PHYSICAL REVIEW E VOLUME 58, NUMBER 6 DECEMBER 1998

Eigenvector-eigenvalue rate calculations for the fluctuating barrier problem: Two examples

Joachim Ankerhold[1] and Philip Pechukas[2]
[1]*Fakultät für Physik, Universität Freiburg, Hermann-Herder Strasse 3, 79104 Freiburg, Germany*
[2]*Department of Chemistry, Columbia University, New York, New York 10027*
(Received 10 July 1998)

By means of the corresponding Fokker-Planck equation two simple systems with fluctuating barriers are studied: the piecewise linear and the piecewise constant model. In the Smoluchowski limit and for dichotomous barrier fluctuations we derive explicit expressions for equilibrium and relaxation eigenvectors and determine the least negative eigenvalue, the relaxation rate, for all values of the barrier fluctuation rate. In particular, the accuracy of an approximate method for solving the eigenvector-eigenvalue problem is demonstrated. [S1063-651X(98)08711-X]

PACS number(s): 05.40.+j, 02.50.−r, 82.20.Mj

I. INTRODUCTION

Escape over a high potential barrier by thermal activation can be found almost everywhere in physics, chemistry, and biology [1]. Particles starting in a well to one side of the barrier stochastically jump over it to reach a well on the other side; at long times the initial nonequilibrium state decays with a constant rate, the so-called relaxation rate, to end up in thermal equilibrium. This dynamics is governed by a Fokker-Planck equation which becomes particularly simple in the overdamped Smoluchowski limit [2]. Then, the eigenvector to the Smoluchowski operator with vanishing eigenvalue, the equilibrium state, can be given explicitly; also the relaxation eigenvector with its least negative eigenvalue, the relaxation rate, is found immediately.

In recent years thermal escape over fluctuating barriers has attracted extensive attention [3,4], especially since the discovery of the ''resonant activation'' phenomenon in 1992 [5]. In many complex systems an additional stochastic process, not in thermal equilibrium, controls thermal diffusion and, thus, acts like a ''gate'' for, e.g., a reaction to occur [6]. In the Smoluchowski limit the mean exit time was calculated analytically for simple models and dichotomous barrier fluctuations [7,8] and numerically for more realistic potentials and continuous fluctuations [4]. However, the conventional Fokker-Planck approach had only been studied in certain limits [9]. The nice simplifications that make the theory of self-adjoint operators applicable to the Smoluchowski operator for static barriers are no longer possible in the fluctuating barrier case. Hence, even the existence of equilibrium and relaxation eigenfunctions is not obvious and a consistent approximate method for calculating the relaxation rate needs to be found.

Recently a rigorous proof was given for the case of dichotomous barrier fluctuations that guarantees at least the existence of these relevant eigenfunctions [10]. Foundations for a practical approach to gain explicit solutions, especially for the relaxation rate, for all values of the barrier fluctuation rate were laid in a subsequent work [11]. Here, we combine results from both studies to illustrate the approximate eigenvector-eigenvalue calculation for two simple models: the piecewise linear and the piecewise constant potential. These two potentials can be seen as limiting cases of generic bistable potentials: double wells with either very large (piecewise linear) or almost vanishing (piecewise constant) curvatures at the barrier top and at the well minima. They not only allow for exact results as explicitly shown for the mean exit time in [7,8] but also lead to transparent expressions that demonstrate nicely the general strategy of the approximation.

The article begins with a brief review of the Fokker-Planck approach for dichotomous barrier fluctuations in the Smoluchowski limit (Sec. II). In the following two sections first the piecewise linear (Sec. III), then the piecewise constant case (Sec. IV) are analyzed. Analytical results are illustrated by numerical examples. Finally, in Sec. V a summary is given.

II. FOKKER-PLANCK OPERATOR

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

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

where V' stands for $dV(x)/dx$, $\epsilon = k_BT$ denotes the thermal energy, and $\rho(x,t)$ is the position probability of the particle at time t. The mathematics to study this dynamics is rather simple: one transforms the Smoluchowski operator $\hat{S}$ to a self-adjoint second-order differential operator by employing an appropriate multiplication operator. Accordingly, the existence of a complete set of eigenfunctions with corresponding real eigenvalues is assured. In particular, the equilibrium eigenfunction $\hat{S}\rho_0 = 0$ is easily found and the least negative eigenvalue $-k$ gives the relaxation rate.

In the case of dichotomous barrier fluctuations between potential surfaces V_1 and V_2 with flipping rate γ 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 to Eq. (1) reads

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

with the matrix Smoluchowski operator

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

However, no simple trick is known to transform $\hat{L}$ to a self-adjoint operator. Consequently, even the existence of equilibrium and relaxation eigenfunctions is not obvious. One way is then to diagonalize $\hat{L}$ exactly which, however, is explicitly possible only for a few model potentials (see Sec. IV). The other way is to prove the existence at least of equilibrium and relaxation eigenfunctions for certain classes of potentials without resorting to the well-developed theory of self-adjoint operators. This is what was done in [10].

