Journal of Statistical Physics, Vol. 41, Nos. 5/6, 1985

Eigenvalues and Eigenfunctions of the Fokker–Planck Equation for the Extremely Underdamped Brownian Motion in a Double-Well Potential

H. Risken[1] **and K. Voigtlaender**[1]

Received April 30, 1985; final July 23, 1985

The eigenvalues and eigenfunctions of the Fokker–Planck equation describing the extremely underdamped Brownian motion in a symmetric double-well potential are investigated. By transforming the Fokker–Planck equation to energy and position coordinates and by performing a suitable averaging over the position coordinate, a differential equation depending only on energy is derived. For finite temperatures this equation is solved by numerical integration, whereas in the weak-noise limit an analytic result for the lowest nonzero eigenvalue is obtained. Furthermore, by using a boundary-layer theory near the critical trajectory, the correction term to the zero-friction-limit result is found.

KEY WORDS: Fokker–Planck equation; double-well potential; eigenvalues; eigenfunctions; low-friction limit; weak-noise limit; boundary-layer theory.

1. INTRODUCTION

As explained in our recent paper,[1] the Brownian motion of particles in a double-well potential has applications in many different fields. In Ref. 1, the corresponding Fokker–Planck equation was solved by the matrix-continued-fraction method. In particular it was shown that the Laplace transform of the time-dependent distribution function (leading to susceptibilities) as well as eigenvalues and eigenfunctions could be obtained by calculating appropriate matrix continued-fractions. This continued-fraction method, however, does not work for very small friction constants. It is the

[1] Abteilung für Theoretische Physik der Universität Ulm, D-7900 Ulm, Federal Republic of Germany.

0022-4715/85/1200-0825$04.50/0

purpose of the present paper to determine the eigenvalues and eigenfunctions in the low-friction limit. For the extremely underdamped case the energy will become nearly a constant of motion, i.e., it will become a slow (relevant) variable, whereas the position or velocity will become a fast (irrelevant) variable (see, for instance, Ref. 2 for a discussion of fast or slow variables). Therefore one should use the energy or a function of the energy like the action integral as the relevant variable in the low-friction limit, as done in Refs. 3–9, leading to eigenvalues of the Fokker–Planck operator, which are in lowest order proportional to the friction constant, i.e.,

$$\lambda = \bar{A}\gamma \tag{1.1}$$

The lowest nonzero eigenvalue λ_1 if well separated from the higher ones determines the exchange rate between the left and the right well. This rate was obtained in the weak-noise limit, i.e., for $\Delta E/(kT) \gg 1$ in Refs. 3–8. (Here ΔE is the energy difference between the minima of the double-well potential and the hump between the wells.) In the present paper the following extensions are made. First we include a boundary-layer theory near the critical trajectory (Section 3). The critical trajectory is the line $E = E_0 = \text{const}$ in phase space, which starts at the maximum of the potential in the middle (see Fig. 1). As it is further shown the distribution function becomes x dependent near the critical trajectory. Next we derive an eigenvalue equation for the energy-dependent eigenfunctions (Section 4). For finite temperatures this eigenvalue equation is solved for the double-well potential (mass $m = 1$)

$$f(x) = d_2 x^2/2 + d_4 x^4/4, \qquad d_2 < 0,\ d_4 > 0 \tag{1.2}$$

by numerical integration. Whereas eigenvalues corresponding to even eigenfunctions are proportional to $\gamma + O(\gamma^2)$, eigenvalues corresponding to odd eigenfunctions are given by $\bar{A}\gamma + \bar{B}\gamma^{3/2} + O(\gamma^2)$. The term proportional to $\gamma^{3/2}$ stems from the boundary condition for the boundary-layer theory. In Section 5 we transform the eigenvalue equation to an integral equation. In the weak-noise limit this integral equation can be solved analytically, leading, besides to the Kramers result, to corrections for somewhat higher damping constants and temperatures. The correction terms to the transition rates proportional to $\gamma^{3/2}$ are explicitly given. A term of this type was also found by Büttiker *et al.*[7] and Büttiker and Landauer,[8a] the proportionality factor was, however, not derived in these references. In Ref. 6a an analytical expression for the escape rate out of a single well was derived; their result, however, does not show a term $\sim \gamma^{3/2}$.

2. BASIC EQUATIONS

The basic equation for the Brownian motion of particles in the potential $f(x)$ is given by the following Fokker–Planck equation in velocity-position space (also called the Kramers equation) for the distribution function $W = W(x, v, t)$

$$\frac{\partial W}{\partial t} = \left\{ -\frac{\partial}{\partial x} v + \frac{\partial}{\partial v} [\gamma v + f'(x)] + \gamma \Theta \frac{\partial^2}{\partial v^2} \right\} W \tag{2.1}$$

In (2.1) we have denoted the friction constant by γ. The noise strength Θ is proportional to the temperature T, i.e., $\Theta = kT$. For small γ the energy

$$E = v^2/2 + f(x) \tag{2.2}$$

becomes a slow variable. One should therefore use E or a function of E like the action integral as one variable.[4] As the other variable we keep the space coordinate x. To retain the full information of the distribution function in position and energy two separate energy-distribution functions, one for each sign of the velocity, have to be taken into account:

$$W_+(x, E, t) = W(x, v(x, E), t)$$
$$W_-(x, E, t) = W(x, -v(x, E), t) \tag{2.3}$$
$$v(x, E) = +2[E - f(x)]^{1/2} \tag{2.4}$$

It should be emphasized that $W_\pm$ are the distribution functions in (x, v) space expressed by x and E coordinates. The distribution functions $\hat{W}_\pm$ in (x, E) space are obtained by dividing $W_\pm$ by the Jacobian

$$\frac{\partial(x, E)}{\partial(x, v)} = \frac{\partial E}{\partial v} = v(x, E) = 2[E - f(x)]^{1/2} \tag{2.5}$$

i.e.,

$$\hat{W}_\pm(x, E, t) = W_\pm(x, E, t)/v(x, E) \tag{2.6}$$

The distribution functions $\hat{W}_\pm$ are not used because the equations for $W_\pm$ have a simpler form.

For further calculations the sum S and the difference D of W_+ and W_- are sometimes more suitable:

$$W_{S,D}(x, E, t) = W_+(x, E, t) \pm W_-(x, E, t) \tag{2.7}$$

For the new variables x, E the Fokker–Planck equation (2.1) for $W_{\pm}$ and for $W_{S,D}$ takes the form

$$\frac{\partial}{\partial t} W_{\pm} = \mp v(x, E) \frac{\partial}{\partial x} W_{\pm} + \gamma v(x, E) \frac{\partial}{\partial E} \left[v(x, E) \left(1 + \Theta \frac{\partial}{\partial E} \right) W_{\pm} \right] \tag{2.8a}$$

$$\frac{\partial}{\partial t} W_{S,D} = -v(x, E) \frac{\partial}{\partial x} W_{D,S} + \gamma v(x, E) \frac{\partial}{\partial E} \left[v(x, E) \left(1 + \Theta \frac{\partial}{\partial E} \right) W_{S,D} \right] \tag{2.8b}$$

At the turning points of the motion without friction, i.e., at x^r, x^l for $E > E_0$ and at $x^r_{1,2}$, $x^l_{1,2}$ for $E < E_0$ (see Fig. 1), both distribution functions W_+ and W_- must agree, i.e.,

$E > E_0$

$$W_+(x^{r,l}, E, t) = W_-(x^{r,l}, E, t) \tag{2.9a}$$

$$W_D(x^{r,l}, E, t) = 0 \tag{2.9b}$$

$E < E_0$

$$W_+(x^{r,l}_{1,2}, E, t) = W_-(x^{r,l}_{1,2}, E, t) \tag{2.10a}$$

$$W_D(x^{r,l}_{1,2}, E, t) = 0 \tag{2.10b}$$

2.1. Ansatz for the Distribution Function

For a physical interpretation of the distribution function we think of an ensemble of noninteracting particles. For a zero damping constant the particles move along the trajectories $E = \text{const}$ (see Fig. 1). For small damping one gets a slow diffusion of the particles perpendicular to their initial trajectories. Because of the motion along the trajectories, the distribution for W becomes independent of the position [the distribution $\hat{W}$ in x–E space is then proportional to the inverse of the velocity see Eq. (2.6)]. Near the critical trajectory, however, this in general is no longer the case as seen as follows. The particles of the ensemble for $E < E_0$ move either in the left or in the right well, whereas for $E > E_0$ they move from the left side to the right side and vice versa. How may particles move from the left well to the right well? First the particles in the left well may be pushed up by the Langevin forces across the critical trajectory $E = E_0$. They then move near

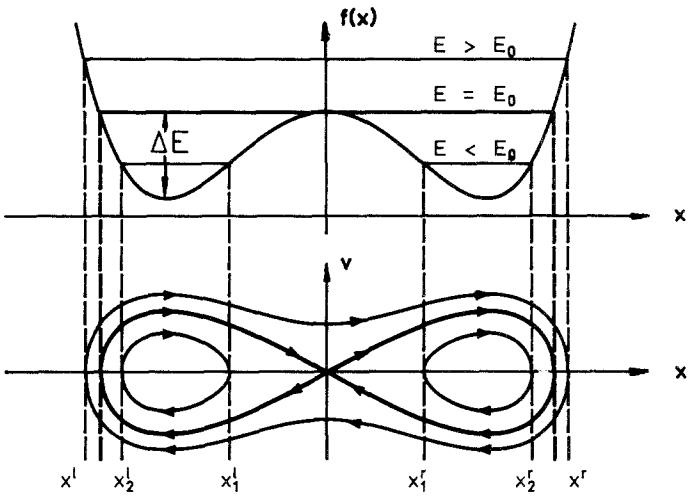


Fig. 1. A typical symmetric double-well potential and its turning points $x_{1,2}^{l,r}$, $x^{l,r}$ (upper part) and three typical trajectories in phase space (lower part).

this trajectory to the right side. Here they may again be pushed by the Langevin forces across the critical trajectory and thus reach the right well with $E<E_0$. For small damping forces this whole process takes place in a small region (boundary layer) near the critical trajectory. As it will turn out later on the thickness of the boundary layer is of the order $\sqrt{\gamma}$. If the distribution functions in the two wells are different (which is always the case if the transition from the left to the right well is considered) one expects a strong diffusion perpendicular to the critical trajectory because of the large gradient of W with respect to E. Furthermore, because of the motion of the particles along the trajectories, we will have an x dependence in this boundary-layer region. We therefore make the following ansatz for the distribution functions $W_{S,D}$:

$$W_S(x, E, t) = \tilde{W}(E, t) + w_S(x, E, t) \qquad \text{for} \quad E > E_0 \qquad (2.11a)$$
$$W_D(x, E, t) = w_D(x, E, t)$$
$$W_S(x, E, t) = \tilde{W}_{l,r}(E, t) + w_S(x, E, t) \qquad \text{for} \quad E < E_0 \qquad (2.11b)$$
$$W_D(x, E, t) = w_D(x, E, t)$$

Here $\tilde{W}(E, t)$ and $\tilde{W}_{l,r}(E, t)$ are functions slowly varying in E depending only on time t and energy E, whereas $w_{S,D}(x, E, t)$ additionally depending on position x, are rapidly varying in E. As it turns out later on $\partial\tilde{W}/\partial E$ and $\partial\tilde{W}_{l,r}/\partial E$ are of the order γ^0, whereas $\partial w_{S,D}/\partial E$ are of the order $\gamma^{-1/2}$. Because of the continuity condition (2.9b), (2.10b), $\tilde{W}_D(E, t)$ must always

be zero. Below the critical energy $E = E_0$ we have two wells. We therefore must distinguish for the E-dependent functions whether we are in the left well (index l, $x < 0$) or in the right well (index r, $x > 0$). The functions $w_{S,D}$ are only different from zero in a boundary-layer region (skin) around the critical trajectory. Thus the functions $w_{S,D}(x, E, t)$ depend very strongly on E. As already mentioned, the thickness of this boundary layer will turn out to be proportional to $\sqrt{\gamma}$.

