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# Reaction rates for fluctuating barriers with asymmetric noise

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Thermally activated escape over a high barrier fluctuating randomly in time is investigated for asymmetric flipping rates. By means of the Fokker–Planck approach approximate methods developed for symmetric noise are applied to calculate the relaxation eigenvector and ultimate relaxation rate for piecewise linear potentials in the Smoluchowski limit. The ranges of validity of these approaches are discussed. Furthermore, the exact result for weak thermal noise but arbitrary barrier flipping rates is derived and its dependence on the asymmetry studied in detail. © *1999 American Institute of Physics.* [S0021-9606(99)51235-X]

## I. INTRODUCTION

Chemical reactions driven by thermal noise can often be visualized as thermally activated escape of Brownian particles over a high potential barrier. This simple model not only describes an archetypical situation in chemistry but also provides the basis to study a variety of phenomena in physics and biology as well.[1] Particularly interesting is the case where the Brownian particles experience a potential barrier that fluctuates randomly in time; in contrast to thermal noise, ''ups'' and ''downs'' can occur on time scales that are shorter than, comparable to, or even much longer than the time scales governing the escape process. In short, the barrier fluctuations act like a ''gate'' for the reaction on the lower potential surface to occur. Examples are the escape of an $O_2$ or CO ligand molecule out of a myoglobin ''pocket,''[2] ion channel kinetics in the lipid cell membrane,[3] and strongly coupled isomerizations.[4] Even for the dynamics of protein folding, and for relaxation in glasses, diffusion over fluctuating barriers might be of some relevance.[5] In all these systems the motion of the Brownian particles is overdamped (Smoluchowski limit) so that inertial effects are negligible. Furthermore, the barrier fluctuations are driven by a process which itself stays far from equilibrium.

Since the discovery of the so-called ''resonant activation'' phenomenon in 1992[6]—the fact that the relaxation rate exhibits a broad maximum for intermediate fluctuation rates—this topic has stimulated extensive research.[7] It was shown in Ref. 8 that the resonance behavior is typical for bistable systems: For very fast barrier fluctuations, the ultimate rate of relaxation is given by the average barrier. For very slow barrier fluctuations, the relaxation rate is determined by the highest barrier. In between there is an intermediate regime where on the one hand barrier fluctuations are slow enough that, during a flip from up to down or vice versa, one has still thermal escape over a static barrier; on the other hand, however, they are so fast that a number of ups and downs must pass before substantial relaxation occurs. In this case the rate is the average rate of the static up and down rates.

In general, however, the calculation of the relaxation rate is very difficult and even the existence and explicit form of the equilibrium state is not clear.[9,10] Analytical and numerical work has focused on one-dimensional bistable potentials and dichotomous or continuous Gaussian barrier fluctuations.[7,11] A direct approach to the relaxation rate is through the Fokker–Planck equation[12] which allows one to determine equilibrium and relaxation eigenfunctions, together with the relaxation rate as the least negative eigenvalue of the Fokker–Planck operator, by employing the separation of time scales in the systems under investigation.[9,13,14] Surprisingly, what has not been studied so far is the case of asymmetric barrier fluctuations: the case—in the simplest version of dichotomous noise—that the flipping rate up differs from the flipping rate down. One might think that this is the typical situation for realistic systems where internal fields give rise to the asymmetry. In the present work we investigate asymmetric barrier flipping rates for a simple bistable potential, namely, the piecewise linear model, which can be seen as the limit of a double well potential with very large frequencies at the barrier and in the wells. It turns out that changing the asymmetry significantly influences the relaxation rate, especially in the resonant activation regime. If the asymmetry could be tuned externally this would allow control of a chemical reaction.

The article is organized as follows: In Sec. II we give a brief introduction to the Fokker–Planck formalism and outline the model. The next section (Sec. III) deals with the approximate methods to evaluate the rate and discusses the specific ranges in parameter space where these approximations can be used. The exact result in the limit of weak thermal noise is derived in Sec. IV to obtain a complete description valid for all values of the fluctuation rates. The article ends with a short conclusion.

## II. FOKKER–PLANCK OPERATOR

In a static potential $V(x)$ thermal diffusion of a particle in the overdamped (Smoluchowski) limit is determined by

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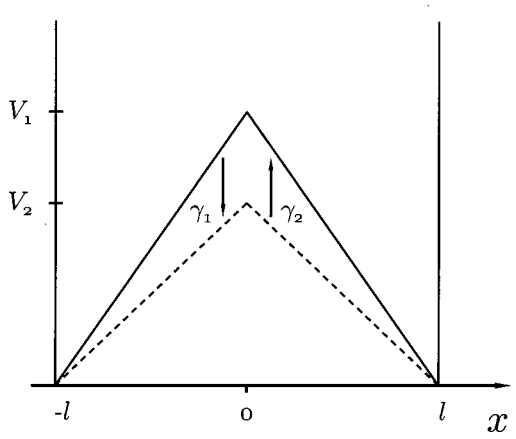


FIG. 1. Piecewise linear potentials.

$$\partial_t \rho = \partial_x [V'(x) + \epsilon \partial_x] \rho \equiv \hat{S} \rho, \tag{1}$$

where $V'$ stands for $dV(x)/dx$, $\epsilon = k_B T$ denotes the thermal energy, and $\rho(x,t)$ is the position probability of the particle at time $t$. (Here time has the dimension length$^2$/energy because we have absorbed a friction constant into it.)