Let us sketch the idea for the equilibrium $\vec{\rho}_0=(\rho_1,\rho_2)$ in symmetric potentials $V_{1,2}(x)$ restricted to the range $[-R,R]$ by reflecting boundary conditions $V_i'\rho_i+\epsilon\rho_i'=0$ at $x=\pm R$. We write $\rho_i(x)=c_i(x)\exp[-V_i(x)/\epsilon]$ and impose $c_i'(0)=0$, $c_i(x)>0$ for all x, and $c_i'(\pm R)=0, i=1,2$. Integrating $\hat{L}\vec{\rho}_0=0$ one gets

$$c_1'(x)\exp[-V_1(x)/\epsilon]=(\gamma/\epsilon)\int_0^x dx'[\rho_1(x')-\rho_2(x')],$$
$$c_2'(x)\exp[-V_2(x)/\epsilon]=-(\gamma/\epsilon)\int_0^x dx'[\rho_1(x')-\rho_2(x')]. \tag{4}$$

If $c_1(0)/c_2(0)$ is sufficiently large, then $\rho_1>\rho_2$ for all x and $c_1'(R)>0$, $c_2'(R)<0$. If $c_1(0)/c_2(0)$ is sufficiently small, then $\rho_1<\rho_2$ for all x and $c_1'(R)<0$, $c_2'(R)>0$. By continuity, there is a ratio $c_1(0)/c_2(0)$ "just right" that the integral from 0 to R of $\rho_1-\rho_2$ vanishes, so $c_1'(R)=c_2'(R)=0$ and we have the equilibrium solution. Similar arguments show that a relaxation eigenfunction $\hat{L}\vec{\rho}_r=-k\vec{\rho}_r$, with $\vec{\rho}_r(x)=-\vec{\rho}_r(-x)$, exists.

In general, much more work is necessary to gain explicit expressions for the quantities of interest due to the entanglement of the potential surfaces in Eq. (2). From a physical point of view the limit of small thermal noise, i.e., high barriers, with the characteristic separation of time scales is relevant for rate calculations. Then, equilibrium and relaxation eigenfunctions are dominated by "Arrhenius-like" exponentials [11] which allows for an asymptotic solution in ϵ. In the following we illustrate how this latter fact together with the above results from the existence proof can be combined to give a powerful method for practical calculations.

III. PIECEWISE LINEAR POTENTIAL

We study diffusion in fluctuating piecewise linear potentials

$$V_i(x)=\begin{cases}v_i(l-x), & 0\le x\le l\\ v_i(l+x), & -l\le x\le 0\end{cases} \tag{5}$$

with $i=1,2$ and $v_1>v_2>0$ (cf. Fig. 1). While in principle for this model the Smoluchowski operator (3) can be diagonalized exactly, we concentrate here on $v_i l/\epsilon\gg 1, i=1,2$ (high barriers) to show the strategy of the approximation.

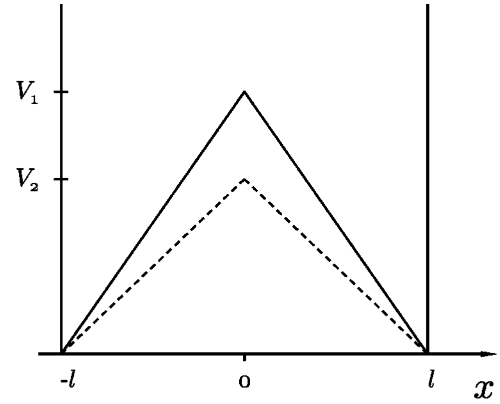

FIG. 1. Piecewise linear potentials.

A. Equilibrium eigenvector

Due to symmetry, $\vec{\rho}_0(x)=\vec{\rho}_0(-x)$, it is sufficient to consider $x>0$ only. One rewrites $\hat{L}\vec{\rho}_0=0$ as a set of first-order differential equations [11]

$$\partial_x\begin{pmatrix}\vec{\rho}_0\\ \vec{\rho}_0{}'\end{pmatrix}=\begin{pmatrix}\mathbf{0} & \mathbf{I}\\ \mathbf{B} & \mathbf{A}\end{pmatrix}\begin{pmatrix}\vec{\rho}_0\\ \vec{\rho}_0{}'\end{pmatrix}, \tag{6}$$

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

$$\mathbf{A}=\begin{pmatrix}v_1/\epsilon & 0\\ 0 & v_2/\epsilon\end{pmatrix},\quad \mathbf{B}=\frac{\gamma}{\epsilon}\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}. \tag{7}$$

By determining eigenvectors and eigenvalues of the four by four matrix in Eq. (6) one generates a basis set for expanding $\vec{\rho}_0$. The proper expansion coefficients are then fixed by invoking the boundary conditions.

