialize to the symmetric case, $V(x)$ and $W(x)$ even in x with maxima at $x = 0$; then to order γ^{-1} the effective potential is

$$V(x) + \gamma^{-1}[W'(x)]^2/2 - \gamma^{-1}\beta\int_0^x dx'\, V'W'^2,$$

and away from $x = 0$ both additions to $V(x)$ are *positive,* which implies that the effective barrier to reaction *decreases* as $\tau_c = \gamma^{-1}$ increases, the effect—as in the dichotomic case—being proportional to the square of the fluctuation.

For small γ we try an expansion in γ: $\rho^{\mathrm{eq}} = \rho_0 + \gamma\rho_1 + \cdots$; $u = u_0 + \gamma u_1 + \cdots$. From (4b) we find $\partial_x u_0 = 0$; solving (4a) and insisting that ρ_0 be non-negative, we find that $\rho_0(x,y) = N(y) \times \exp\{-\beta[V(x) + yW(x)]\}$; integrating (4b) over x, we find that $N(y) = \exp(-y^2/2)/Z(y)$, where $Z(y) = \int dx \exp[-\beta(V + yW)]$. As should be the case, in the limit $\gamma \to 0$ ρ^{eq} is a Gaussian distribution of the static (fixed γ) equilibria in x. Again specialize to the symmetric case and suppose that the barrier modulation $W(x)$ is nonzero only around $x = 0$; then $V(0) + yW(0)$ is the static (fixed y) barrier and—since $V(0) \gg k_BT$ and $W(0) \ll V(0)$—$Z(y)$ does not depend strongly on y. Integrating $\rho_0(x,y)$ over y, we find that the Arrhenius factor for barrier passage is now $\exp[-\beta V(0)]\langle\exp[-\beta yW(0)]\rangle$, where $\langle\exp[-\beta yW(0)]\rangle = \exp[\beta^2 W(0)^2/2]$ is the average over the Gaussian distribution of y. This is precisely the rate enhancement given by averaging the instantaneous rates $k(y) = k_V\exp[-\beta yW(0)]$ over the Gaussian distribution of y.

But we have made a mistake. *To speak of a single effective barrier to relaxation makes no sense if γ is so small that τ_c is comparable to or greater than the time of barrier passage.* In fact, in the static limit $\gamma = 0$ we have a continuous spectrum of barriers and rates, with barrier heights extending up to infinity and rates extending down to zero because arbitrarily large positive fluctuations are permitted by a Gaussian distribution [4]. Nevertheless, the calculation of the last paragraph has meaning: It applies to the region $k_V \ll \gamma \ll k_r$, where k_r is a rate of intrawell relaxation, *provided* the equilibrium solution of the Fokker-Planck equation (3) in this region does not differ much from ρ_0. This will be the case unless the "perturbation" $\gamma\partial_y[(y + \partial_y)\rho_0]$ has nonzero projection on the relaxation eigenfunction $\phi(x|y)$ of the Fokker-Planck operator $L(y)$ for motion in the potential $V(x) + yW(x)$, $L(y)\phi(x|y) = -k(y)\phi(x|y)$, where $L(y) = \partial_x(V' + yW' + \beta^{-1}\partial_x)$. In the symmetric case, by symmetry, there is no such projection: ρ_0 is even in x; $\phi(x|y)$ is odd. We do not pause to analyze the general case but instead look to the time-dependent Fokker-Planck equation to see if a rate exists at all in the small γ regime.

We are looking for the solution with the lowest positive eigenvalue of $-\gamma\partial_y^2\rho - \gamma\partial_y(y\rho) - L(y)\rho = k(\gamma)\rho$. We write $\rho(x,y) \cong \rho(y)\phi(x|y)$ and replace $L(y)$ by its eigenvalue $-k(y)$: $-\gamma\partial_y^2\rho - \gamma\partial_y(y\rho) + k(y)\rho = k(\gamma)\rho$. This is a Born-Oppenheimer type of approximation, and it is justified in the standard way, by noting that the separation of levels in the "potential" $k(y)$—which is $O(k_V)$—is much smaller than the gap between $k(y)$ and higher "potentials," which is $O(k_r)$.

In the symmetric case $k(y) = k_V\exp[-\beta yW(0)]$ and the lowest eigenvalue $k(\gamma)$ is easily calculated, in harmonic oscillator approximation, to be

$$k(\gamma) = \gamma\{\bar{y}^2/4 + \bar{y}/2\beta\Delta + [(1 + \beta\Delta\bar{y})^{1/2} - 1]/2\}, \tag{5}$$

where $\Delta \equiv W(0)$ and $\bar{y}$ is determined by the equation $\gamma\bar{y}/2 = \beta\Delta k_V\exp(-\beta\Delta\bar{y})$. The separation of this eigenvalue from the next one up is $\gamma(1 + \beta\Delta\bar{y})^{1/2}$.

If $\gamma \gg k_V$, $\bar{y}$ is small, $\bar{y} \cong 2\beta\Delta k_V/\gamma$, and we find $k(\gamma) \cong k_V(1 + \beta^2\Delta^2/2)$, in agreement with what we found above by effective potentials. The next eigenvalue to be determined is separated from k by γ, so the relaxation is well described by a single exponential.

If $\gamma \ll k_V$, $\bar{y}$ is large, and it is easier to regard γ as a function of $\bar{y}$, the limit being $\bar{y} \to \infty$; then $k \cong \gamma\bar{y}^2/4 = \beta\Delta k_V\bar{y}\exp(-\beta\Delta\bar{y})/2$. The rate goes to zero, as expected, there being no limit on the height of the possible barriers, but it does so trailing a near continuum of slightly higher rates behind it, for the eigenvalue separation in this limit is $\gamma(\beta\Delta\bar{y})^{1/2} \ll \gamma\bar{y}^2/4$. In this regime the relaxation is not simply exponential with rate constant k, but slightly faster, going as $t^{-1/2}\exp(-kt)$ [5].

In summary, our calculations for both dichotomic and Gaussian fluctuations support a simple physical picture of activated processes with fluctuating barriers: If fluctuations are fast, we are in the "motional narrowing" regime in which the rate is determined by the average barrier; if fluctuations are slow, we are near the static limit and the slowest process is ultimately rate determining; the third characteristic rate—the average rate, the rate averaged over the distribution of barrier heights—is the rate observed when the time scales of barrier fluctuation and barrier passage are comparable, and this average rate is greater than the rate in either the fast or the slow fluctuation limit.

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