2.2. Equation of Motion for $\tilde{W}$ and $\tilde{W}_{l,r}$

Outside the boundary layer the distribution function does not depend on x. We first insert (2.11) with $w = 0$ into the Fokker–Planck equation and average over the time T along a trajectory $E = \text{const}$. The time T should be small compared to the time $1/\gamma$ in which $W(E, t)$ changes its value appreciably. Because of

$$\int \cdots dt = \int \cdots \frac{dx}{v(x, E)} \tag{2.12}$$

we may as well divide (2.8b) [or (2.8a)] by $v(x, E)$ and take an x average. The term containing $(\partial/\partial x)$ then drops out and we finally arrive at

$$E > E_0 \colon T(E) \frac{\partial}{\partial t} \tilde{W} = \gamma \frac{\partial}{\partial E} I(E) \left(1 + \Theta \frac{\partial}{\partial E}\right) \tilde{W} \tag{2.13}$$

$$E < E_0 \colon T_{r,l}(E) \frac{\partial}{\partial t} \tilde{W}_{r,l} = \gamma \frac{\partial}{\partial E} I_{r,l}(E) \left(1 + \Theta \frac{\partial}{\partial E}\right) \tilde{W}_{r,l} \tag{2.14}$$

Here $I(E)$, $T(E)$ are defined by $(E > E_0)$

$$\begin{aligned} I(E) &= 2 \int_{x^l(E)}^{x^r(E)} v(x, E)\, dx \\ T(E) &= I'(E) = 2 \int_{x^l(E)}^{x^r(E)} dx/v(x, E) \end{aligned} \tag{2.15}$$

and $I_{r,l}(E)$, $T_{r,l}(E)$ by $(E < E_0)$

$$\begin{aligned} I_r(E) &= 2 \int_{x_1^r(E)}^{x_2^r(E)} v(x, E)\, dx, \qquad I_l(E) = 2 \int_{x_2^l(E)}^{x_1^l(E)} v(x, E)\, dx \\ T_r(E) &= I_r'(E) = 2 \int_{x_1^r(E)}^{x_2^r(E)} dx/v(x, E) \\ T_l(E) &= I_l'(E) = 2 \int_{x_2^l(E)}^{x_1^l(E)} dx/v(x, E) \end{aligned} \tag{2.16}$$

The second expression in (2.15) is twice the time a particle needs to travel from x^l to x^r, i.e., it is the round-trip time for particles with energy $E > E_0$, whereas $T_r(E)$ in (2.16) is twice the time a particle needs to travel from x_1^r to x_2^r, i.e., it is the round-trip time for particles with energy $E < E_0$ in the right well. Correspondingly $T_l(E)$ is the round-trip time in the left well. The expression $I(E)$ and $I_{r,l}(E)$ are the action integrals for energies $E > E_0$ and $E < E_0$, respectively. In the last case l and r refer to left and right well. At the critical energy E_0 we obviously have

$$I(E_0 + 0) = I_l(E_0 - 0) + I_r(E_0 - 0) \tag{2.17}$$

2.3. Symmetric Potential

Further on we shall restrict ourselves to a symmetric double-well potential

$$f(x) = f(-x), \qquad x^r = -x^l, \qquad x_1^r = -x_1^l, \qquad x_2^r = -x_2^l \tag{2.18}$$

We then define $I(E)$ and $T(E)$ for $E < E_0$ by

$$\begin{aligned} I_l(E) &= I_r(E) = I(E)/2 \\ T_l(E) &= T_r(E) = T(E)/2 \end{aligned} \tag{2.19}$$

and (2.17) simplifies to

$$I(E_0 + 0) = I(E_0 - 0) \equiv I(E_0)$$

Notice that $I(E)$ for $E < E_0$ is now twice the action integral in one well and that $T(E)$ for $E < E_0$ is twice the round-trip time in one well. We introduced a factor 2 in the definition of $T(E)$ and $I(E)$ for $E < E_0$, because then the action integral is continuous at $E = E_0$ [see (2.17)].

2.4. Explicit Expressions for the Potential (1.2)

For the potential (1.2) the turning points as well as the action variable $I(E)$ and its derivative can be given analytically. Obviously for the critical energy E_0 we have $E_0 = 0$.
We now introduce the abbreviations

$$a = (|d_2|/d_4)^{1/2}[1 + (1 + 4d_4E/d_2^2)^{1/2}]^{1/2} \tag{2.20a}$$

$$b = (|d_2|/d_4)^{1/2}[-1 + (1 + 4d_4E/d_2^2)^{1/2}]^{1/2} \tag{2.20b}$$

$$c = (|d_2|/d_4)^{1/2}[1 - (1 + 4d_4E/d_2^2)^{1/2}]^{1/2} \tag{2.20c}$$

$$\bar{\alpha} = [1 + (1 + 4d_4E/d_2^2)^{1/2}]/[2(1 + 4d_4E/d_2^2)^{1/2}] \tag{2.20d}$$

It should be noted that a and $\bar{\alpha}$ are valid for $E \geqslant -d_2^2/(4d_4)$, whereas b is only valid for $E \geqslant 0$ and c for $-d_2^2/(4d_4) \leqslant E \leqslant 0$. The turning points for the bistable potential (1.2) are given by

$$x^r = -x^l = a \qquad \text{for} \quad E \geqslant 0$$

$$x_2^r = -x_2^l = a \qquad \text{for} \quad -d_2^2/(4d_4) \leqslant E \leqslant 0$$

$$x_1^r = -x_1^l = c \qquad \text{for} \quad -d_2^2/(4d_4) \leqslant E \leqslant 0$$

$I(E)$ and $T(E)$ can be expressed by the complete elliptic integrals of the first and second kind, $\mathbf{K}$ and $\mathbf{E}$,[16] i.e.,

(i) $E > 0$:

$$I(E) = (2/3)(2d_4)^{1/2}(a^2+b^2)^{1/2} \times [b^2\mathbf{K}(\bar{\alpha}) - 2(|d_2|/d_4)\,\mathbf{E}(\bar{\alpha})] \tag{2.21a}$$

$$T(E) = 4(2/d_4)^{1/2}(a^2+b^2)^{-1/2}\,\mathbf{K}(\bar{\alpha}) \tag{2.22a}$$

(ii) $-d_2^2/(4d_4) \leqslant E < 0$:

$$I(E) = (4a/3)(2d_4)^{1/2}[|d_2|/d_4\,\mathbf{E}(1/\bar{\alpha}) - c^2\mathbf{K}(1/\bar{\alpha})] \tag{2.21b}$$

$$T(E) = 4(2/d_4)^{1/2}\,a^{-1}\mathbf{K}(1/\bar{\alpha}) \tag{2.22b}$$

They are plotted in Fig. 2. By expanding the elliptic integrals, we can derive the following asymptotic expressions:

(i) for $E \gtrapprox -d_2^2/(4d_4) = E_{\min}$,

$$I(E) = \pi\,|d_2|^{3/2}/(\sqrt{2}\,d_4)[(1+4d_4E/d_2^2) + (3/32)(1+4d_4E/d_2^2)^2] \tag{2.21b'}$$

$$T(E) = 2\pi\sqrt{2}\,|d_2|^{-1/2}[1+(3/16)(1+4d_4E/d_2^2)] \tag{2.22b'}$$

(ii) for $E \lessapprox E_0 = 0$,

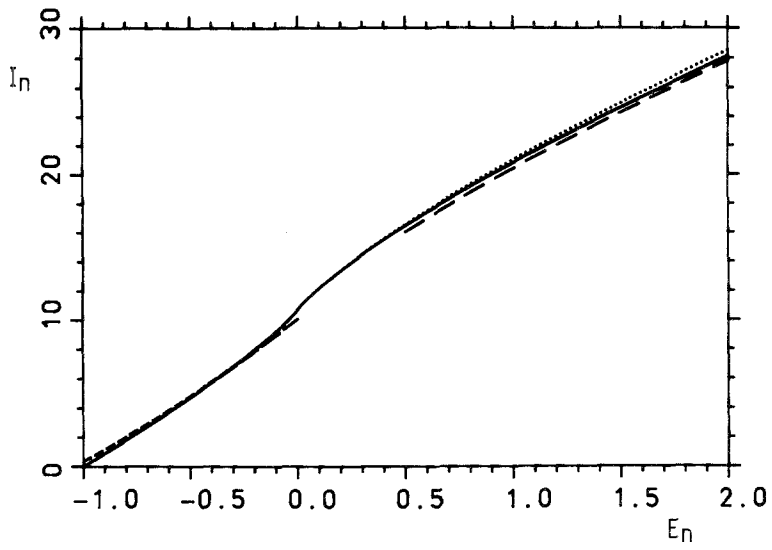
$$I(E) = (8\,|d_2|^{3/2}/3d_4)\{1-3(d_4\,|E|/d_2^2) \times [1+\ln 16d_2^2/(d_4\,|E|)]\} \tag{2.21b''}$$

$$T(E) = |d_2|^{-1/2}\{2\ln 16d_2^2/(d_4\,|E|) + (d_4\,|E|/d_2^2)[(3/2)\ln 16d_2^2/(d_4\,|E|) - 1]\} \tag{2.22b''}$$

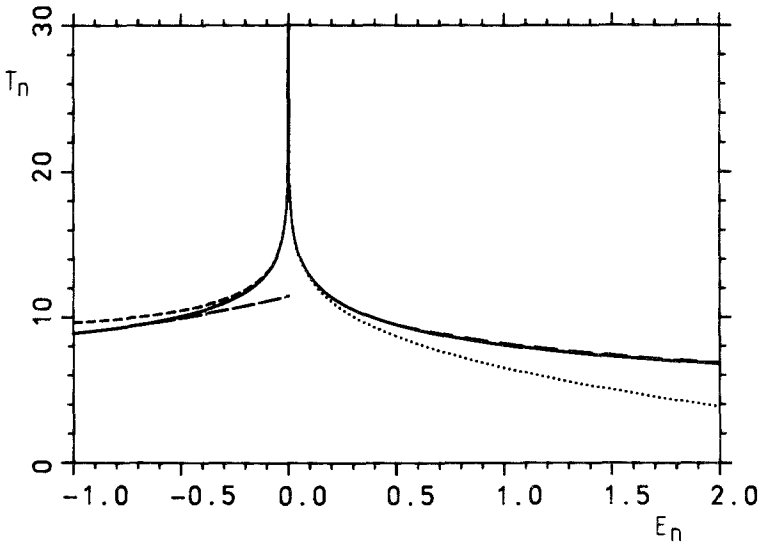
(iii) for $E \gtrapprox E_0 = 0$,

$$I(E) = (8\,|d_2|^{3/2}/3d_4)\{1+3(d_4E/d_2^2) \times [1+\ln 16d_2^2/(d_4E)]\} \tag{2.21a''}$$

$$T(E) = |d_2|^{-1/2}\{2\ln 16d_2^2/(d_4E) - (d_4E/d_2^2)[(3/2)\ln 16d_2^2/(d_4E)+1]\} \tag{2.22a''}$$



(a)



(b)

Fig. 2. The action integrals (2.21) and the periods (2.22) (solid lines) as well as the asymptotic expressions (2.21′), (2.21″), (2.22′), (2.22″) as a function of the energy for the double-well potential (1.2). Here we used the normalized variables $E_n = 4d_4 E d_2^{-2}$, $T_n = T\,|d_2|^{1/2}$ and $I_n = 4d_4 I\,|d_2|^{-3/2}$.

(iv) for $E \gg d_2^2/4d_4$,

$$I(E) = (4\,|d_2|^{3/2}/3d_4)(4d_4E/d_2^2)^{3/4} \times \{\mathbf{K}(1/2) + (3/2)(4d_4E/d_2^2)^{-1/2} \times [2\mathbf{E}(1/2) - \mathbf{K}(1/2)] + [3d_2^2/(32d_4E)]\,\mathbf{K}(1/2)\} \quad (2.21a')$$

$$T(E) = 4\,|d_2|^{-1/2}(4d_4E/d_2^2)^{-1/4} \times \{\mathbf{K}(1/2) + (1/2)(4d_4E/d_2^2)^{-1/2} \times [2\mathbf{E}(1/2) - \mathbf{K}(1/2)] - (d_2^2/32d_4E)\,\mathbf{K}(1/2)\} \quad (2.22a')$$

In (2.21a'), (2.22a') we expanded the elliptic integrals at $\alpha = 1/2$ in Taylor series. Onodera[17] has also given these expansions, but without the correction terms proportional to $E^{-1/2}$ and E^{-1}.

The asymptotic expansions (2.21'), (2.21''), (2.22'), (2.22'') are also shown in Fig. 2. As seen, they approximate the corresponding expressions in the appropriate regions very well. The weak logarithmic singularity of $T(E)$ at $E = E_0$ does not lead to serious difficulties in solving the differential equations (2.13), (2.14).