In the case of dichotomous barrier fluctuations between potential surfaces $V_1$ and $V_2$ with flipping rates $\gamma_1$ ($V_1 \to V_2$) and $\gamma_2$ ($V_2 \to V_1$), respectively, two densities $\rho_1(x,t)$ and $\rho_2(x,t)$ are needed: $\rho_i(x,t)$, $i=1,2$ are the densities to find the particle at time $t$ at position $x$ and the potential in state $V_i$. The analog of Eq. (1) reads

$$\partial_t \begin{pmatrix} \rho_1 \\ \rho_2 \end{pmatrix} = \hat{L}(\gamma_1, \gamma_2) \begin{pmatrix} \rho_1 \\ \rho_2 \end{pmatrix}, \tag{2}$$

with the matrix-Smoluchowski operator

$$\hat{L}(\gamma_1, \gamma_2) = \begin{pmatrix} \hat{S}_1 - \gamma_1 & \gamma_2 \\ \gamma_1 & \hat{S}_2 - \gamma_2 \end{pmatrix}. \tag{3}$$

In the following we are interested in the least negative eigenvalue, $k(\gamma_1, \gamma_2)$, which defines the relaxation rate $k$, and the corresponding relaxation eigenvector of the operator $\hat{L}(\gamma_1, \gamma_2)$. Unfortunately, a general solution to this problem for arbitrary potential surfaces is not known and even its existence is not obvious at all.[9] The case of symmetric noise $\gamma_1 = \gamma_2$ has been investigated intensively. Then, the existence of equilibrium and relaxation eigenfunctions can be proven;[9] moreover, in the limit of small thermal noise, i.e., high barriers, approximate methods to determine the relaxation rate have been developed by exploiting the characteristic separation of time scales.[14]

In contrast, little is known for the case of asymmetric flipping rates $\gamma_1 \neq \gamma_2$. In particular, the quality of the approximate methods is not clear and a simple estimate shows that there are regions in parameter space where none of these approaches can be applied. Thus, we consider here a simple model, namely, diffusion in fluctuating piecewise linear potentials (cf. Fig. 1)

$$V_i(x) = \begin{cases} v_i(l-x), & 0 \leqslant x \leqslant l \\ v_i(l+x), & -l \leqslant x \leqslant 0, \end{cases} \tag{4}$$

$i=1,2$ and $v_1 > v_2 > 0$, which allows for an exact analytical solution. It is convenient to scale out the thermal energy $\epsilon$ by dividing Eq. (3) by $\epsilon$ and then reusing the same symbols; thus, $\hat{L}/\epsilon$ is renamed $\hat{L}$, $\gamma_1/\epsilon$ is now $\gamma_1$, etc. The condition that the thermal noise be weak, that the thermal energy $\epsilon$ be small compared to the barrier heights, is then $v_2 l \gg 1$. We write

$$\gamma_1 = \frac{\gamma}{\alpha}, \quad \gamma_2 = \gamma\alpha, \tag{5}$$

with asymmetry parameter $\alpha$. Consequently, for $\gamma > 0$ the limits $\alpha \to 0$ and $\alpha \to \infty$ correspond to frozen potential surfaces in states $V_2$ and $V_1$, respectively. Now, the relaxation rate is defined by the proper solution to

$$\hat{L}(\gamma, \alpha) \vec{\rho}_r = -k(\gamma, \alpha) \vec{\rho}_r, \tag{6}$$

with relaxation eigenvector $\vec{\rho}_r$. Using the notation $\vec{\rho}_r = (\phi_1, \phi_2)$ we set $\vec{\rho}_r(0) = (\phi_1(0), \phi_2(0)) = 0$, by symmetry of the potential around $x=0$, and impose reflecting boundary conditions $V_i' \phi_i + \phi_i' = 0$, $i=1,2$ at $x = \pm l$.

## III. APPROXIMATE EIGENVECTORS AND EIGENVALUES

From a physical point of view the limit of small thermal noise is relevant for rate calculations. Then, the two exponentially large time scales corresponding to the relaxation processes in the static potentials are well separated from the time scales for intrawell relaxation. This allows for an approximate diagonalization of the Fokker–Planck operator in the regions of slow and moderate to fast fluctuation rates, respectively.