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

$$\mathbf{B}\vec{w}+\lambda\mathbf{A}\vec{w}=\lambda^2\vec{w}. \tag{8}$$

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

$$\lambda^3-2\lambda^2\frac{\overline{v}}{\epsilon}+\lambda\frac{v_1v_2-2\epsilon\gamma}{\epsilon^2}+\frac{2\gamma\overline{v}}{\epsilon^2}=0, \tag{9}$$

with the average slope

$$\overline{v}=\frac{v_1+v_2}{2}. \tag{10}$$

For the components one has

$$\vec{w}_1=\begin{pmatrix}1\\ -x_1\end{pmatrix},\quad \vec{w}_2=\begin{pmatrix}x_2\\ 1\end{pmatrix},\quad \vec{w}_3=\begin{pmatrix}1\\ 1\end{pmatrix},\quad \vec{w}_4=\begin{pmatrix}1\\ -x_4\end{pmatrix}, \tag{11}$$

where

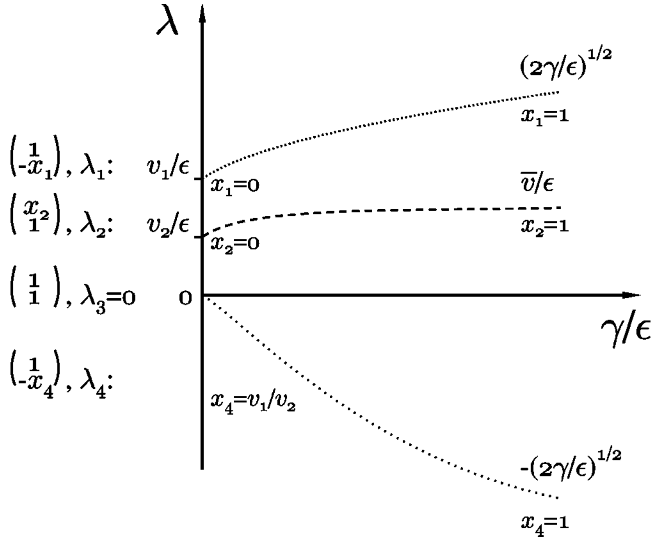

FIG. 2. Eigenvalues of Eq. (8) as functions of γ/ϵ. The components of the corresponding eigenvectors are also specified for $\gamma=0$ and $\gamma/\epsilon\to\infty$. See text for details.

$$x_1=\frac{\epsilon\lambda_1-v_1}{\epsilon\lambda_1-v_2},\quad x_2=\frac{\epsilon\lambda_2-v_2}{v_1-\epsilon\lambda_2},\quad x_4=\frac{\epsilon\lambda_4-v_1}{\epsilon\lambda_4-v_2}. \tag{12}$$

Since **A** and **B** are constant matrices Eq. (9) is easy to solve but explicit expressions are lengthy and not very instructive. Instead Fig. 2 collects the behavior of eigenvectors and eigenvalues as the fluctuation rate γ varies from $\gamma=0$ to $\gamma\to\infty$. Two eigenvalues λ_1 and λ_4 diverge for large γ while only λ_2 saturates, thus, interpolating between v_2/ϵ and the average slope $\bar{v}/\epsilon$. 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

$$\vec{\rho}_0(x)=\sum_{j=1}^{4} a_j(x)\vec{w}_j \tag{13}$$

into Eq. (6) immediately leads to

$$a_j(x)=b_j\,\exp(\lambda_j x),\quad j=1,\ldots,4 \tag{14}$$

with constants b_j. Without loss of generality we set $b_2=1$ in what follows. The reflecting boundary condition $c_i'(l)=0$ is solved by setting the integral from 0 to l of $\rho_1-\rho_2$ equal to zero [see (4)]. Retaining only those terms that may become exponentially large, we have

$$\begin{aligned}0&=\int_0^l dx[\rho_1(x)-\rho_2(x)]\\&=\frac{x_2-1}{\lambda_2}\exp(\lambda_2 l)+\frac{1+x_1}{\lambda_1}\exp(\lambda_1 l)b_1\end{aligned} \tag{15}$$

so that

$$b_1=\frac{\lambda_1(1-x_2)}{\lambda_2(1+x_1)}\exp[-(\lambda_1-\lambda_2)l] \tag{16}$$

turns out to be exponentially small. The condition $c_i'(0)=0$ is equivalent to $v_i\rho_i+\epsilon\rho_i'=0$ from which the remaining constants b_3 and b_4 follow. We neglect the exponentially small b_1 contribution and find

$$b_3=-\frac{x_2(\epsilon\lambda_2+v_1)+b_4(\epsilon\lambda_4+v_1)}{v_1}, \tag{17}$$

$$b_4=\frac{v_1v_2(1-x_2)+\epsilon\lambda_2(v_1-v_2x_2)}{v_1v_2(1+x_4)+\epsilon\lambda_4(v_2+v_1x_4)}. \tag{18}$$