3. BOUNDARY-LAYER THEORY

As already explained in Section 2 the x-independent functions $\tilde{W}(E, t)$, $\tilde{W}_{l,r}(E, t)$ alone cannot always describe the process in the entire region. Here the x-dependent functions w_S and w_D must also be taken into account in the boundary-layer region around the critical trajectory $E = E_0$. Because the functions w_S and w_D are rapidly varying in E we may neglect the first derivative with respect to E in (2.8) compared to the second one and replace $v(x, E)$ in (2.8) by

$$v(x, E) \to v(x, E_0) \quad (3.1)$$

It follows from (3.4), (3.5) that the thickness of the boundary layer, i.e., the region in which w_S and w_D give an essential contribution to the distribution function, is of the order $\sqrt{\gamma}$.

If we consider a time scale of the distribution functions of the order $1/\gamma$ the time derivative of w_S and w_D need not be taken into account in (2.8b), because in the boundary layer of thickness $\sqrt{\gamma}$ a quasistationary distribution is established in a time scale of the order γ^0.

Therefore the equations (2.8b) for the x-dependent functions reduce to

$$\partial w_{S,D}/\partial x = \gamma\Theta v(x, E_0)\,\partial^2 w_{D,S}/\partial E^2 \quad (3.2)$$

If we introduce the variable u defined by

$$u(x) = \pi \int_0^x v(\xi, E_0)\, d\xi \Big/ \int_0^{x^r(E_0)} v(\xi, E_0)\, d\xi \tag{3.3}$$

i.e., $u > 0$ for $x > 0$ and $u < 0$ for $x < 0$, (3.2) may be written

$$\partial w_{S,D}/\partial u = [\Theta^2/(2\alpha^2)]\, \partial^2 w_{D,S}/\partial E^2 \tag{3.4}$$

where α is given by

$$\alpha = [2\pi\Theta/\gamma I(E_0)]^{1/2} \tag{3.5}$$

In deriving (3.4) we have used $x_1^r(E_0) = 0$, $x_2^r(E_0) = x^r(E_0)$, (2.16), (2.19) and

$$du/dx = 4\pi v(x, E_0)/I(E_0) \tag{3.6}$$

For the double-well potential (1.2) $u(x)$ specializes to

$$u(x) = \pi \frac{x}{|x|}\left[1 - \left(1 - \frac{d_4}{2\,|d_2|}\, x^2\right)^{3/2}\right] \tag{3.3a}$$

3.1. Continuity Conditions at $E = E_0$

We now have to match the distribution functions (2.11a, b) and their derivatives at $E = E_0$, i.e.,

$$\begin{aligned}
\tilde{W}(E_0 + 0, t) + w_S(x, E_0 + 0, t) &= \tilde{W}_{l,r}(E_0 - 0, t) + w_S(x, E_0 - 0, t) \\
\partial(\tilde{W} + w_S)/\partial E|_{E = E_0 + 0} &= \partial(\tilde{W}_{l,r} + w_S)/\partial E|_{E = E_0 - 0} \\
w_D(x, E_0 + 0, t) &= w_D(x, E_0 - 0, t) \\
\partial w_D/\partial E|_{E = E_0 + 0} &= \partial w_D/\partial E|_{E = E_0 - 0}
\end{aligned} \tag{3.7}$$

In the first two equations the index l is valid for $x < 0$ and the index r for $x > 0$. In order to proceed further we assume that initially the distribution function depends outside the boundary-layer region $E \approx E_0$ only on the slow variable E. Furthermore we split the distribution function into two parts. In the first part the distribution functions are equally distributed inside the wells ($E < E_0$) and arbitrary outside the wells ($E > E_0$). In the second part the distribution is opposite in the wells ($E < E_0$) and zero outside the wells ($E > E_0$). Because of the linearity of the Fokker–Planck equation we can treat both cases separately.

3.2. Equal Probabilities in the Wells

If the initial conditions are such that $W_S(x, E, 0) = \tilde{W}_l(E, 0) = \tilde{W}_r(E, 0)$ for $E < E_0$ and $W_S(x, E, 0) = W(E, 0)$ for $E > E_0$ we will have

$$\tilde{W}_l(E, t) = \tilde{W}_r(E, t) = \tilde{W}(E, t) \tag{3.8}$$

In this case the additional x-dependent functions w_S and w_D need not be taken into account and both boundary conditions (3.7) read

$$\begin{aligned} &\tilde{W}(E_0 + 0, t) = \tilde{W}(E_0 - 0, t) \\ &\left.\frac{\partial \tilde{W}(E, t)}{\partial E}\right|_{E = E_0 + 0} = \left.\frac{\partial \tilde{W}(E, t)}{\partial E}\right|_{E = E_0 - 0} \end{aligned} \tag{3.9}$$

3.3. Opposite Probabilities in the Wells

If the initial conditions are such that $W_S(|x|, E, 0) = \tilde{W}_r(E, 0) = -\tilde{W}_l(E, 0) = -W_S(-|x|, E, 0)$ for $E < E_0 - \Delta E$ and $W_S(x, E, 0) = 0$ for $E > E_0 + \Delta E$ (ΔE is the thickness of the boundary region $\sim\sqrt{\gamma}$) then we have outside the boundary layer

$$\begin{aligned} &\tilde{W}_r(E, t) = -\tilde{W}_l(E, t) \qquad \text{for} \quad E < E_0 - \Delta E \\ &\tilde{W}(E, t) = 0 \qquad\qquad\quad \text{for} \quad E > E_0 + \Delta E \end{aligned} \tag{3.10}$$

In this case the x-dependent functions w_S and w_D must be taken into account, because otherwise the boundary conditions (3.7) cannot be fulfilled. For opposite probabilities in the wells, $w_S(x, E, t)$ is antisymmetric in x and therefore, from (3.2), $w_D(x, E, t)$ is symmetric in x, i.e.,

$$\begin{aligned} w_S(|x|, E, t) &= -w_S(-|x|, E, t) \\ w_D(|x|, E, t) &= w_D(-|x|, E, t) \end{aligned} \tag{3.11}$$

It then follows from (3.7) that we have to consider now the boundary conditions

$$\begin{aligned} &w_S(|x|, E_0 + 0, t) = \tilde{W}_r(E_0 - 0, t) + w_S(|x|, E_0 - 0, t) \\ &\left.\frac{\partial w_S(|x|, E, t)}{\partial E}\right|_{E = E_0 + 0} = \left.\frac{\partial \tilde{W}_r(E, t)}{\partial E}\right|_{E = E_0 - 0} \\ &\qquad\qquad + \left.\frac{\partial w_S(|x|, E, t)}{\partial E}\right|_{E = E_0 - 0} \\ &w_D(|x|, E_0 + 0, t) = w_D(|x|, E_0 - 0, t) \\ &\left.\frac{\partial w_D(|x|, E, t)}{\partial E}\right|_{E = E_0 + 0} = \left.\frac{\partial w_D(|x|, E, t)}{\partial E}\right|_{E = E_0 - 0} \end{aligned} \tag{3.12}$$

By these relations $\partial \tilde{W}_r(E, t)/\partial E$ at $E = E_0 - 0$ and $\tilde{W}_r(E_0 - 0, t)$ are linearly coupled. This coupling may be written in the form

$$\tilde{W}_{r,l}(E_0 - 0, t) + \kappa(\Theta/\alpha)\, \partial \tilde{W}_{r,l}(E, t)/\partial E \,|_{E = E_0 - 0} = 0 \tag{3.13}$$

The additional factor Θ/α with α given by (3.5) is introduced because we then get a relation for κ without any dependence on γ and Θ. Mixed boundary conditions of the type (3.13) are often encountered in heat-conduction problems.[11] A similar relation [(11.122) of Ref. 9] was used for the Brownian motion in an inclined cosine potential.

3.4. Determination of κ and of the *x*-Dependent Functions

Solutions of (3.2) with the symmetry property (3.11), fulfilling (2.9b) and (2.10b) and decreasing for energies outside the boundary region are given by [the variable u is defined in (3.3)]

(i) $E > E_0$:

$$\begin{aligned} w_D(u, E) &= w_0 \sum_{n=0}^{\infty} \mathrm{Im}\{a_n \exp[-\alpha(n+1/2)^{1/2}(1+i)(E-E_0)/\Theta]\} \\ &\quad \times \cos(n+1/2)u \\ w_S(u, E) &= w_0 \sum_{n=0}^{\infty} \mathrm{Re}\{a_n \exp[-\alpha(n+1/2)^{1/2}(1+i)(E-E_0)/\Theta]\} \\ &\quad \times \sin(n+1/2)u \end{aligned} \tag{3.14}$$

(ii) $E < E_0$:

$$\begin{aligned} w_D(u, E) &= -w_0 \sum_{n=1}^{\infty} \mathrm{Im}\{b_n \exp[\alpha\sqrt{n}\,(1+i)(E-E_0)/\Theta]\} \\ &\quad \times \sin n|u| \\ w_S(u, E) &= w_0 \sum_{n=1}^{\infty} \mathrm{Re}\{b_n \exp[\alpha\sqrt{n}\,(1+i)(E-E_0)/\Theta]\} \\ &\quad \times (u/|u|) \cos nu \end{aligned} \tag{3.15}$$

Here the real and imaginary parts are denoted by Re and Im. The index $n = 0$ must be excluded in (3.15) because w_S would otherwise contain an x-independent function. For further consideration it is convenient to choose the common factor w_0 according to

$$w_0 = \mp(\Theta/\alpha)\, \partial \tilde{W}_{r,l}(E, t)/\partial E \,|_{E = E_0 - 0} \tag{3.16}$$

Inserting (3.14), (3.15) into the boundary condition (3.12), using (3.13), (3.16), and dividing by w_0 we arrive at

$$\begin{aligned}
&\sum_{n=0}^{\infty} a_n^{(r)} \sin(n+1/2)|u| = \kappa + \sum_{n=1}^{\infty} b_n^{(r)} \cos nu \\
&\sum_{n=0}^{\infty} (-a_n^{(r)} + a_n^{(i)})(n+1/2)^{1/2} \sin(n+1/2)|u| \\
&\qquad = -1 + \sum_{n=1}^{\infty} (b_n^{(r)} - b_n^{(i)}) \sqrt{n} \cos nu \\
&\sum_{n=0}^{\infty} a_n^{(i)} \cos(n+1/2)u = -\sum_{n=1}^{\infty} b_n^{(i)} \sin n|u| \\
&\sum_{n=0}^{\infty} (a_n^{(r)} + a_n^{(i)})(n+1/2)^{1/2} \cos(n+1/2)u \\
&\qquad = \sum_{n=1}^{\infty} (b_n^{(r)} + b_n^{(i)}) \sqrt{n} \sin n|u|
\end{aligned} \tag{3.17}$$

From (3.17) the constant κ and the coefficients $a_n = a_n^{(r)} + ia_n^{(i)}$ and $b_n = b_n^{(r)} + ib_n^{(i)}$ can be determined (see the Appendix A).

The approximate results read

$$\begin{aligned}
a_n^{(r)} &= y(n+1/2)^{-1} + z(n+1/2)^{-3/2} + \hat{a}_n^{(r)}, && n = 0, 1, 2,... \\
a_n^{(i)} &= -z(n+1/2)^{-3/2} + \hat{a}_n^{(i)}, && n = 0, 1, 2,... \\
b_n^{(r)} &= -zn^{-3/2} + \hat{b}_n^{(r)}, && n = 1, 2,... \\
b_n^{(i)} &= yn^{-1} - zn^{-3/2} + \hat{b}_n^{(i)}, && n = 1, 2,...
\end{aligned} \tag{3.18}$$

where κ, y, and z are given by

$$\kappa = 0.8554, \qquad y = 0.3992, \qquad z = 0.1093 \tag{3.19}$$

and where the coefficients $\hat{a}_n^{(r)}$, $\hat{a}_n^{(i)}$, $\hat{b}_n^{(r)}$, $\hat{b}_n^{(i)}$ are listed in Table I.