### A. Slow fluctuations

For flipping rates sufficiently smaller than the intrawell relaxation rates it was first shown in Ref. 8 for symmetric noise ($\alpha = 1$) that $\hat{L}$ can be diagonalized approximately taking into account only a basis of equilibrium and relaxation eigenfunctions of the static potentials $V_1, V_2$ with relaxation rates

$$k_i = v_i^2 \exp(-v_i l), \quad i = 1,2. \tag{7}$$

Along these lines, the eigenvalue of interest $-k(\gamma, \alpha)$ of (3) is given as the least negative eigenvalue of

$$\begin{pmatrix} -k_1 - \gamma_1 & \gamma_2 \\ \gamma_1 & -k_2 - \gamma_2 \end{pmatrix}. \tag{8}$$

As a result we obtain

$$k(\gamma, \alpha) = k_+ + \gamma_+ - \sqrt{k_-^2 + \gamma_+^2 - 2\gamma_- k_-}, \tag{9}$$

where we introduced sum and difference rates

$$k_\pm = \frac{k_2 \pm k_1}{2}, \quad \gamma_\pm = \frac{\gamma_1 \pm \gamma_2}{2} \equiv \frac{1 \pm \alpha^2}{2\alpha} \gamma. \tag{10}$$

This result is valid as long as $\gamma_1, \gamma_2$ are *both* much smaller than the second negative eigenvalue of $\hat{S}_2$ which is of order $v_2^2$ (for details see Sec. III C). Accordingly, one finds from Eq. (9) in the limit $\gamma \to 0$

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$$k(\gamma,\alpha)\approx k_1+\frac{\gamma}{\alpha}+O(\gamma^2), \tag{11}$$

while in the so-called resonant activation regime ($\gamma_+ \gg k_-$) the relaxation rate saturates at

$$k(\gamma,\alpha)\to\frac{k_2+\alpha^2 k_1}{1+\alpha^2}. \tag{12}$$

Hence, tuning the asymmetry parameter $\alpha$ allows for varying the relaxation rate between $k_2$ and $k_1$; for potential fluctuations which are large compared to $\epsilon$, i.e., $k_2 \gg k_1$, this leads to a significant slowing down (or acceleration) of the relaxation process, see also Sec. IV.

### B. Moderate to fast fluctuations

To determine the relaxation rate for larger values of $\gamma$ we start by taking the sum of the two coupled differential equations $\hat{L}\vec{\rho}_r=-k\vec{\rho}_r$ and integrating from 0 to $l$; with $\vec{\rho}_r=(\phi_1,\phi_2)$ one gets

$$k=\frac{\phi_1'(0)+\phi_2'(0)}{\int_0^l dx[\phi_1(x)+\phi_2(x)]}. \tag{13}$$

Next, in the case of symmetric noise an approximate solution for $\gamma \gg k_2$ was derived[13,14] by setting $k\approx 0$ in Eq. (6) and solving $\hat{L}\vec{\rho}_r=0$. It was shown that this procedure gives indeed a quantitatively good description all the way up from the resonant activation region to the region of motional narrowing $\gamma\to\infty$. Due to the separation of time scales there is a broad parameter range where the approximation for slow barrier fluctuations and that for moderate to fast fluctuations are both applicable, thus, providing the relaxation rate for all $\gamma$. Here, for asymmetric noise we try the same strategy; however, as we will discuss at the end, the matching region in $(\gamma,\alpha)$ parameter space shrinks as $\alpha$ deviates from 1 and eventually does not exist anymore for sufficiently large $\alpha$.

Due to symmetry, $\vec{\rho}_r(x)=\vec{\rho}_r(-x)$, it is sufficient to consider $x>0$ only. One rewrites $\hat{L}\vec{\rho}_r=0$ as a set of first-order differential equations[14]

$$\partial_x\begin{pmatrix}\vec{\rho}_r\\ \vec{\rho}_r'\end{pmatrix}=\begin{pmatrix}\mathbf{0} & \mathbf{I}\\ \mathbf{B} & \mathbf{A}\end{pmatrix}\begin{pmatrix}\vec{\rho}_r\\ \vec{\rho}_r'\end{pmatrix}, \tag{14}$$

where $\mathbf{I}$ denotes the two-dimensional identity and

$$\mathbf{A}=\begin{pmatrix}v_1 & 0\\ 0 & v_2\end{pmatrix},\quad \mathbf{B}=\frac{\gamma}{\alpha}\begin{pmatrix}1 & -\alpha^2\\ -1 & \alpha^2\end{pmatrix}. \tag{15}$$

By determining eigenvectors and eigenvalues of the four by four matrix in (14) one generates a basis set for expanding $\vec{\rho}_r$. The proper expansion coefficients are then fixed by invoking the proper boundary conditions.

The eigenvectors are obtained as $\vec{\sigma}_j=(\vec{w}_j,\lambda_j\vec{w}_j)$, $j=1,\ldots,4$ where eigenvalues $\lambda_j$ and components $\vec{w}_j$ follow from

$$\mathbf{B}\vec{w}+\lambda\mathbf{A}\vec{w}=\lambda^2\vec{w}. \tag{16}$$

In particular, one finds one vanishing eigenvalue $\lambda_3=0$ corresponding to the equilibrium of the $\gamma$-process. The remaining three real eigenvalues are determined by the cubic equation

$$-2\gamma_+(\lambda-\overline{v_\alpha})+\lambda(\lambda-v_1)(\lambda-v_2)=0, \tag{17}$$

with the $\alpha$ weighted average slope

$$\overline{v_\alpha}=\frac{v_1\alpha^2+v_2}{1+\alpha^2}. \tag{18}$$

For the components one has

$$\vec{w}_1=\begin{pmatrix}1\\ -x_1\end{pmatrix},\quad \vec{w}_2=\begin{pmatrix}x_2\\ 1\end{pmatrix},\quad \vec{w}_3=\begin{pmatrix}1\\ 1/\alpha^2\end{pmatrix},\quad \vec{w}_4=\begin{pmatrix}1\\ -x_4\end{pmatrix}, \tag{19}$$

where

$$x_1=\frac{\lambda_1-v_1}{\lambda_1-v_2},\quad x_2=\frac{\lambda_2-v_2}{v_1-\lambda_2},\quad x_4=\frac{\lambda_4-v_1}{\lambda_4-v_2}. \tag{20}$$