Retaining only terms that grow exponentially with x, one therefore has

$$\vec{\rho}_0(x)=\exp\left(\frac{v_2x}{\epsilon}\right)\begin{pmatrix}0\\1\end{pmatrix}+\frac{v_1}{v_2}\exp\left[-\frac{(v_1-v_2)l-v_1x}{\epsilon}\right]\begin{pmatrix}1\\0\end{pmatrix} \tag{19}$$

in the limiting case $\gamma\to 0$, and

$$\vec{\rho}_0(x)=\exp\left(\frac{\bar{v}x}{\epsilon}\right)\begin{pmatrix}1\\1\end{pmatrix} \tag{20}$$

in the limit $\gamma\to\infty$.

B. Relaxation eigenvector

The eigenvector $\vec{\rho}_r$ associated to the least negative eigenvalue of $\hat{L}$, which determines the relaxation rate k, dominates the dynamics of an initial nonequilibrium distribution in Eq. (2) for long times. For a high static barrier with slope v one simply finds from $\hat{S}\rho_r=-k\rho_r\approx 0$ the function $\rho_r\approx\exp(vx/\epsilon)-1$. The rate is calculated by integrating the Smoluchowski equation from 0 to l,

$$k=-\frac{\int_0^l dx\hat{S}\rho_r}{\int_0^l dx\rho_r}=\epsilon\frac{\rho_r'(0)}{\int_0^l dx\rho_r}\approx\frac{v^2}{\epsilon}\exp\left(-\frac{vl}{\epsilon}\right). \tag{21}$$

As already mentioned above for fluctuating barriers of the type (5) an exact diagonalization of $\hat{L}$ is in principle possible even though rather lengthy. Here, however, we want to proceed in the spirit of the small ϵ expansion to arrive at transparent expressions. For this purpose we consider the "small" γ range and the "moderate to large" γ range separately. In the first case the operator $\hat{L}$ can be diagonalized approximately for *any* potential (for details see [9]) taking into account only a basis of equilibrium and relaxation eigenfunctions of the static potentials $V_{1,2}$ with relaxation rates $k_{1,2}$. The relevant least negative eigenvalue is

$$k(\gamma)=\frac{k_1+k_2}{2}+\gamma-\left[\gamma^2+\frac{(k_1-k_2)^2}{4}\right]^{1/2}. \tag{22}$$

As expected $k(0)=k_1$ while for $\gamma\gg(k_2-k_1)$ the rate saturates at $k(\gamma)=(k_1+k_2)/2\approx k_2/2$ in the so-called resonant activation region. This result is valid as long as γ is much smaller than the second negative eigenvalue of $\hat{S}_2$ which is of order v_2^2/ϵ.

To determine the relaxation rate for larger values of γ we start by integrating $\hat{L}\vec{\rho}_r=-k\vec{\rho}_r$ from 0 to l; with the notation $\vec{\rho}_r=(\phi_1,\phi_2)$ we get [see (21)]

$$k=\epsilon\frac{\phi_1'(0)+\phi_2'(0)}{\int_0^l dx[\phi_1(x)+\phi_2(x)]}. \tag{23}$$

Next, an approximate solution for $\gamma \gg k_1, k_2$ is derived by setting $k\approx 0$ and solving $\hat{L}\vec{\rho}_r=0$. Consequently, $\int_0^l(\phi_1-\phi_2)\approx 0$, see Eq. (4). This then looks just like the problem we already solved in the preceding section, with a different boundary condition at $x=0$. $\vec{\rho}_r$ is expanded according to Eq. (13) again with $b_2=1$ and b_1 as specified in Eq. (16). Up to exponentially small terms the condition $\vec{\rho}_r(0)=0$ leads to

$$b_3=-\frac{1+x_2x_4}{1+x_4},\quad b_4=\frac{1-x_2}{1+x_4}. \tag{24}$$

Hence,

$$\phi_1'(0)+\phi_2'(0)\approx\lambda_2(1+x_2)+\lambda_4\frac{(1-x_4)(1-x_2)}{1+x_4} \tag{25}$$

and

$$\int_0^l dx[\phi_1(x)+\phi_2(x)] \approx \frac{(1+x_2)\exp(\lambda_2 l)}{\lambda_2}+b_1\frac{(1+x_1)\exp(\lambda_1 l)}{\lambda_1} \approx \exp(\lambda_2 l)\,\frac{(1+x_1)(1+x_2)+(1-x_1)(1-x_2)}{\lambda_2(1+x_1)}. \tag{26}$$