3.5. Determination of W_+ and W_-

According to (3.13) and (3.16) we have for the x-independent part the Taylor expansion near $E \lessapprox E_0$

$$\tilde{W}_{r,l}(E, t) = g_{r,l}(\kappa - \xi)\, w_0, \qquad \xi \leqslant 0 \tag{3.20}$$

Table I. The Coefficients $\hat{a}_n^{(r)}, \ldots, \hat{b}_n^{(i)}$ of (3.18) up to $n=5$ (Computed for $N=100$)

n	$\hat{a}_n^{(r)}$	$\hat{a}_n^{(i)}$	$\hat{b}_n^{(r)}$	$\hat{b}_n^{(i)}$
0	0.0175	−0.0838	—	—
1	0.0003	−0.0103	0.0337	0.0022
2	−0.0002	−0.0037	0.0085	0.0005
3	−0.0002	−0.0019	0.0038	0.0002
4	−0.0002	−0.0011	0.0022	0.0002
5	−0.0002	−0.0008	0.0014	0.0001

where ξ and $g_{r,l}$ are given by

$$\xi = \alpha(E-E_0)/\Theta = [2\pi/\gamma I(E_0)\,\Theta]^{1/2}(E-E_0) \tag{3.21}$$

and

$$g_r = 1, \qquad g_l = -1 \tag{3.22}$$

Thus near $E \approx E_0$ the functions $W_\pm$ read [cf. (2.7), (2.11)]

$$W_\pm = \tfrac{1}{2}[g_{r,l}(\kappa-\xi)\,w_0 + w_S \pm w_D] \qquad \text{for} \quad \xi \leqslant 0, \text{ i.e., for} \quad E \leqslant E_0 \tag{3.23}$$

and

$$W_\pm = \tfrac{1}{2}[w_S \pm w_D] \qquad \text{for} \quad \xi \geqslant 0, \text{ i.e., for} \quad E \geqslant E_0 \tag{3.24}$$

For positive x (positive u) $g_r = 1$ and for negative x, (negative u) $g_l = -1$ has to be used. In Fig. 3a the functions

$$W_\pm^{\text{red}} = \tfrac{1}{2}[g_{r,l}\kappa w_0 + w_S \pm w_D] \qquad \text{for} \quad \xi \leqslant 0 \tag{3.25}$$

are plotted as a function of u for constant $\xi \leqslant 0$ and in Fig. 3b (3.24) as a function of u for constant $\xi \geqslant 0$. We have omitted in Fig. 3a the term $-g_{r,l}\xi w_0$ of (3.23) because it would otherwise have dominated the plot for large negative ξ. In the plots the sum in (3.14), (3.15) was taken up to $n = N = 1000$, whereas for $n = 0, \ldots, 5$ the numerically calculated a_n and b_n had been used. For $n = 6, \ldots, N$ we have employed the asymptotic expansion (3.18) without the $\hat{a}_n$ and $\hat{b}_n$ terms.

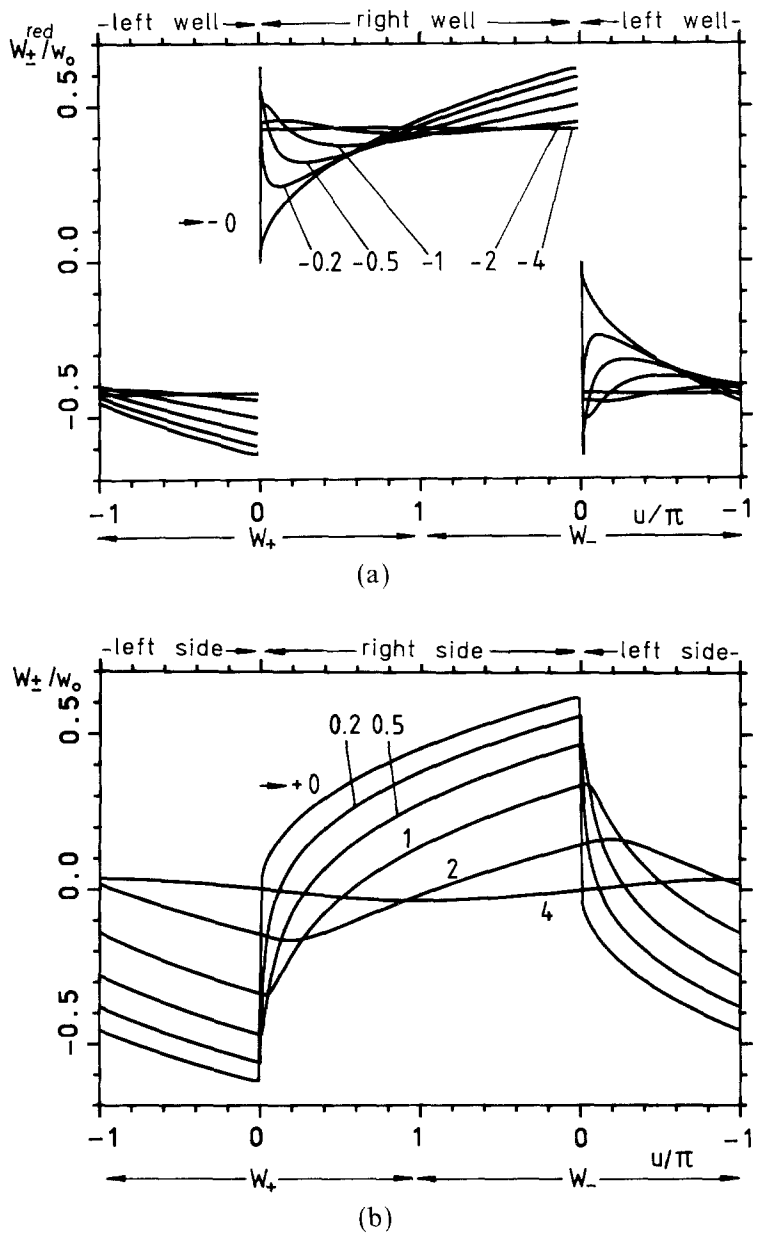


Fig. 3. The distribution (3.25) and (3.24) in the boundary layer as a function of u for various negative (a) and positive (b) ξ values. The limit values $\xi \to -0$ and $\xi \to +0$ are also shown. In the figure the corresponding regions for W_+ and W_- and for the right and left well or right and left side are also indicated.

3.6. Asymptotic Expressions

Inserting (3.18) into (3.13) and neglecting the small terms $\hat{b}_n^{(r)}$ and $\hat{b}_n^{(i)}$ we get for $E \to E_0 - 0$

$$w_D = -w_0[yf_1(|u|) - zf_2(|u|)]$$
$$w_S = -w_0 \frac{u}{|u|} zf_3(u) \tag{3.26}$$

where $f_i(u)$ are defined by

$$f_1(u) = \sum_{n=1}^{\infty} n^{-1} \sin nu = (\pi - u)/2 \qquad \text{for} \quad 0 \leqslant u \leqslant 2\pi \tag{3.27}$$

$$f_2(u) = \sum_{n=1}^{\infty} n^{-3/2} \sin nu \approx (2\pi u)^{1/2} \qquad \text{for} \quad 0 \leqslant u \ll 1 \tag{3.28}$$

$$f_3(u) = \sum_{n=1}^{\infty} n^{-3/2} \cos nu \approx \sum_{n=1}^{\infty} n^{-3/2} - (2\pi u)^{1/2} = \zeta(3/2) - (2\pi u)^{1/2}$$
$$\text{for} \quad 0 \leqslant u \ll 1 \tag{3.29}$$

In (3.29) ζ is Riemann's ζ function. Whereas $f_1(u)$ jumps at $u = 0$, f_2 and f_3 are continuous with square root dependence near $u = 0$ for $u \geqslant 0$. This square root dependence is clearly seen in Figs. 3a, b for the $\xi = 0$ line. [The approximate expressions (3.28), (3.29) can be found by integration of (2.1) of Chap. V in Ref. 14.] Notice the change of periodicity in the boundary layer. Inside the wells, i.e., for $\xi < 0$, the functions are periodic in u with 2π, whereas above the critical energy E_0, i.e., for $\xi > 0$ the combination of W_+ and W_- are periodic with $2 \times 2\pi$, compare also Fig. 1.

In Fig. 4 the distributions (3.23), (3.24) are shown as a function of ξ for various u values. Here the continuous dependence of the functions and of their derivatives at $\xi = 0$ for $u \neq 0$ is clearly seen. Neglecting the x-dependent functions in (3.23) we notice that the functions are zero at the energy E_M defined by

$$\xi_M = \frac{\alpha}{\Theta}(E_M - E_0) = \kappa \tag{3.30}$$

The length $\xi_M = \kappa$ is similar to the Milne extrapolation length in the kinetic boundary layer for the Fokker–Planck equation with an absorbing wall; see for instance Ref. 13.

We want to emphasize that the boundary-layer distributions in the variables ξ and u are independent of the special form of the symmetric

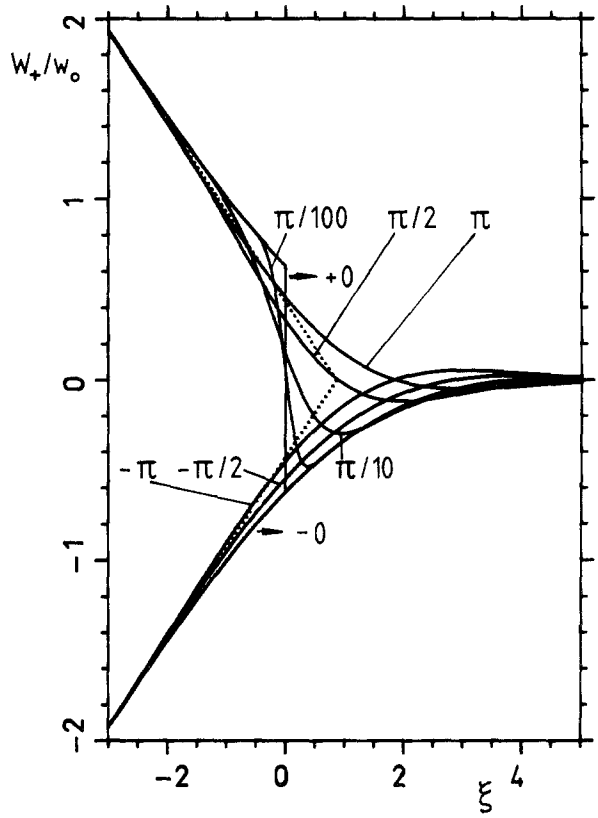


Fig. 4. The distributions (3.23), (3.24) in the boundary layer as a function of ξ for various u values. The dotted lines show the u-independent part in (3.23).

double-well potential. For asymmetric or metastable potentials, however, the boundary-layer distributions will be different. For a metastable potential, for instance, where the right side of the potential in Fig. 1 will go to negative-infinite values, particles cannot enter into the left side for $E > E_0$ and $v < 0$, they can only leave the well for $E > E_0$ and $v > 0$. Whereas the ansatz (3.15) can still be used inside the well of the metastable potential, the ansatz (3.14) does not fulfill the boundary condition of the situation described above and has therefore to be modified. The factor κ in (3.13) will differ from the value in (3.19). Preliminary calculations[18] lead for a metastable potential to the value

$$\kappa \approx 1.46 \tag{3.31}$$

3.7. Connection to the Work of Büttiker, Harris, and Landauer

To describe the influence of small but finite damping Büttiker *et al.*[7] and Büttiker and Landauer[8a] introduced a factor $\alpha_{\mathrm{BHL}} > 1$, which connects the divergence of the probability current in E direction with the probability density itself. Because of the large change of their distribution β within the boundary layer we may neglect the first derivative in their equation (3.4) and thus obtain in their (BHL) notation

$$\eta I_{\mathrm{BHL}} kT(d^2\beta/dE^2) = \alpha_{\mathrm{BHL}}\beta \tag{3.32}$$

This relation has to be compared with our Eq. (3.13). Differentiating (3.13) and using again (3.13) we have (omitting the indices)

$$\begin{aligned}\kappa^2(\Theta/\alpha)^2(d^2W/dE^2)\,|_{E=E_0-0} &= -\kappa(\Theta/\alpha)(dW/dE)\,|_{E=E_0-0} \\ &= W\,|_{E=E_0}\end{aligned} \tag{3.33}$$

Because their action integral I_{BHL} and our action integral [cf. (2.16) and (2.19)] are connected by $I(E_0) = 2I_l(E_0) = 2I_{\mathrm{BHL}}$ and because our α is defined by (3.5) we obtain by comparing (3.32) and (3.33) ($\eta = \gamma$, $kT = \Theta$)

$$\alpha_{\mathrm{BHL}} = \pi/\kappa^2 \tag{3.34}$$

Thus we are able to determine their ad hoc factor α_{BHL}. It should be noted that Büttiker, Harris, and Landauer applied their method to a metastable potential. As already mentioned, our κ in (3.19) is valid for a double-well potential. The factor $\alpha_{\mathrm{BHL}}^{(D)}$ for a double-well potential thus has the value

$$2\alpha_{\mathrm{B}} = \alpha_{\mathrm{BHL}}^{(D)} \approx 4.293 \tag{3.35}$$

Büttiker[8b] has defined a constant α_{B} for the double-well potential, which is just twice the $\alpha_{\mathrm{BHL}}^{(D)}$.