Since $\mathbf{A}$ and $\mathbf{B}$ are constant matrices (17) is easy to solve but explicit expressions are lengthy and not very instructive. In principle, the solutions follow from those of the symmetric case[13] by replacing $\gamma\to\gamma_+$ and $\overline{v_1}\to\overline{v_\alpha}$. Hence, there are two eigenvalues $\lambda_1$ and $\lambda_4$ that diverge like $\pm\sqrt{2\gamma_+}$, respectively, as $\gamma_+\to\infty$ while the eigenvalue $\lambda_2$ interpolates between $v_2$ and $\overline{v_\alpha}$. We note that $\gamma_+\to\infty$ is not only reached by $\gamma\to\infty$ for fixed $\alpha>0$ but also by $\alpha\to\infty$ or $\alpha\to 0$ for fixed $\gamma>0$. Accordingly, we have $x_1=x_2=0$ for $\gamma_+=0$ and $x_1,x_2,x_4\to 1$ in the limit $\gamma_+\to\infty$.

Now, inserting the expansion

$$\vec{\rho}_r(x)=\sum_{j=1}^{4} a_j(x)\vec{w}_j, \tag{21}$$

into (14) immediately leads to

$$a_j(x)=b_j\exp(\lambda_j x),\quad j=1,\ldots,4, \tag{22}$$

with constants $b_j$. Without loss of generality we put $b_2=1$ in the sequel. The reflecting boundary condition at $x=l$ is solved by taking the difference of the coupled equations $\hat{L}\vec{\rho}_r=0$, integrating from 0 to $l$, and neglecting exponentially small terms. Thus, the condition is equivalent to

$$\int_0^l dx[\phi_1(x)-\alpha^2\phi_2(x)]=0. \tag{23}$$

Inserting the expansion (21) and again retaining only those terms that may become exponentially large, we have

$$0=\int_0^l dx[\phi_1(x)-\alpha^2\phi_2(x)]$$

$$=\frac{x_2-\alpha^2}{\lambda_2}\exp(\lambda_2 l)+\frac{1+\alpha^2 x_1}{\lambda_1}\exp(\lambda_1 l)b_1, \tag{24}$$

so that

$$b_1=\frac{\lambda_1(\alpha^2-x_2)}{\lambda_2(1+\alpha^2 x_1)}\exp[-(\lambda_1-\lambda_2)l], \tag{25}$$

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turns out to be exponentially small. From the condition $\vec{\rho}_r(0)=0$ follow the remaining constants $b_3$ and $b_4$. We neglect the exponentially small $b_1$ contribution and find

$$b_3=-\alpha^2\frac{1+x_2x_4}{1+\alpha^2x_4}, \tag{26}$$

$$b_4=\frac{\alpha^2-x_2}{1+\alpha^2x_4}. \tag{27}$$

Hence,

$$\phi_1'(0)+\phi_2'(0)\approx\lambda_2(1+x_2)+\lambda_4\frac{(1-x_4)(\alpha^2-x_2)}{1+\alpha^2x_4}, \tag{28}$$

and

$$\begin{aligned}\int_0^l dx[\phi_1(x)+\phi_2(x)]&\approx\frac{(1+x_2)\exp(\lambda_2 l)}{\lambda_2}+b_1\frac{(1-x_1)\exp(\lambda_1 l)}{\lambda_1}\\&\approx\exp(\lambda_2 l)\frac{(1+\alpha^2x_1)(1+x_2)+(1-x_1)(\alpha^2-x_2)}{\lambda_2(1+\alpha^2x_1)}.\end{aligned} \tag{29}$$

This way we gain from (13)

$$k(\gamma,\alpha)\approx\frac{\lambda_2}{1+\alpha^2}\exp(-\lambda_2 l)\frac{[\lambda_2(1+x_2)(1+\alpha^2x_4)+\lambda_4(\alpha^2-x_2)(1-x_4)](1+\alpha^2x_1)}{(1+x_1x_2)(1+\alpha^2x_4)}. \tag{30}$$

For small $\gamma_+$ (but still $\gamma_+\gg k_2$) we find

$$k\approx\frac{\lambda_2^2}{1+\alpha^2}\exp(-\lambda_2 l)\approx\frac{v_2^2}{1+\alpha^2}\exp(-v_2 l)=\frac{k_2}{1+\alpha^2}, \tag{31}$$

the rate in the resonant activation regime while for $\gamma_+\to\infty$ follows

$$k\approx\left[\frac{\lambda_2}{1+\alpha^2}\exp(-\lambda_2 l)\right](1+\alpha^2)\lambda_2\approx\bar{v}_\alpha^2\exp(-\bar{v}_\alpha l), \tag{32}$$

the rate in the $\alpha$ dependent average potential.