This way we gain from Eq. (23)

$$k\approx\frac{\epsilon\lambda_2}{2}\exp(-\lambda_2 l)\times\frac{[\lambda_2(1+x_2)(1+x_4)+\lambda_4(1-x_2)(1-x_4)](1+x_1)}{(1+x_1x_2)(1+x_4)}. \tag{27}$$

For small γ (but still $\gamma\gg k_2$) we find

$$k\approx\frac{\epsilon\lambda_2}{2}\exp(-\lambda_2 l)\approx\frac{v_2}{2\epsilon}\exp\left(-\frac{v_2 l}{\epsilon}\right)=\frac{k_2}{2}, \tag{28}$$

the rate for resonant activation. For $\gamma\to\infty$ we find

$$k\approx\left[\frac{\epsilon\lambda_2}{2}\exp(-\lambda_2 l)\right]2\lambda_2\approx\frac{\overline{v}^2}{\epsilon}\exp\left(-\frac{\overline{v}l}{\epsilon}\right), \tag{29}$$

the rate in the average potential. The region of resonant activation where both expressions (22) and (27) match is very broad and extends from γ of order k_2 to γ of order v_2^2/ϵ.

To illustrate our results we show the relaxation rate as a function of the barrier fluctuation rate in Fig. 3. As parameters we chose $l=1$ and barrier heights $v_1/\epsilon=9$ and $v_2/\epsilon=6$ to test the small ϵ approximation even for realistic parameters. According to Eq. (22) the rate grows from $\gamma=0$ with increasing γ to reach the broad resonant activation regime, see Fig. 3(a). With further increasing fluctuation rate Eq. (27) gives an again decreasing relaxation rate to arrive finally at Eq. (29), see Fig. 3(b). To compare our approximations with exact results we calculated $\vec{\rho}_r$ along the lines described in Sec. III A exactly. The appropriate boundary conditions first provide the coefficients in the eigenvector expansion and then a nonlinear equation for the rate. As can be seen in Fig. 3 deviations mainly occur for moderate γ values where effects of $\exp(-\lambda_1 l)$ terms are still present. In particular, while the upper limit of Eq. (22) is $k=(k_1+k_2)/2$ the lower limit of Eq. (27) is $k=k_2/2$. Anyway, the combination of these two formulas gives an excellent approximation also for moderate barrier heights and the accuracy improves with decreasing ϵ and increasing V_1-V_2.

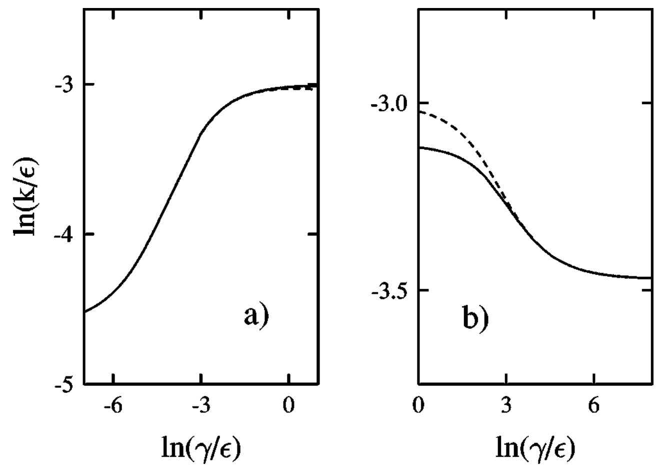

FIG. 3. Relaxation rate for the piecewise linear potential as a function of the barrier fluctuation rate. The solid line shows the approximate formulas (22) in (a) and (27) in (b). The dashed line is the exact result. Parameters are $l=1$, $v_1/\epsilon=9$, and $v_2/\epsilon=6$.

IV. SQUARE BARRIER POTENTIAL

The starting point for calculating eigenfunctions to the Smoluchowski operator $\hat{L}$ in the small ϵ limit is Eq. (8). As seen this equation describes relevant correlations between the stochastic processes of barrier crossings and barrier fluctuations. The general scheme illustrated for a simple model potential in the preceding section can now be applied to more realistic potentials. However, this eigenvector-eigenvalue equation becomes unusable for singular potentials. Hence, we derive here the exact solution for a piecewise constant potential in a somewhat different way. The symmetric bistable potentials with square barriers are given by (cf. Fig. 4)

$$V_i(x)=\begin{cases}0, & a\le x\le l\\ V_i, & -a\le x\le a\\ 0, & -l\le x\le -a\end{cases},\quad i=1,2. \tag{30}$$

A. Equilibrium eigenvector

For the solution of $\hat{L}\vec{\rho}_0=0$ with $\vec{\rho}_0(x)=\vec{\rho}_0(-x)$ we impose $\vec{\rho}_0'(0)=0$ and $\vec{\rho}_0'(\pm l)=0$. Furthermore, we are looking