Using the κ value for a metastable potential (3.31) we have

$$\alpha_{\mathrm{BHL}}^{(M)} \approx 1.47 \tag{3.36}$$

4. EIGENVALUES AND EIGENFUNCTIONS

We now want to determine the eigenvalues and eigenfunctions for a symmetric double-well potential. Outside the boundary layer the eigenfunctions are assumed to be independent of x. Inserting the ansatz

$$\begin{aligned}\tilde{W}_{r,l}(E, t) &= 2g_{r,l}\varphi(E)\, e^{-\lambda t} \qquad \text{for} \quad E_{\min} \leqslant E < E_0 \\ \tilde{W}(E, t) &= 2\varphi(E)\, e^{-\lambda t} \qquad \text{for} \quad E_0 < E\end{aligned}$$

in (2.13), (2.14) leads for symmetric ($g_r = g_l = 1$) as well as for antisymmetric eigenfunctions ($g_r = -g_l = 1$) to the eigenvalue equation

$$\left[\frac{d}{dE} I(E)\left(1 + \Theta \frac{d}{dE}\right) + AT(E)\right] \varphi(E)$$
$$= \Theta I(E)\, \varphi''(E) + [I(E) + \Theta T(E)]\, \varphi'(E)$$
$$+ (1 + A)\, T(E)\, \varphi(E) = 0 \tag{4.1}$$

where $I(E)$ and $T(E)$ are the action integral and its derivative introduced in Section 2, and A is defined by

$$A = \lambda/\gamma \tag{4.2}$$

4.1. Boundary Condition at $E = E_{\min}$

Because of

$$\begin{aligned} I(E) &= I(E_{\min}) + I'(E_{\min})(E - E_{\min}) + \cdots \\ &= T(E_{\min})(E - E_{\min}) + \cdots \end{aligned} \tag{4.3}$$

we obtain from (4.1) for $E = E_{\min}$

$$\Theta \varphi'(E_{\min}) + (1 + A)\, \varphi(E_{\min}) = 0 \tag{4.4}$$

Thus at $E = E_{\min}$ the derivative of φ is coupled to φ itself.

4.2. Boundary Conditions at $E = E_0$ for Even Eigenfunctions

For even eigenfunctions $\varphi(E)$ is different from zero for $E > E_0$. At $E = E_0$, φ and its derivative must be continuous:

$$\begin{aligned} \varphi(E_0 - 0) &= \varphi(E_0 + 0) \\ \varphi'(E_0 - 0) &= \varphi'(E_0 + 0) \end{aligned} \tag{4.5}$$

As explained in Section 3 no x-dependent functions occur near $E = E_0$. For $E \to \infty$ the boundary condition for even functions is such that φ should vanish fast enough, so that all the moments exist. [Then $\varphi'(E)$ will also vanish.]

4.3. Boundary Condition at $E = E_0$ for Odd Eigenfunctions

For odd eigenfunctions $\varphi(E)$ is zero for $E > E_0$. In the boundary layer near $E \approx E_0$ x-dependent functions must by taken into account leading to the boundary condition [cf. (3.13); notice $I(E_0) = 2I_r(E_0)$]

$$\begin{aligned} \varphi(E_0 - 0) &= -\kappa(\Theta/\alpha)\, \varphi'(E_0 - 0) \\ &= -\kappa[\gamma I(E_0)\, \Theta/(2\pi)]^{1/2}\, \varphi'(E_0 - 0) \end{aligned} \tag{4.6}$$

By these boundary conditions the eigenvalues and the eigenfunctions up to a normalization constant are uniquely determined.

4.4. Numerical Determination of Eigenfunctions and Eigenvalues

Even eigenfunctions and eigenvalues are determined as follows. First (4.1) for $E < E_0$ was integrated by a Runge–Kutta procedure starting with $\varphi(E_{\min})$ and $\varphi'(E_{\min})$ given by (4.4) with a certain value for λ. At $E = E_0$ we use (4.5) and integrate (4.1) to larger E. The eigenvalue follows from the requirement, that $\varphi(E_{\max}, \lambda)$ vanishes at some large value $E_{\max}$. A similar method was already used to calculate the eigenvalues for the Brownian motion in periodic potentials.[15]

To calculate odd eigenfunctions and eigenvalues we also integrate (4.1) by a Runge–Kutta procedure starting with $\varphi(E_{\min})$ and $\varphi'(E_{\min})$ given by (4.4) with an estimated eigenvalue. The correct eigenvalue is now determined by (4.6). Whereas for even eigenfunctions $A = \lambda(\gamma)/\gamma$ is independent of γ, for odd eigenfunctions $A = \lambda(\gamma)/\gamma$ depends on γ.

4.5. Dependence of $A(\gamma)$ for Small γ

Because the right-hand side in (4.6) is a small quantity, we may express the eigenvalue $A(\gamma) = \lambda(\gamma)/\gamma$ for finite γ in terms of the eigenvalue $A(0) = A_0 = \lambda(0)/\gamma$ and of the eigenfunction φ^0 in the zero-friction limit, i.e., by using the boundary condition

$$\varphi(E_0 - 0) = 0 \tag{4.6a}$$

instead of (4.6).

As shown in Appendix B $A = \lambda/\gamma$ can be expressed by

$$A(\gamma) = \frac{\lambda(\gamma)}{\gamma} = A_0 \left(1 - \frac{\kappa}{\alpha} B\right) = A_0(1 - \kappa[I(E_0)\, \gamma/(2\pi\Theta)]^{1/2}\, B) \tag{4.7}$$

where B is given by

$$B = \frac{I(E_0 - 0)[\Theta(d\varphi^0/dE) \mid_{E=E_0}]^2}{A(0) \int_{E_{\min}}^{E_0} T(E) \exp[-(E_0 - E)/\Theta][\varphi^0(E)]^2 \, dE} \tag{4.8}$$

Thus $A = \lambda/\gamma$ depends linearly on $\sqrt{\gamma}$ for odd eigenfunctions.

4.6. Results

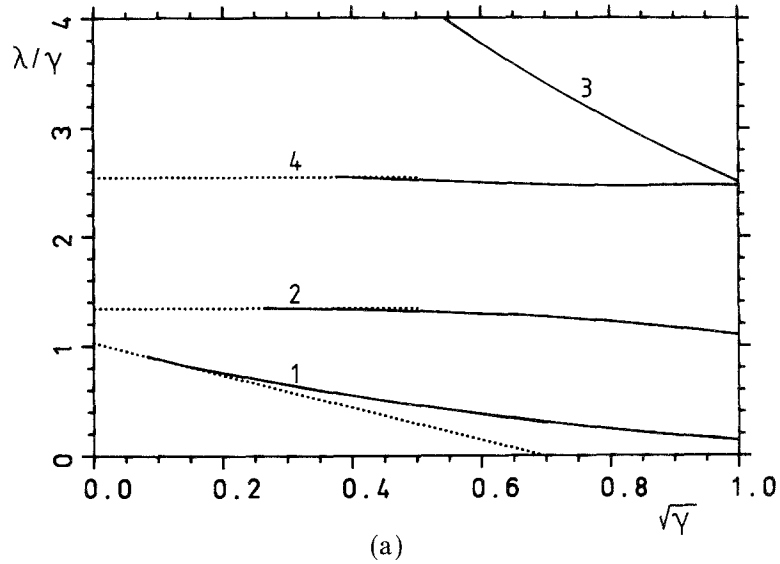
In Fig. 5 the lowest nonzero eigenvalues λ/γ for the double-well potential (1.2) in the normalization $-d_2 = d_4 = 1$ [see (2.25) of Ref. 1] as obtained by the integration procedure discussed above are shown and compared to those obtained by the matrix-continued-fraction method of Ref. 1. The potential difference of (1.2) between the hump in the middle and the minimum is given by

$$\Delta E = d_2^2/4d_4 \tag{4.9}$$

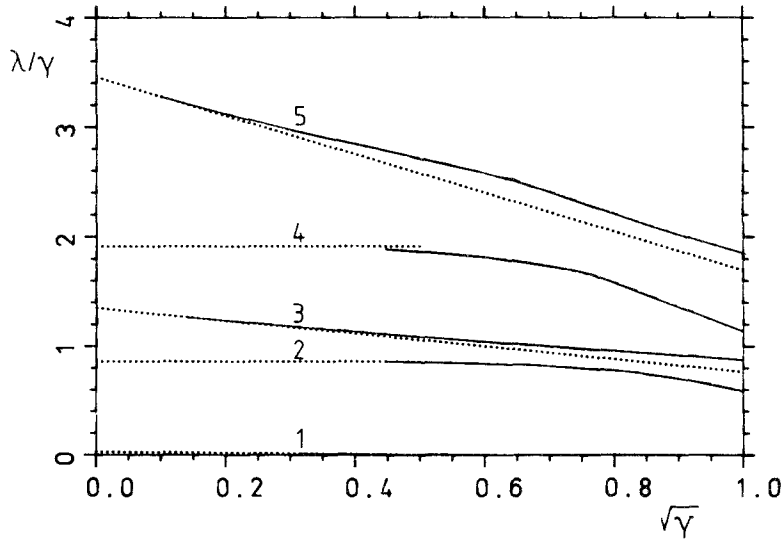
As mentioned in Ref. 1 the ratio

$$\Delta E/(kT) = d_2^2/4d_4\Theta = 1/4\tilde{\Theta} \tag{4.10}$$

is the same for different normalizations. In Fig. 5 the eigenvalues are shown for the high-temperature $\Delta E = kT$ and for the low-temperature $\Delta E = 5kT$. (An approximate expression for the lowest nonzero eigenvalue valid already for $\Delta E = 5kT$ is derived in Section 5.) As seen in Fig. 5 eigenvalues belonging to even eigenfunctions (even numbers) do not depend linearly on $\sqrt{\gamma}$ for small γ, whereas eigenvalues belonging to odd eigenfunctions (odd numbers) depend linearly on $\sqrt{\gamma}$ for small γ. The corresponding even and odd eigenfunctions in the limit $\gamma \to 0$ are shown in Fig. 6. Owing to the boundary condition (4.6a) the odd eigenfunctions are zero for $E > E_0 = 0$, whereas the even eigenfunctions extend into this region. This extension of the even eigenfunctions in the region $E > E_0 = 0$ is very pronounced for $\Delta E = kT$, but it is less noticeable for the lower temperature $\Delta E = 5kT$. For lower temperatures the different boundary conditions (4.5), (4.6a) for even and odd eigenfunctions only lead to a slightly different influence of the eigenfunctions. In Fig. 6b, for instance, the eigenfunctions 0 and 1 nearly coincide. Because of the different boundary conditions even and odd eigenvalues do not need to alternate. For the low-temperature $\Delta E = 5kT$ the five lowest eigenvalues alternate, whereas for the higher-temperature $\Delta E = kT$ the third eigenvalue is larger than the fourth one for $\gamma < 1$; cf. Fig. 5a. For finite γ the boundary condition (4.6) should be used instead of (4.6a). In Fig. 7 the lowest normalized odd eigenfunction is shown for a finite γ and for comparison for the limit $\gamma \to 0$. The normalization of the eigenfunctions is explained in Appendix C. With the help of this eigenfunction and the



(a)



(b)

Fig. 5. The eigenvalues $A = \lambda/\gamma$ calculated by means of the matrix-continued-fraction method as a function of $\sqrt{\gamma}$ (Ref. 1, Section 4) shown by solid lines and the eigenvalues obtained by the Runge–Kutta integration of (4.1) by dotted lines for the normalized $(-d_2 = d_4 = 1)$ double-well potential (1.2) for $\Delta E/kT = 1$ (a) and $\Delta E/kT = 5$ (b). The numbers correspond to the eigenfunctions for $\gamma \to 0$ in Fig. 6.