### C. Validity of the approximations

The results Eq. (9) and Eq. (30) provide the relaxation rate $k(\gamma,\alpha)$ for all values of $\gamma$ only if for fixed $\alpha$ there is a region where both results match up to exponentially small corrections. In this section we analyze the domains of validity for the above approximations.

In the case of slow barrier fluctuations, as already mentioned, the diagonalization in the subspace of the relaxation eigenfunctions for the static potentials is valid so long as $\gamma/\alpha$ and $\gamma\alpha$ are both much smaller than the second negative eigenvalue of $\hat{S}$, which is of order $v_2^2$. In $(\gamma,\alpha)$ parameter space this gives rise to two curves (see Fig. 2): for $\alpha\leqslant 1$ the line $\gamma/\alpha=\eta v_2^2$ with arbitrary but fixed parameter $\eta\ll 1$ [line (1) in Fig. 2] defines the upper bound, while for $\alpha>1$ the line $\gamma/\alpha=\eta v_2^2$ [line (2) in Fig. 2] is essential. The corresponding area (region I) is the shaded domain in Fig. 2. Physically, in region I the system has enough time to relax to equilibrium in the potential wells after each flip so that one has basically escape over static barriers.

The procedure outlined in Sec. III B is applicable for sure (in the limit $\epsilon\to 0$) if the reflecting boundary condition can be solved by Eq. (23). The corrections neglected there follow by taking the difference of the coupled equations $\hat{L}\vec{\rho}_r=-k\vec{\rho}_r$ and integrating from 0 to $l$; employing Eq. (13) we get

$$\int_0^l dx[\gamma_1\phi_1(x)-\gamma_2\phi_2(x)]=-\phi_2'(0)+k\int_0^l dx\,\phi_2(x). \tag{33}$$

Since $\phi_i$ provide exponentially large contributions while $\phi_2'(0)$ is of order 1 and $k$ exponentially small, the right hand side in Eq. (33) is always of lower order than the left hand side if $\gamma_1,\gamma_2\gg k$. This means $\gamma\gg k_2/\alpha$ for $\alpha\leqslant 1$ and $\gamma\gg k_2\alpha$ for $\alpha>1$. However, for $\alpha<1$ there is an even weaker condition: in the range where $\gamma_+$ is sufficiently smaller than $v_2$ the limit $k\approx k_2/(1+\alpha^2)$ applies; accordingly, the right hand side is then of order $\alpha^2$, thus vanishing for $\alpha\to 0$. Further, in the limit $\epsilon,\alpha\to 0$ where $k_2\gg\alpha^2k_1$, the upper limit in

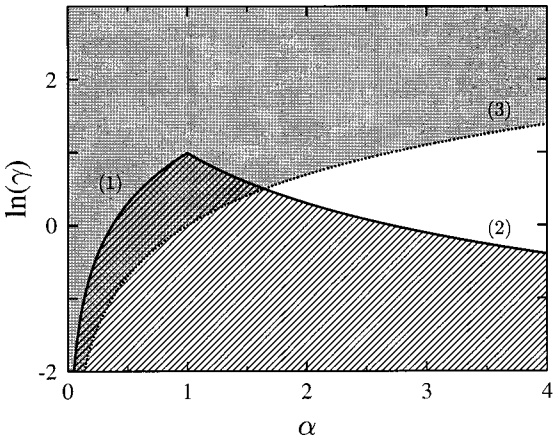


FIG. 2. Ranges of validity for the various approximations. In the shaded area (region I) the approximation for slow barrier fluctuations Eq. (9) applies while in the gray domain (region II), that for moderate to fast fluctuations, Eq. (30) works. The solid line (1) corresponds to the curve $\gamma=\eta\alpha v_2^2$, the line (2) to $\gamma=\eta v_2^2/\alpha$, and the dotted line (3) to $\gamma=\eta' k_2\alpha$ (see text for details). Parameters were chosen according to Fig. 3.

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the slow fluctuation range Eq. (12) coincides with $k \approx k_2/(1+\alpha^2)$; this upper limit holds for $\gamma_+ \gg k_-$, i.e., $\gamma \gg k_2\alpha$. Hence, the validity of the moderate to fast fluctuation procedure is restricted from below by the line $\gamma = \eta' k_2 \alpha$ with arbitrary but fixed $\eta' \gg 1$ [line (3) in Fig. 2] for all $\alpha$. In this region II, barrier fluctuations are so fast that the distributions in states $v_1$ and $v_2$ differ only near the top of the barrier; from up to down and back to up there is no time for intrawell relaxation anymore.