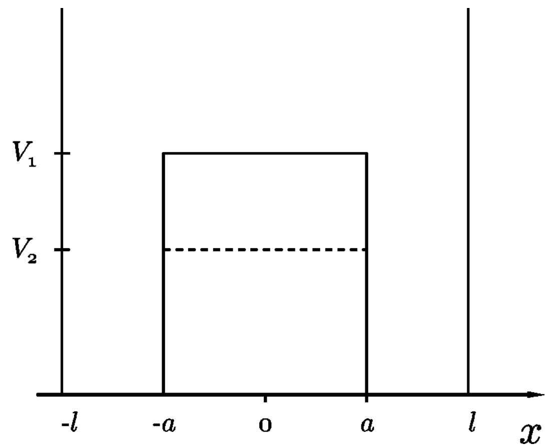

FIG. 4. Piecewise constant potentials.

for symmetric solutions with $\vec{\rho}_0'(a^+)=\vec{\rho}_0'(a^-)$ where a^+ denotes the upper and a^- the lower limit to a.

Due to symmetry we again need only to consider the range $0 \leqslant x \leqslant l$ which is separated in ranges I, $a < x \leqslant l$, and II, $0 \leqslant x < a$. The general solution in I is straightforward,

$$\vec{\rho}_0=(a_1 x+a_2)\begin{pmatrix}1\\1\end{pmatrix}+[a_3 \sinh(\xi x)+a_4 \cosh(\xi x)]\begin{pmatrix}1\\-1\end{pmatrix}, \tag{31}$$

with $\xi=\sqrt{2\gamma/\epsilon}$. In II the general solution looks like Eq. (31) with coefficients $b_j, j=1,\ldots,4$ where $\vec{\rho}_0'(0)=0$ requires $b_1=b_3=0$. We also set $a_2=1$ without loss of generality. Then we have *six* conditions—four at $x=a$, two at $x=l$—and *five* coefficients to satisfy them. Magically—the magic of the equilibrium solution, see after Eq. (4) where adjusting *one* parameter satisfies *two* conditions—it all works out. After tedious but simple algebra one obtains within $a < x \leqslant l$

$$\vec{\rho}_0(x)=\begin{pmatrix}1-f(\xi,x)\cosh(\xi x)/\cosh(\xi a)\\1+f(\xi,x)\cosh(\xi x)/\cosh(\xi a)\end{pmatrix}, \tag{32}$$

with the function

$$f(\xi,x)=\frac{[1-\tanh(\xi l)\tanh(\xi x)]\eta_-}{1-\tanh(\xi l)\coth(\xi a)-\eta_+[1-\tanh(\xi l)\tanh(\xi a)]} \tag{33}$$

and the abbreviation

$$\eta_\pm=\frac{1}{2}\left[\exp\left(-\frac{V_2}{\epsilon}\right)\pm\exp\left(-\frac{V_1}{\epsilon}\right)\right]. \tag{34}$$

For $0 \leqslant x < a$ follows

$$\vec{\rho}_0(x)=[1-f(\xi,a)]\exp\left(-\frac{V_1}{\epsilon}\right)\begin{pmatrix}g_+(\xi,x)\\g_-(\xi,x)\end{pmatrix}+[1+f(\xi,a)]\exp\left(-\frac{V_2}{\epsilon}\right)\begin{pmatrix}g_-(\xi,x)\\g_+(\xi,x)\end{pmatrix}, \tag{35}$$

with

$$g_\pm(\xi,x)=\frac{1}{2}\pm\frac{\cosh(\xi x)}{2\cosh(\xi a)}. \tag{36}$$

While the limit $\gamma=0$ leads to $\phi_i(x\in I)=\exp(V_i/\epsilon)\phi_i(x\in II)=\text{const}, i=1,2$ the case $\gamma\rightarrow\infty$ is more interesting. If $V_i/\epsilon \gg 1$ one has for $|x-a|\gg 1/\xi$ in range I simply $\vec{\rho}_0=(1,1)$ and in II $\vec{\rho}_0=\eta_+(1,1)$. Inside a region around $x=a$ with width of order $2/\xi$ the eigenfunction becomes nonconstant,

$$\vec{\rho}_0(x)=\begin{pmatrix}1+\eta_- \exp(-\delta\xi)\\1-\eta_- \exp(-\delta\xi)\end{pmatrix}, \tag{37}$$

in range I with $\delta=x-a$ and

$$\vec{\rho}_0(x)=\frac{1}{2}\exp\left(-\frac{V_1}{\epsilon}\right)\begin{pmatrix}1+\exp(\delta\xi)\\1-\exp(\delta\xi)\end{pmatrix}+\frac{1}{2}\exp\left(-\frac{V_2}{\epsilon}\right)\begin{pmatrix}1-\exp(\delta\xi)\\1+\exp(\delta\xi)\end{pmatrix} \tag{38}$$

in range II.