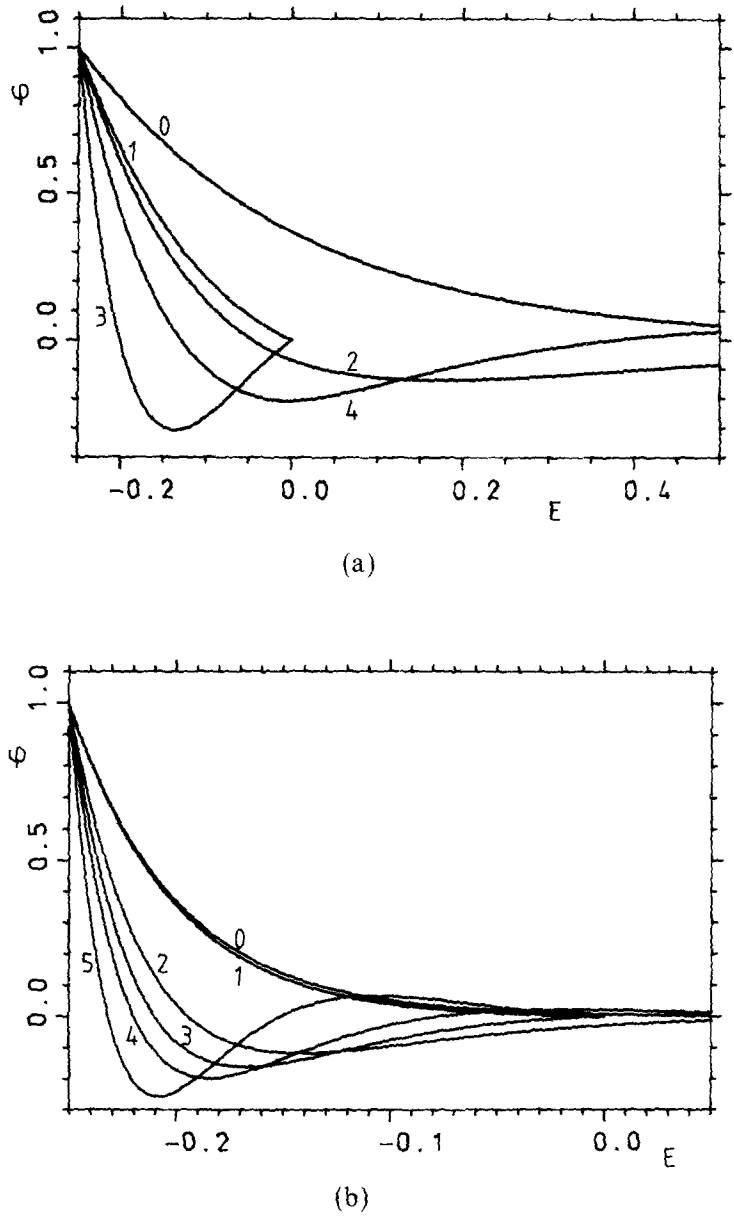


Fig. 6. The unnormalized eigenfunction $\varphi(E)$ obtained by numerical integration of (4.1) with the boundary condition (4.5) for even and (4.6a) for odd eigenfunctions in the limit $\gamma \to 0$. As in Fig. 5 we have used the normalized ($-d_2 = d_4 = 1$) double-well potential and the ratios $\Delta E/kT = 1$ (a) and $\Delta E/kT = 5$ (b).

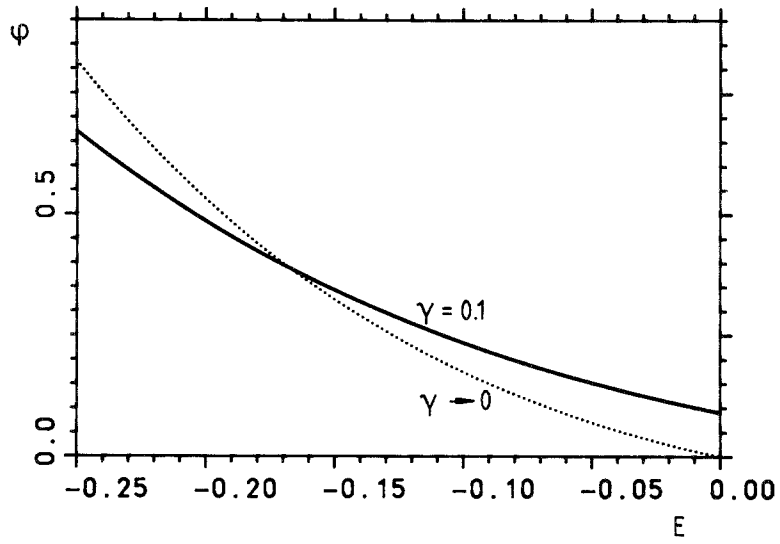


Fig. 7. The normalized eigenfunction of the lowest nonzero eigenvalue for $\Delta E = kT$ and for $\gamma = 0.1$ (solid line) and $\gamma \to 0$ (dotted line) for the normalized potential (1.2).

boundary-layer theory of Section 3 the eigenfunction belonging to the lowest nonzero eigenvalue can be plotted in phase space. Starting with the coordinates x, v in phase space, we obtain first the energy (2.2). The u values are obtained according (3.3) or (3.3a) for $E = E_0$. For other energies u may approximately be calculated by (3.3), where E_0 is replaced by E and the lower bounds in the integrals are replaced by $x_1'(E)$ for $E < E_0$. The result for the eigenfunction with the lowest nonzero eigenvalue is shown in Fig. 8a. In Fig. 8b the normalized eigenfunction obtained by the matrix-continued-fraction method is shown for comparison. Though the value $\gamma = 0.1$ is still a little bit too large for applying the low-friction-limit theory, both functions agree quite well for energies below and slightly above the critical energy E_0. Well above the critical energy deviations occur. These deviations are expected, because (3.2) is valid only near the critical trajectory. It should also be noted that near the origin $x = v = 0$, the low-friction-limit theory fails. Because the velocity $v(x, E_0)$ is zero for $x = 0$ the approximations made are no longer valid.

4.7. Complex Eigenvalues

As discussed in Ref. 19 (see also Section 11.9.1 of Refs. 9 and 20) a contraction of some of the eigenfunctions toward the minima of the poten-

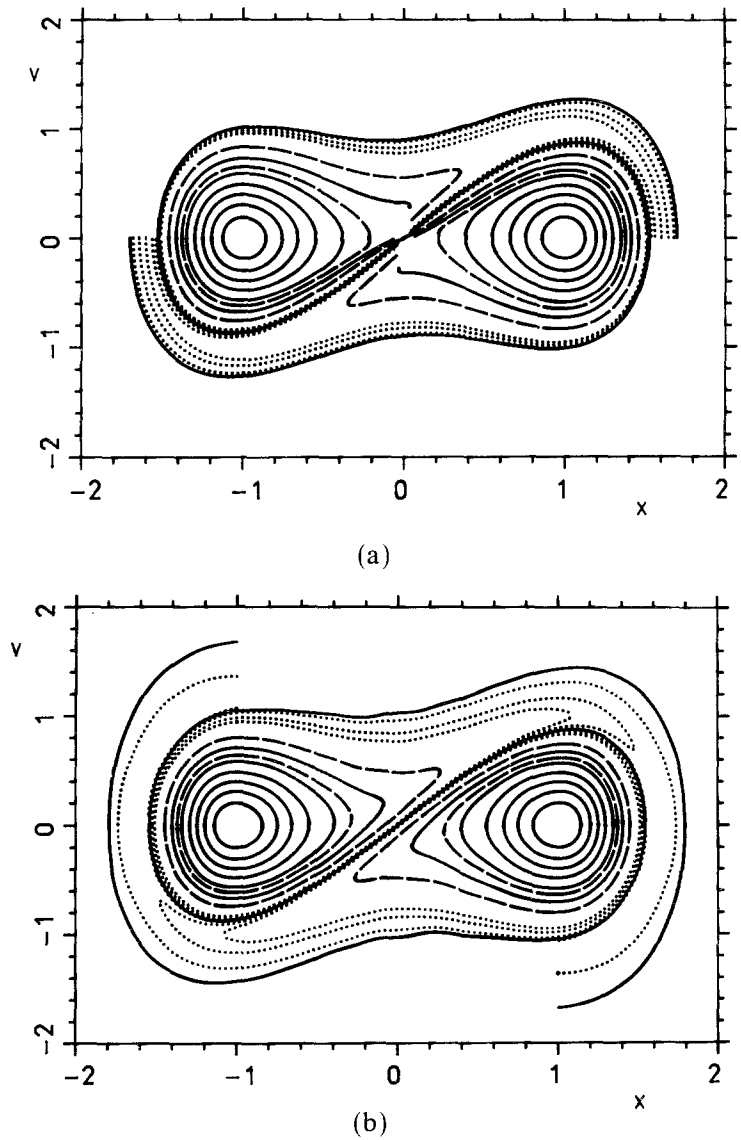


Fig. 8. Altitude charts of the eigenfunction Φ_1 of the lowest nonzero eigenvalue of the normalized potential (1.2) for $\gamma = 0.1$ and $\Delta E = kT$ as obtained by the low-friction-limit theory (a) and by the matrix-continued-fraction theory of Ref. 1 (b). The lines $\Phi_1 = c = \text{const}$ are shown for $c = 0$, ± 0.1, ± 0.2, ± 0.3, ± 0.4, ± 0.5, ± 0.6 (solid lines), $c = \pm 0.05$, ± 0.15 (broken lines), $c = \pm 0.001$, ± 0.005, ± 0.01 (dotted lines). The wavy behavior of the nodal curve $\Phi_1 = 0$ in Fig. 8b indicates that the dimension of the matrices was not large enough for this low friction-constant.

tial occurs for complex eigenvalues and anharmonic potentials in the low-friction limit. The eigenvalues can then be obtained analytically [see (3.27) of Ref. 19 or (11.301) of Ref. 9]. In contrast to the periodic potential example treated in Ref. 19, the matrix-continued-fraction method for a double-well potential could not be carried out to such low friction-constants with our computer that an unequivocal correspondence between these eigenvalues and the analytical eigenvalues could be found.

5. LOWEST NONZERO EIGENVALUE IN THE WEAK-NOISE LIMIT

In this Section we derive an expression in the low-temperature limit $\Theta \to 0$. As discussed in detail in Section 6 this limit is valid only if γ is still much smaller than Θ, i.e., the condition $\Theta \gg \gamma$ must still be satisfied, see also the remark following (5.23). To derive an analytical expression for the lowest nonzero eigenvalue we transform the differential equation (4.1) together with the boundary conditions (4.4) and (4.6a) (i.e., in the limit $\gamma \to 0$) into an integral equation. Formal integration of (4.1) leads to

$$\Theta\varphi' + \varphi = -[A_0/I(E)] \int_{E_{\min}}^{E} T(E')\, \varphi(E')\, dE' \tag{5.1}$$

The boundary condition (4.4) is automatically fulfilled by (5.1), because of

$$\lim_{E \to E_{\min}} \frac{1}{I(E)} \int_{E_{\min}}^{E} T(E')\, \varphi(E')\, dE' = \varphi(E_{\min}) \tag{5.2}$$

Considering the right-hand side of (5.1) as an inhomogeneous part we obtain by using (4.6a)

$$\varphi(E) = (A_0/\Theta)\, e^{-E/\Theta} \int_{E}^{E_0} \frac{e^{E'/\Theta}}{I(E')} \int_{E_{\min}}^{E'} T(E'')\, \varphi(E'')\, dE''dE' \tag{5.3}$$

The integral equation (5.3) can be transformed to a Fredholm integral equation by using a proper partial integration. Introducing

$$y(E) = \int_{E}^{E_0} [e^{E'/\Theta}/I(E')]\, dE' \tag{5.4}$$

and the kernel

$$\begin{aligned} K(E, E') &= \Theta^{-1} e^{-E/\Theta} y(E)\, T(E') \qquad \text{for} \quad E' < E \\ &= \Theta^{-1} e^{-E/\Theta} y(E')\, T(E') \qquad \text{for} \quad E' > E \end{aligned} \tag{5.5}$$

the integral equation reads

$$\varphi(E) = A_0 \int_{E_{\min}}^{E_0} K(E, E')\, \varphi(E')\, dE' \tag{5.6}$$

Here we will consider only odd eigenfunctions, though a similar procedure is also valid for the even eigenfunctions (see also Ref. 15, Section 5). In the weak-noise limit (i.e., $\Theta \to 0$) we may write

$$y(E) = \Theta e^{E_0/\Theta} / I(E_0) = y_0 \qquad \text{for} \quad E_0 - E \ll \Theta \tag{5.7}$$

Hence $K(E, E')$ then factorizes and we have

$$\varphi(E) = \Theta^{-1} A_0\, y_0 e^{-E/\Theta} \int_{E_{\min}}^{E_0} T(E')\, \varphi(E')\, dE' \tag{5.8}$$

Multiplying (5.8) with $T(E)$, integrating the resulting equation, and using

$$M = \int_{E_{\min}}^{E_0} T(E)\, e^{-E/\Theta}\, dE \approx \Theta T(E_{\min})\, e^{-E_{\min}/\Theta} \tag{5.9}$$

for small Θ, we thus arrive at the following result for the eigenvalue:

$$\lambda = \gamma A_0 = \gamma \frac{\Theta}{M y_0} = \gamma \frac{I(E_0)}{\Theta T(E_{\min})}\, e^{-(E_0 - E_{\min})/\Theta} \tag{5.10}$$

This expression is similar to the one derived by Kramers[3] a long time ago. The corresponding eigenfunction may be obtained from (5.6) by iteration. As seen from (5.8) the zeroth approximation to the eigenfunction is (c is a normalization constant)

$$\varphi(E) = c e^{-E/\Theta} \tag{5.11}$$

This function is not valid near $E \approx E_0$ because it does not fulfill the boundary condition (4.6a). After insertion of (5.11) either into (5.3) or equivalently into (5.6) we obtain in a better approximation

$$\varphi(E) = A_0 c \int_{E_{\min}}^{E_0} K(E, E')\, e^{-E'/\Theta}\, dE' \tag{5.12}$$

which fulfills the boundary condition (4.6a) as best seen from the equivalent expression (5.3).