As can be seen in Fig. 2 the domain where regions I and II overlap is broad for $\alpha \leqslant 1$ but tends to vanish for moderate $\gamma$ and sufficiently large $\alpha$. Thus, for larger asymmetry, i.e., $\gamma_1$ sufficiently smaller than $\gamma_2$, the above approximations give the relaxation rate only in distinct ranges of the $(\gamma,\alpha)$ parameter space. In between these regions barrier fluctuations act on quite different time scales: they are neither both smaller than the typical time for intrawell relaxation nor both larger than the average interwell escape time. While the flipping rate $\gamma_1$ is small enough that the system can equilibrate to the upper potential surface before it jumps back to the lower one, the rate $\gamma_2$ is not. Thus, we have thermal activation over an almost static barrier $v_1$ coupled to an escape over $v_2$ from a nonequilibrium well distribution. As a consequence, the diagonalization procedure does not work. Further, since in the limit $\epsilon \to 0$ we have $k_2 \gg k_1$, in the $v_2$ state still a substantial loss of population occurs meaning that the relaxation rate is given as a kind of average rate [but not as in Eq. (12)] and cannot be described by relaxation in only one effective potential. What is always possible, however, to gain a complete result is an approximation based only on the assumption of weak thermal noise $\epsilon \to 0$ and to avoid the separation in small and moderate to large $\gamma$; this is what we do in the next section.

## IV. EXACT RELAXATION RATE

To evaluate the relaxation rate for arbitrary $\gamma,\alpha$ but $\epsilon \to 0$ is just a little exercise in keeping track of the exponentially small expansion parameter $k$ by solving $\hat{L}\vec{\rho}_r = -k\vec{\rho}_r$ perturbatively along the lines described in Sec. III B. As a warm up let us briefly sketch the one-dimensional case with slope $v$. The equation $-v\rho_r' + \rho_r'' = -k\rho_r$ is simply fulfilled by an exponential ansatz $\rho_r \propto \exp(\lambda x)$ with the solutions

$$\lambda_+ = \frac{v}{2} + \sqrt{\frac{v^2}{4} - k} \approx v - \frac{k}{v}, \quad \lambda_- = \frac{v}{2} - \sqrt{\frac{v^2}{4} - k} \approx \frac{k}{v}, \tag{34}$$

where the approximations follow by retaining at most terms linear in $k$. Thus, inserting $\rho_r = \exp(\lambda_+ x) + b\exp(\lambda_- x)$ into $\rho_r(0) = 0$ fixes first $b = -1$; second, the reflecting boundary condition at $x = l$ is solved by expanding up to terms linear in $k$ leading to the rate as in Eq. (7).

For the fluctuating barrier case we again rewrite $\hat{L}\vec{\rho}_r = -k\vec{\rho}_r$ as a set of first-order differential equations. One obtains the result specified in Eq. (14), however, with the matrix $\mathbf{B}$ replaced by

$$\tilde{\mathbf{B}} = \begin{pmatrix} \gamma/\alpha - k & -\gamma\alpha \\ -\gamma/\alpha & \gamma\alpha - k \end{pmatrix}. \tag{35}$$

The corresponding eigenvalues of the four by four matrix are determined by $\mathrm{Det}[\tilde{\mathbf{B}} + \tilde{\lambda}\mathbf{A} - \tilde{\lambda}^2] = 0$. To proceed in the sense of the $\epsilon \to 0$ asymptotics we write the four eigenvalues as $\tilde{\lambda}_i = \lambda_i + \delta\lambda_i, i = 1,\ldots,4$ where the $\lambda_i$ follow by putting $k = 0$ in Eq. (35). Then, as in Sec. III B one has $\lambda_3 = 0$ while $\lambda_1, \lambda_2, \lambda_4$ are given by the cubic equation Eq. (17). Furthermore, it turns out that by retaining only the dominant corrections for $\epsilon \to 0$ one obtains $\delta\lambda_3 \approx \delta\lambda_4 \approx 0$ and $\delta\lambda_i = -k\sigma_i, i = 1,2$ with

$$\sigma_i = \frac{\overline{v_\alpha}\lambda_i[v_1\Delta_{i1} + v_2\Delta_{i2}] - 2\gamma_+ v_1 v_2}{\overline{v_\alpha} v_1 v_2[\lambda_i(\Delta_{i1} + \Delta_{i2}) - 2\gamma_+ + \Delta_{i1}\Delta_{i2}]}. \tag{36}$$

Here, we used the abbreviation

$$\Delta_{ij} = \lambda_i - v_j. \tag{37}$$

The leading order contributions to the eigenvectors are found as specified in Eqs. (19), (20) and $k$-dependent corrections provide only negligible small contributions in the final rate expression.

Next, $\vec{\rho}_r$ is expanded according to Eq. (21) where the boundary conditions fix the corresponding coefficients. Since here we seek for a solution which reduces to the relaxation eigenfunction in potential $v_1$ for $\gamma_+ \to 0$ and to that in potential $\overline{v_\alpha}$ for $\gamma_+ \to \infty$ it is convenient to put $b_3 = 1$. Inserting $\vec{\rho}_r$ into the four boundary conditions [two from $\vec{\rho}_r(0) = 0$, two reflecting boundary conditions at $x = l$] and neglecting exponentially small terms determines first $b_1, b_2, b_4$, and eventually after straightforward but lengthy algebra leads to a nonlinear equation for $k$. To solve this equation is a little tricky: The naive way would be to proceed as in the one-dimensional case and to expand up to terms linear in $k$. However, as we learned in Sec. III A, in the small $\gamma$ range terms linear in $k$ dominate only for $\gamma \gg k$ while for smaller flipping rates $k^2$ contributions are necessary. This way, the full equation is formally expanded as $a_0 + a_1 k + a_2 k^2 + O(k^3) = 0$. In fact, by determining the leading order terms in the coefficient $a_2$ it turns out that for all $\gamma \gg k$ the $k^2$ term is negligibly small against the linear term. Hence, it suffices to retain in $a_2$ only those terms that give relevant contributions for small $\gamma$. This simplifies the perturbation theory enormously. The coefficient $a_0$ is easy while $a_1$ just requires some tedious algebra. As the final result we obtain for the relaxation rate in the limit $\epsilon \to 0$ (but for arbitrary $\gamma_+$) the compact formula