In contrast to the piecewise linear case, here the limit $\gamma\rightarrow\infty$ does not lead to the eigenfunction for the average potential but instead to the average of the eigenfunctions for the static potentials. This shows that there are no correlations between thermal diffusion over square barriers and barrier fluctuations.

B. Relaxation eigenvector

We have to look for an antisymmetric eigenfunction $\vec{\rho}_r(x)=-\vec{\rho}_r(-x)$, i.e., $\vec{\rho}_r(0)=0$. As a warmup let us briefly address a static barrier with height $V/\epsilon \gg 1$. For $a=l/2$ the expressions simplify considerably and one derives for the eigenfunction in I ($a < x \leqslant l$), $\rho_r=\cos[\kappa(l-x)]$; in II ($0 \leqslant x < a$), $\rho_r=\exp[-V/(2\epsilon)]\sin(\kappa x)$ with $\kappa^2=k/\epsilon$; the rate follows as

$$k=\frac{4\epsilon}{l^2}\arctan\left[\exp\left(-\frac{V}{2\epsilon}\right)\right]^2\approx\frac{4\epsilon}{l^2}\exp\left(-\frac{V}{\epsilon}\right). \tag{39}$$

For fluctuating barriers the general solution in I is obtained as

$$\vec{\rho}_r=[a_1 \sin(\kappa x)+a_2 \cos(\kappa x)]\begin{pmatrix}1\\1\end{pmatrix}+[a_3 \sin(\lambda x)+a_4 \cos(\lambda x)]\begin{pmatrix}1\\-1\end{pmatrix}, \tag{40}$$

with $\lambda^2=\kappa^2-2\gamma/\epsilon$. For $\lambda^2<0$ we use the analytic continuation of trigonometric to hyperbolic functions. Correspondingly, the solution in II has constants $b_j, j=1,\ldots,4$ where the node at $x=0$ requires $b_2=b_4=0$. The continuity conditions at $x=a$ and the reflecting boundary conditions at $x=l$ give rise to six homogeneous linear equations for the six remaining integration constants, with a nontrivial solution only if the determinant of the coefficients vanishes, thus fixing the eigenvalue k. One obtains the transcendent equation

$$\tan(\kappa a)\tan[\kappa(l-a)]\{\eta_1\eta_2-\eta_+ \cot(\lambda a)\cot[\lambda(l-a)]\}+\cot(\lambda a)\cot[\lambda(l-a)]-\eta_+=0, \tag{41}$$

with $\eta_i = \exp(-V_i/\epsilon), i=1,2$ and $\eta_+ = (\eta_1 + \eta_2)/2$. Again let us consider for simplicity the special case $a = l/2$. Then Eq. (41) may be written as

$$\tan(\kappa l/2)^2 \tan(\lambda l/2)^2 - \eta_+ \tan(\lambda l/2)^2 \times \left[1 + \frac{\sin(\kappa l/2)^2}{\sin(\lambda l/2)^2}\right] + \eta_1 \eta_2 = 0. \quad (42)$$

For $\gamma = 0$ Eq. (42) exhibits two solutions, namely, the rates k_1 and k_2 for the static barriers V_1 and V_2, Eq. (39), respectively. For $\gamma \ll 2\epsilon/l^2$ an expansion of the trigonometric functions applies leading us to Eq. (22). In the opposite limit $\gamma \gg 2\epsilon/l^2$ we have [since $\tanh(|\lambda| l/2) \approx 1$] the result

$$k = \frac{4\epsilon}{l^2} \arctan(\sqrt{\eta_+ + \eta_1 \eta_2})^2 \approx \frac{k_1 + k_2}{2}. \quad (43)$$

Hence for all $\gamma \gg k_2$ the resonant activation rate applies.

Finally, for completeness, the eigenvector: for $\gamma = 0$ we recover the eigenfunction for the static case in the potential V_1. In the opposite limit $\gamma \to \infty$ (and high barriers), outside the vicinity of $x = a$ (i.e., $|x - a| \gg 1/\xi$), one has $\vec{\rho}_r \approx (1,1)$ in I and $\vec{\rho}_r \approx (\eta_+ x/a)(1,1)$ in II; inside, for $|x - a| \lesssim 1/\xi$, we obtain ''connection formulas'' like those derived for the equilibrium in Eqs. (37) and (38) that are, however, lengthy and not very illuminating. More important is to notice that as for the equilibrium vector for $\gamma \to \infty$ the relaxation eigenvector does not tend to the eigenvector in the average potential but instead to the average of the eigenvectors in the static potentials. The boundary conditions are assured by slight deviations in the close vicinity around $x = a$.