The validity of the expression (5.10) can be extended to somewhat higher temperatures Θ by evaluating (5.7), (5.9) more accurately. Instead of (5.9) we have

$$\begin{aligned} M &= \int_{E_{\min}}^{E_0} [T(E_{\min}) + T'(E_{\min})(E - E_{\min})]\, e^{-E/\Theta}\, dE \\ &= T(E_{\min})\, \Theta \exp(-E_{\min}/\Theta)[1 + \Theta T'(E_{\min})/T(E_{\min})] \end{aligned} \tag{5.13}$$

For the double-well potential (1.2) we thus get

$$T'(E_{\min})/T(E_{\min}) = 3d_4/4d_2^2 \tag{5.14}$$

$$M = 2\pi(2/|d_2|)^{1/2}\, \Theta \exp(d_2^2/4d_4\Theta)\,(1 + 3d_4\Theta/4d_2^2) \tag{5.13a}$$

The evaluation of (5.4) is more complicated, because $I(E)$ generally cannot be expanded in a power series at $E = E_0$. For the double-well potential (1.2) with $E_0 = 0$ the exact expression of $I(E)$ in terms of the complete elliptic integrals is given by (2.21). Using the asymptotic expression (2.21″) we have

$$I(E_0) = 8\,|d_2|^{3/2}/3d_4 \tag{5.15}$$

$$\begin{aligned} I^{-1}(E) \approx I^{-1}(E_0)[1 + 3(d_4\,|E|/4d_2^2) \\ \times\, (1 + \ln 16d_2^2/d_4|E|)] \end{aligned} \tag{5.16}$$

Insertion in (5.4) leads to

$$\begin{aligned} y_0 = \Theta \exp(E_0/\Theta)\, I^{-1}(E_0) \\ \times\, \{1 + 3(d_4\Theta/4d_2^2)[\ln(16d_2^2/d_4\Theta) + C]\} \end{aligned} \tag{5.17}$$

where

$$C = 1 - \int_0^\infty x e^{-x} \ln x\, dx = 0.5772... \tag{5.18}$$

is Euler's constant. Further insertion leads to

$$\begin{aligned} \frac{\lambda}{\gamma} = A_0 = \frac{\Theta}{My_0} = \frac{2\sqrt{2}\, d_2^2}{3\pi d_4 \Theta} \exp(-d_2^2/(4d_4\Theta)) \\ \times\, \{1 - 3(d_4\Theta/4d_2^2)[1 + C + \ln(16d_2^2/d_4\Theta)]\} \end{aligned} \tag{5.19}$$

Next we include the correction terms proportional to $\gamma^{3/2}$. By (4.7), (4.8) this correction term can be expressed by the eigenvalue and eigenfunction

with boundary condition (4.6a). To derive B we first have to know $\varphi'(E_0)$. Using (5.5), (5.12) we have

$$\begin{aligned}\varphi'(E_0) &= A_0 c \int_{E_{\min}}^{E_0} \frac{dK(E_0, E')}{dE_0} e^{-E'/\Theta}\, dE' \\ &= -A_0 c \int_{E_{\min}}^{E_0} \frac{1}{\Theta} \frac{T(E')}{I(E_0)} e^{-E'/\Theta}\, dE' \\ &= -\frac{A_0 c M}{\Theta I(E_0)}\end{aligned} \tag{5.20}$$

Inserting the simpler relation (5.11) in the denominator we thus obtain

$$B = \frac{A_0 M}{I(E_0)} e^{E_0/\Theta} = \frac{\Theta}{y_0 I(E_0)} e^{E_0/\Theta} \tag{5.21}$$

To derive the last expression we used $A_0 = \Theta/M y_0$. Without the correction terms $\sim\Theta$ we have (5.7) and obtain

$$B = 1 \tag{5.22}$$

Hence without the correction terms in Θ we obtain for the eigenvalue (4.7)

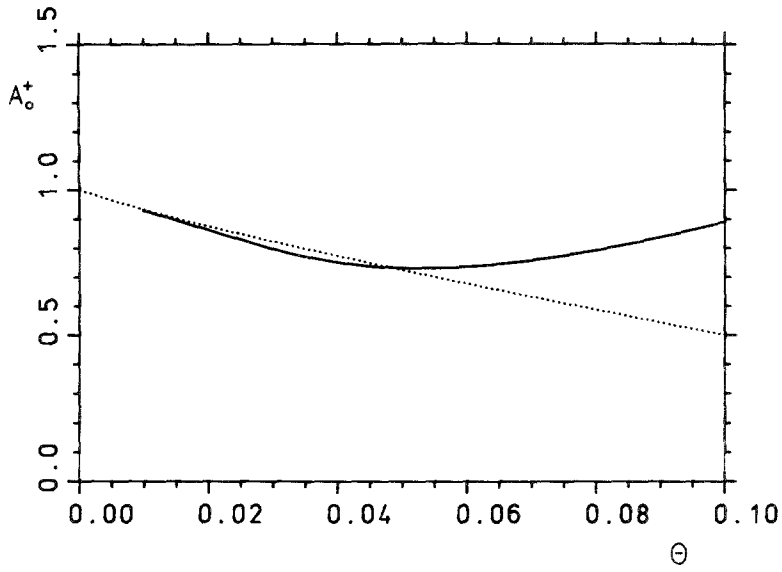
$$\lambda = \gamma \frac{I(E_0)}{\Theta T(E_{\min})} e^{-(E_0 - E_{\min})/\Theta} \left\{1 - \kappa \left[\frac{I(E_0)}{2\pi\Theta}\gamma\right]^{1/2}\right\} \tag{5.23}$$

Because the second term in the brackets, which is the correction term proportional to $\gamma^{3/2}$, should be small compared to the first term, obviously the relation $\gamma \ll \Theta$ should be fulfilled (see also the discussion in Section 6).

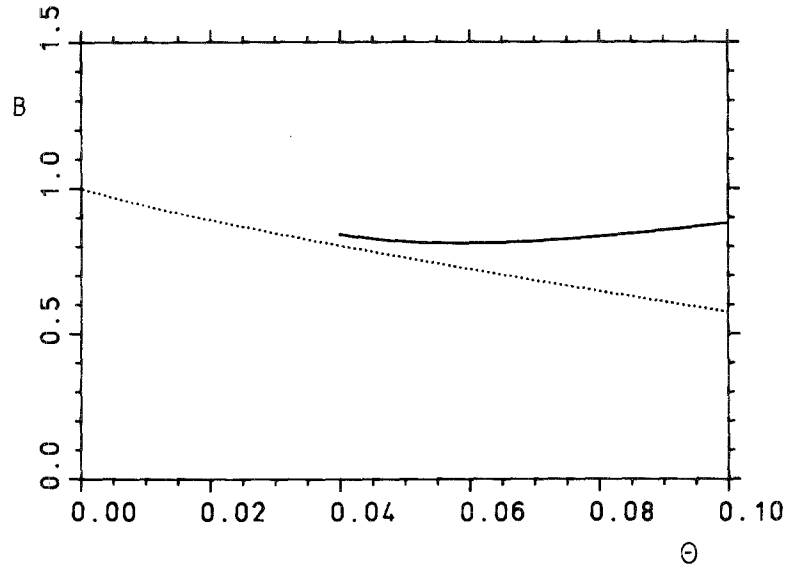
For small γ this value ($r_{\mathrm{BHL}} = \lambda$) agrees with (3.11) of Ref. 7, if the factor α_{BHL} is given by (3.34). [Note that in the low-friction limit without the boundary-layer theory we have the same boundary condition $\varphi(E_0) = 0$ for the first eigenfunction of the double-well potential and of a metastable potential. Both eigenvalues therefore agree in lowest order.] For a comparison one should use $kT = \Theta$, $\eta = \gamma$, $I_b = I_l(E_0) = I(E_0)/2$, $\omega_A = 2\pi/T_l(E_{\min}) = 4\pi/T(E_{\min})$, $E_b = E_0 - E_{\min}$. The expression (5.23) is only valid if the additional term proportional to $\sqrt{\gamma}$ in the last factor of (5.23) is small compared to 1.

Using the more accurate result (5.17) for the double-well potential (1.2) we get

$$B = 1 - \frac{3d_4\Theta}{4d_2^2}\left[\ln(16d_2^2/d_4\Theta) + C\right] \tag{5.22a}$$



(a)



(b)

Fig. 9. The asymptotic expression (5.19), (5.25) (a) and (5.22a) (b) as a function of Θ (dotted lines) and the results (5.25) and (4.8) as obtained by numerical integration of (4.1) (solid lines).

The final result for the double-well potential (1.2) reads

$$\lambda = \gamma \frac{2\sqrt{2}\, d_2^2}{3\pi\, d_4 \Theta} \exp\left(\frac{-d_2^2}{4 d_4 \Theta}\right) \times \{1 - \underline{3(d_4\Theta/4d_2^2)[1 + C + \ln(16 d_2^2/d_4\Theta)]}\} \times \{1 - \kappa[16\,|d_2|^{3/2}\,\gamma/(3\pi d_4\Theta)]^{1/2} \times [1 - \underline{3(d_4\Theta/4d_2^2)(\ln(16 d_2^2/d_4\Theta) + C)}]\} \tag{5.24}$$

Underlined terms are the corrections with respect to finite Θ. To check the approximate expressions (5.19) and (5.22a) we have plotted in Fig. 9 the factor

$$A_0^+ = A_0 \frac{3\pi d_4 \Theta}{2\sqrt{2}\, d_2^2} \exp\left(\frac{d_2^2}{4 d_4 \Theta}\right) \tag{5.25}$$

and B as a function of the temperature Θ and compared these quantities to those obtained from numerical integration of (4.1). It is clearly seen that (5.19) and (5.22a) are the asymptotic expressions for small Θ. The expression (5.24) without the underlined terms was compared with the matrix-continued-fraction result in Fig. 6a of Ref. 1 and Fig. 2 of Ref. 10.

6. DISCUSSION AND CONCLUSION

By introducing energy and position variables we have shown that the eigenvalues as well as the eigenfunctions of the Fokker–Planck equation for a double-well potential can be calculated in the low-friction limit. By considering a boundary-layer theory in the region of the critical trajectory eigenvalues of odd eigenfunctions have the form $\bar{A}\gamma + \bar{B}\gamma^{3/2}$ whereas the term proportional to $\gamma^{3/2}$ is missing for eigenvalues of even eigenfunctions. Furthermore the complicated distribution near the critical trajectory was obtained (see Figs. 3, 4, and 8). (For a recent dispute about the distributions near the critical trajectories, see the comments of Büttiker and Landauer[21] and Carmeli and Nitzan.[22]) Eigenvalues and eigenfunctions obtained by the present method agree very well with those obtained by the matrix-continued-fraction method of Ref. 1 for low friction-constants. For a recent review article on escape rates from a metastable state, see Ref. 23.