$$k(\gamma,\alpha) = \Lambda - \sqrt{\Lambda^2 - \Gamma}. \tag{38}$$

Here,

$$\Lambda = \frac{\sigma_1[\Delta_{22} + \kappa_2(1+\rho_2)] + \sigma_2[\Delta_{11} + \kappa_1(1+\rho_1)]}{2\sigma_1\sigma_2}, \tag{39}$$

and

$$\Gamma = \frac{\kappa_1\kappa_2(1+\chi_0) + \kappa_1(\Delta_{22} + \chi_1) + \kappa_2(\Delta_{11} + \chi_2)}{(1 + x_1 x_2)\sigma_1\sigma_2}. \tag{40}$$

Thereby

$$\kappa_i = v_i \exp(-\lambda_i l), \tag{41}$$

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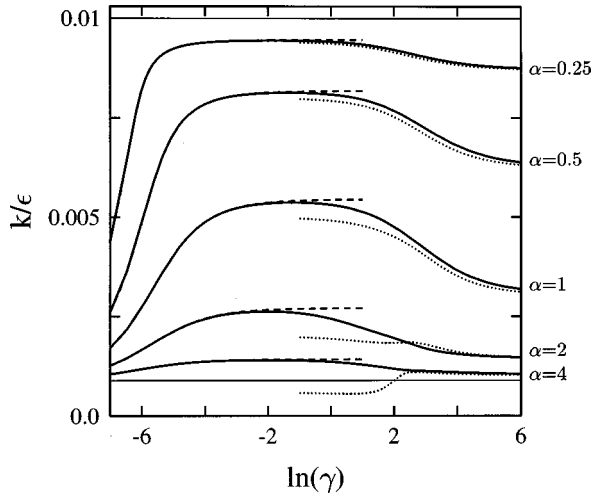


FIG. 3. Relaxation rates for the piecewise linear potential as a function of the barrier fluctuation rate and for various asymmetry parameters $\alpha$. The thick solid lines show the exact result (38). The dashed lines represent Eq. (9) and the dotted lines Eq. (30). The thin solid lines depict the static rates $k_2$ (top line) and $k_1$ (bottom line). Parameters are $l=1$, $v_1=12$, and $v_2=9$.

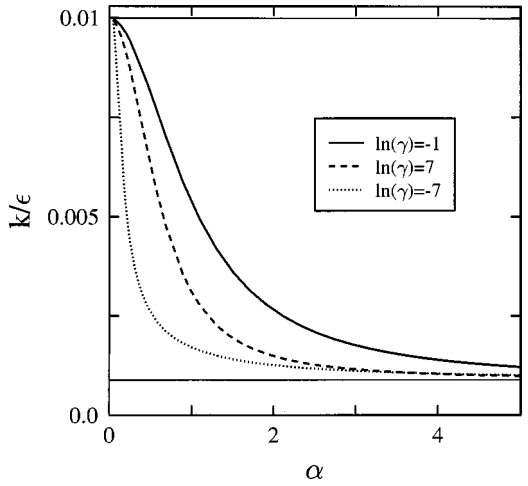


FIG. 4. Relaxation rates for the piecewise linear potential as a function of the asymmetry parameter $\alpha$ for fixed barrier fluctuation rate. The thin solid lines show the static rates $k_2$ (top line) and $k_1$ (bottom line). Parameters are as in Fig. 3.

while the $\rho_i, i=1,2$ and $\chi_i, i=0,1,2$ are not very illuminating and specified in the Appendix. In particular, these terms are negligible for all $\gamma \ll v_2$.

Let us briefly discuss some limits of the above result: for $\gamma_+ \to 0$ it is $\Delta_{11}=\Delta_{22}=0$ so that $\sigma_i=1/v_i$; with $\kappa_i=k_i/v_i$ we find $\Lambda=(k_1+k_2)/2$ and $\Gamma=k_1k_2$ bringing us back to $k=k_1$. In the opposite limit $\gamma_+ \to \infty$ the eigenvalue $\lambda_1$ diverges and thus with $\Delta_{11}$ and $\Delta_{12}$ also $\Lambda$ and $\Gamma$; however, since $\Gamma/\Lambda^2 \to 0$ an expansion of the square root gives with $x_1=x_2=1$ the right answer, $k \to \Gamma/(2\Lambda)=k(\overline{v_\alpha})$. The intermediate case $k_2 \ll \gamma_+ \ll v_2^2$ goes as follows: to lowest order $\Delta_{ii}=\gamma_+/v_i$ and $\sigma_i=1/v_i$; $\rho_i$ and $\chi_i$ can be neglected; correspondingly, one rederives the result in Eq. (9).