For the same parameters as in the piecewise linear case, $l = 1$, $V_1/\epsilon = 9$, and $V_2/\epsilon = 6$, we calculated in Fig. 5 the relaxation rate from Eq. (42). For comparison also the approximate formula (22) is shown. Once the rate reaches the resonant activation regime it begins to saturate at Eq. (43). In contrast to the mean exit time which is nearly independent of γ for small and large γ [8], the rate becomes constant only in the latter range.

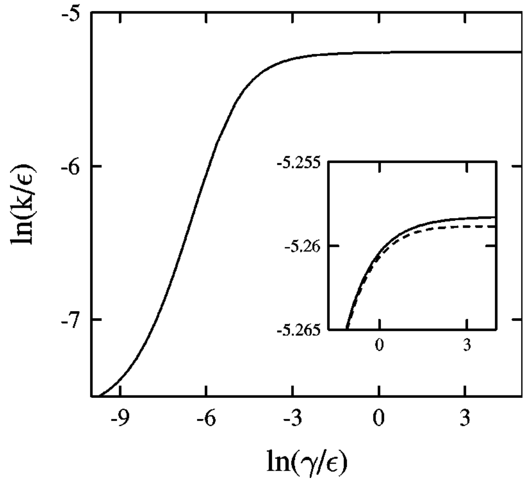

FIG. 5. Relaxation rate for the piecewise constant potential as a function of the barrier fluctuation rate. The solid line represents the exact result from Eq. (42) while the dashed line shows the approximate expression (22). Parameters are $l = 1$, $V_1/\epsilon = 9$, and $V_2/\epsilon = 6$.

V. SUMMARY

In this paper we studied the Fokker-Planck equation for two simple versions of the fluctuating barrier problem, namely, dichotomous barrier fluctuations for piecewise linear and piecewise constant potentials. Due to the properties of the corresponding Smoluchowski operator even the mathematical existence of equilibrium and relaxation eigenvectors is not obvious. For the piecewise linear case we applied an approximate method for solving the eigenvector-eigenvalue problem which becomes exact in the limit of vanishing thermal noise. The idea is to determine eigenvalues and eigenvectors of the ''potential matrix'' and to use this basis set for expanding the desired eigenfunction. The coefficients in this expansion are then fixed by the appropriate boundary conditions. This way we combined general results from previous work [10,11]. The procedure not only gives a nice mathematical picture of the underlying physics but also shows that for sufficiently large barrier fluctuation rates both potential surfaces get strongly entangled to build up an effective potential for thermal barrier crossing. It turned out that even for moderate barrier heights the least negative eigenvalue, the relaxation rate, is obtained with sufficient accuracy for the method to be applicable in more realistic systems. For the piecewise constant potential the potential matrix becomes singular so that eigenvectors and eigenvalues were calculated exactly. In contrast to the previous case there are no correlations between stochastic barrier crossings and stochastic barrier fluctuations; as a consequence, an effective potential does not exist and the relaxation rate saturates in the region of resonant activation.

So far investigations for fluctuating barrier systems have been focused on the Smoluchowski limit. The simple models analyzed here, however, can be used to elucidate also ''kinetic'' effects of finite damping.

ACKNOWLEDGMENTS

Part of this work was done during an extended visit of J.A. at Columbia University. Financial support was provided by the Alexander von Humboldt Foundation and the National Science Foundation (Grant No. CHE-9633796).

[1] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[2] H. Risken, *The Fokker-Planck Equation* (Springer, Berlin, 1989).
[3] J. Maddox, Nature (London) **359**, 771 (1992).
[4] For a review see, e.g., R. Zwanzig, Acc. Chem. Res. **23**, 148 (1990); P. Reimann and P. Hänggi, in *Stochastic Dynamics*, edited by L. Schimansky-Geier and T. Pöschel, Lecture Notes

in Physics Vol. 484 (Springer, Berlin, 1997), p. 127.
[5] C. R. Doering and J. C. Gadoua, Phys. Rev. Lett. **69**, 2318 (1992).
[6] N. Agmon and J. J. Hopfield, J. Chem. Phys. **78**, 6947 (1983); A. Szabo, D. Shoup, S. H. Northrup, and J. A. McCammon, *ibid.* **77**, 4484 (1982).
[7] M. Bier and R. D. Astumian, Phys. Rev. Lett. **71**, 1649 (1993).
[8] U. Zürcher and C. R. Doering, Phys. Rev. E **47**, 3862 (1993).
[9] P. Pechukas and P. Hänggi, Phys. Rev. Lett. **73**, 2772 (1994).
[10] P. Pechukas and J. Ankerhold, Chem. Phys. **235**, 5 (1998).
[11] J. Ankerhold and P. Pechukas, Physica A (to be published).