In Fig. 3 the result Eq. (38) is shown as a function of $\gamma$ and for various values of $\alpha$. For the set of parameters $v_1=12$, $v_2=9$ and $l=1$, this asymptotic result coincides practically with the exact one. As can be seen the intermediate resonant activation maximum of $k(\gamma,\alpha)$ becomes rather flat for small and large $\alpha$. For $\alpha \to 0$ the change from $k=k_1$ $(\gamma=0)$ to $k \approx k_2$ occurs very steeply while for large $\alpha$ the rate is practically given by $k_1$. Obviously, for moderate $\gamma$ the rate changes drastically by varying $\alpha$. Also shown in Fig. 3 are the approximate results for slow and moderate to fast fluctuations. As already discussed in Sec. III C the combination of both methods performs excellently for $\alpha \lesssim 1$. Particularly, decreasing $\gamma$ from the large $\gamma$ range, the effective potential surface approximation Eq. (30) begins to underestimate the exact rate when relaxation over two almost static barriers tends to occur. This effect becomes distinct for $\alpha > 1$ where, for moderate $\gamma$, none of these approaches gives reliable results.

The dependence of the relaxation rate $k(\gamma,\alpha)$ on $\alpha$ is depicted in Fig. 4 for fixed very small, moderate, and very large $\gamma$ (same set of parameters as for Fig. 3). While in the extreme limits the change in $\alpha$ is basically restricted to small values of $\alpha$, intermediate $\gamma$ values give rise to a significant drop of the rate over a broad $\alpha$ range.

## V. CONCLUSIONS

The influence of asymmetric barrier flipping rates on the relaxation rate in a simple bistable potential has been studied by means of the Fokker–Planck approach. Approximate methods to gain the rate for slow and moderate to fast fluctuations, respectively, give excellent results for large regions of parameter space. They definitely fail for moderate fluctuation rates and asymmetries where the system spends more time in the upper potential surface than in the lower one but still not much enough to dominate the relaxation rate completely. Physically, in this range, escape over the almost static higher barrier is coupled to escape over the lower barrier from a nonequilibrium well distribution. To achieve a complete description we also derived a result which avoids any assumption about the magnitude of barrier flipping rates and relies only on the asymptotics of weak thermal noise $\epsilon \to 0$.

Interestingly, the dependence of the relaxation rate on the asymmetry can be used to tune the relaxation process from fast to slow and vice versa. Think of the fluctuating barrier system as two strongly coupled isomerizations; suppose the asymmetry of the isomerization process that generates barrier fluctuations for the other isomerization could be influenced by an external field; then, fluctuating potentials would allow control of the rate of a chemical reaction. Perhaps the present work will stimulate experimentalists at least to think about the possibility of realizing such a control.

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## APPENDIX: COEFFICIENTS IN THE EXACT RATE EXPRESSION

Here, we specify the somewhat lengthy coefficients in the asymptotic rate expression Eq. (38). In the function $\Lambda$ in Eq. (39) we have

$$\rho_1 = x_1 x_2 \frac{\nu_2}{\nu_1} + \frac{1+\alpha^2 x_1}{\nu_1(1+\alpha^2 x_4)}(x_2 x_4 \eta_2 + \eta_1),$$
$$\rho_2 = x_1 x_2 \frac{\nu_1}{\nu_2} + \frac{\alpha^2 - x_2}{\nu_2(1+\alpha^2 x_4)}(x_4 \eta_2 - x_1 \eta_1), \tag{A1}$$

with

$$\eta_i = \nu_i + \exp(\lambda_4 l)(\lambda_4 - \nu_i), \quad i = 1,2. \tag{A2}$$

These coefficients vanish for $\gamma_+ \to 0$; for $\gamma_+ \to \infty$ we find $\rho_1 \to \nu_2/\nu_1 + (\nu_1+\nu_2)/\nu_1$ and $\rho_2 \to \nu_1/\nu_2$.

The function $\Gamma$ in Eq. (40) contains

$$\chi_0 = -\frac{\alpha^2 \nu_1 x_4 \eta_2 + \nu_2 \eta_1}{\nu_1 \nu_2 (1+\alpha^2 x_4)};$$
$$\chi_1 = \Delta_{21} x_1 x_2 \frac{\nu_2}{\nu_1} - \frac{1+\alpha^2 x_1}{\nu_1(1+\alpha^2 x_4)}(x_2 x_4 \eta_2 \Delta_{21} + \eta_1 \Delta_{22});$$
$$\chi_2 = \Delta_{12} x_1 x_2 \frac{\nu_1}{\nu_2} - \frac{\alpha^2 - x_2}{\nu_2(1+\alpha^2 x_4)}(x_4 \eta_2 \Delta_{11} - x_1 \eta_1 \Delta_{12}). \tag{A3}$$

For $\gamma \ll \nu_2$ these coefficients give negligibly small contributions to the rate and are relevant only for moderate $\gamma_+$.


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