Finally we want to discuss the approximate regions of applicability for various procedures to obtain the first nonzero eigenvalue. The approximate regions for the normalized variables $\tilde{\Theta} = kT/4\Delta E$ and $\tilde{\gamma} = \gamma/|d_2|^{1/2}$ are shown in Fig. 10. In the weak-noise limit $\tilde{\Theta} \to 0$ we can use Kramer's rate, i.e., (4.4a) of Ref. 1, if the damping constant $\tilde{\gamma}$ is appreciably larger than the temperature $\tilde{\Theta}$. In the low-friction limit $\tilde{\gamma} \to 0$ we can apply the results

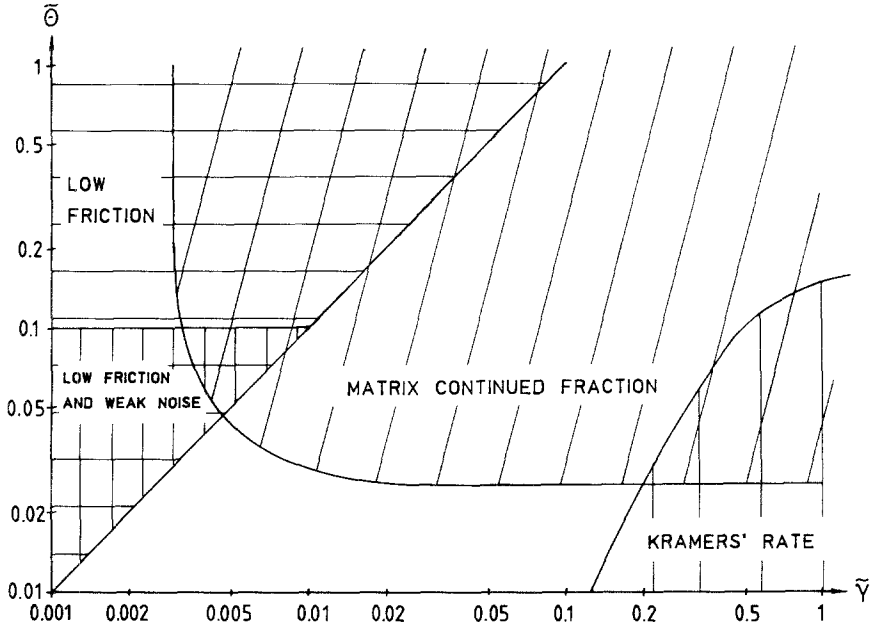


Fig. 10. Approximate regions of validity for various approximation methods to obtain the first nonzero eigenvalue are shown by different lining. The various methods are: matrix-continued-fraction method of Ref. 1; Kramers' rate [see for instance (4.4a) of Ref. 1]; low-friction theory (Section 4); low-friction case and weak-noise case (Section 5). The normalized parameters of the bistable potential (1.2) are $\tilde{\Theta} = kT/4\Delta E = d_4 kT/d_2^2$, $\tilde{\gamma} = \gamma/|d_2|^{1/2}$.

presented here if the temperature $\tilde{\Theta}$ is appreciably larger than $\tilde{\gamma}$, see also the remark following (5.23). Whereas for $\tilde{\Theta} \ll 1$ ($\tilde{\gamma}$ must then still be appreciably smaller than $\tilde{\Theta}$) analytical results can be given, one has to use a numerical integration procedure for larger temperature $\tilde{\Theta}$. The restriction of the matrix-continued-fraction method is that the normalized temperature $\tilde{\Theta}$ as well as the normalized friction constant $\tilde{\gamma}$ should be not too small. If both the temperature $\tilde{\Theta}$ and the friction constant $\tilde{\gamma}$ are of the same order and both become very small, we do not know a suitable method for calculating the transition rate. (One may of course use a suitable interpolation method connecting both analytical results, like a Padé approximation, as done by Skinner and Wolynes.[24])

ACKNOWLEDMENTS

We wish to thank Dr. R. Landauer and Dr. M. Büttiker, IBM Watson Research Center, for stimulating correspondence and discussions. Further-

more we wish to thank Dr. H. D. Vollmer for reading the manuscript and for giving us many valuable comments on to improve it.

APPENDIX A

To determine the coefficients $a_n^{(r)}$, $a_n^{(i)}$, $b_n^{(r)}$, $b_n^{(i)}$ and the constant κ from (3.17) we first expand $\sin(n+1/2)|u|$ and $\sin n|u|$ in the series

$$\sin(m+1/2)\,|u| = A_m + \sum_{n=1}^{\infty} A_{mn} \cos nu \tag{A1}$$

$$\sin m|u| = \sum_{n=0}^{\infty} B_{mn} \cos(n+1/2)u \tag{A2}$$

with

$$\begin{aligned} A_n &= [\pi(n+1/2)]^{-1} \\ A_{mn} &= [\pi(m+n+1/2)]^{-1} + [\pi(m-n+1/2)]^{-1} \\ B_{mn} &= [\pi(m+n+1/2)]^{-1} + [\pi(m-n-1/2)]^{-1} \end{aligned} \tag{A3}$$

Insertion of (A1) into the first and second equation in (3.17) leads to equations where only $\cos nu$ ($n = 0, 1, 2,...$) terms occur. Similarly by the insertion of (A2) into the third and fourth equation of (3.17) leads to equations where only $\cos(n+1/2)u$ terms occur. Equating the coefficients we thus obtain the following infinite system of equations:

$$b_n^{(r)} - \sum_{m=0}^{\infty} A_{mn} a_m^{(r)} = 0, \qquad n = 1, 2, 3,... \tag{A4}$$

$$\kappa - \sum_{m=0}^{\infty} A_m a_m^{(r)} = 0 \tag{A5}$$

$$\sum_{m=0}^{\infty} (m+1/2)^{1/2} A_{mn}(-a_m^{(r)} + a_m^{(i)}) + \sqrt{n}(-b_n^{(r)} + b_n^{(i)}) = 0, \qquad n = 1,2,... \tag{A6}$$

$$\sum_{m=0}^{\infty} (m+1/2)^{1/2} A_m(a_m^{(r)} - a_m^{(i)}) = -1 \tag{A7}$$

$$a_n^{(i)} + \sum_{m=1}^{\infty} B_{mn} b_m^{(i)} = 0, \qquad n = 0, 1, 2,... \tag{A8}$$

$$(n+1/2)^{1/2}(a_n^{(r)} + a_n^{(i)}) - \sum_{m=1}^{\infty} B_{mn} \sqrt{m}(b_m^{(r)} + b_m^{(i)}) = 0, \qquad n = 0, 1, 2,... \tag{A9}$$

By replacing the coefficients according to

$$b_n^{(r)} \to -(-1)^n a_n^{(i)} \qquad a_n^{(r)} \to -(-1)^n b_n^{(i)}$$
$$b_n^{(i)} \to (-1)^n a_n^{(r)} \qquad a_n^{(i)} \to (-1)^n b_n^{(r)}$$
$$C_n = (-1)^n A_n \qquad C_{mn} = (-1)^{m+n} A_{mn} \qquad S_{mn} = -(-1)^{m+n} B_{mn}$$

we obtain the same equations which occurred in the problem of Brownian motion in a cosine potential [see (A6)–(A9) of Ref. 12]. To solve the infinite system (A4)–(A9) we have to truncate it. Putting the coefficients $a_n^{(r,i)}$ and $b_n^{(r,i)}$ equal to zero for $n \geqslant N+1$ we have $4N+3$ unknowns, namely, $2N\, b_1^{(r,i)} \cdots b_N^{(r,i)}$, $(2N+2)\, a_0^{(r,i)} \cdots a_N^{(r,i)}$, and the constant κ. Because the number of equations must be the same, the index n runs in the interval $1 \leqslant n \leqslant N$ in (A4) and (A6), in the interval $0 \leqslant n \leqslant N$ in (A8), and only in the interval $0 \leqslant n \leqslant N-1$ in (A9). The total number of equations is thus $4N+3$: $4N+1$ for (A4), (A6), (A8), (A9) and 2 for (A5), (A7). If we solve (A4)–(A9) for large N, we guess the form (3.18) with small $\hat{a}_n^{(r)}, \ldots, \hat{b}_n^{(i)}$ for large n. This form is also consistent with analytical investigations of (A4)–(A9) for large n. Assuming that $\hat{a}_n^{(r)}, \ldots, \hat{b}_n^{(i)}$ are zero for $n > N$, we thus obtain

$$-c_n y - (n^{-3/2} + g_n)\, z + \hat{b}_n^{(r)} - \sum_{m=0}^{N} A_{mn} \hat{a}_m^{(r)} = 0, \qquad n = 1, 2, \ldots, N \tag{A10}$$

$$\kappa - c_0 y - g_0 z - \sum_{m=0}^{N} A_m \hat{a}_m^{(r)} = 0 \tag{A11}$$

$$(e_n - n^{-1/2})\, y + 2c_n z + \sqrt{n}(\hat{b}_n^{(r)} - \hat{b}_n^{(i)}) + \sum_{m=0}^{N} (n+1/2)^{-1/2} A_{mn} (\hat{a}_m^{(r)} - \hat{a}_m^{(i)}) = 0, \qquad n = 1, 2, \ldots, N \tag{A12}$$

$$e_0 y + 2c_0 z + \sum_{m=0}^{N} (m+1/2)^{1/2} A_m (\hat{a}_m^{(r)} - \hat{a}_m^{(i)}) = -1 \tag{A13}$$

$$d_n y - [h_n + (n+1/2)^{-3/2}]\, z + \hat{a}_n^{(i)} + \sum_{m=1}^{N} B_{mn} \hat{b}_m^{(i)} = 0, \qquad n = 0, 1, 2, \ldots, N+1 \tag{A14}$$

$$[(n+1/2)^{-1/2} - f_n]\, y + 2d_n z + (n+1/2)^{1/2} (\hat{a}_n^{(r)} + \hat{a}_n^{(i)}) - \sum_{m=1}^{N} m^{1/2} B_{mn} (\hat{b}_m^{(r)} + \hat{b}_m^{(i)}) = 0, \qquad n = 0, 1, 2, \ldots, N \tag{A15}$$

The quantities c_0, c_n,..., h_n are defined by

$$
\begin{aligned}
c_0 &= \sum_{m=0}^{\infty} \frac{A_m}{m+1/2} = \frac{\pi}{2} \\
c_n &= \sum_{m=0}^{\infty} \frac{A_{mn}}{m+1/2} = 0, && n = 1, 2, 3... \\
d_n &= \sum_{m=1}^{\infty} \frac{B_{mn}}{m} = 4\pi^{-1}(2n-1)^{-2}, && n = 0, 1, 2, 3,... \\
e_0 &= \sum_{m=0}^{\infty} \frac{A_m}{m+1/2} = \pi^{-1}(2\sqrt{2}-1)\,\zeta(3/2) \\
e_n &= \sum_{m=0}^{\infty} \frac{A_{mn}}{(m+1/2)^{1/2}}, && n = 1, 2, 3,... \\
f_n &= \sum_{m=1}^{\infty} \frac{B_{mn}}{m^{1/2}}, && n = 0, 1, 2, 3,... \\
g_0 &= \sum_{m=0}^{\infty} \frac{A_m}{(m+1/2)^{3/2}} = \pi^{-1}(4\sqrt{2}-1)\,\zeta(5/2) \\
g_n &= \sum_{m=0}^{\infty} \frac{A_{mn}}{(m+1/2)^{3/2}}, && n = 1, 2, 3,... \\
h_n &= \sum_{m=1}^{\infty} \frac{B_{mn}}{m^{3/2}}, && n = 0, 1, 2, 3,...
\end{aligned}
\tag{A16}
$$

where ζ is Riemann's zeta function.

The sums not given analytically in (A16) can be calculated numerically by summation up to a large index M (e.g., 10 000) and by evaluating the remaining terms according to Euler's sum rule. Because we now have $4N+5$ unknowns (κ, y, z, $\hat{a}_0^{(r,i)} \cdots \hat{a}_N^{(r,i)}$, $\hat{b}_1^{(r,i)} \cdots \hat{b}_N^{(r,i)}$) the number of equations must also be $4N+5$. Therefore the index n in one of the equations, which we have chosen to be (A14), must run to $N+1$. By introducing proper vector and matrix notations and by using appropriate intermediate analytical steps the calculations can be reduced to one inversion of a $(N+2)\times(N+2)$ matrix plus proper multiplications instead of one inversion of a $(4N+5)\times(4N+5)$ matrix, if (A10)–(A15) had been used directly. The results for $N=100$ are given in (3.19) and Table I. The coefficients $\hat{a}_n^{(r)}$,..., $\hat{b}_n^{(i)}$ for $n>5$, not shown in the table, are less than 10^{-3}. With lesser accuracy the constant κ has been already determined in Ref. 12.

APPENDIX B

To derive (4.7), (4.8) we make a perturbation expansion in terms of $\kappa/\alpha \sim \sqrt{\gamma}$. Inserting

$$\frac{\lambda}{\gamma} \equiv A = A_0 \left(1 - \frac{\kappa}{\alpha} B\right), \qquad A_0 = A(0) \tag{B1}$$

$$\varphi(E) = \varphi^{(0)}(E) + \frac{\kappa}{\alpha} \varphi^{(1)}(E) \tag{B2}$$

into (4.2), (4.4), (4.6) we obtain in the order $(\kappa/\alpha)^0$

$$\left[\frac{d}{dE} I(E) \left(1 + \Theta \frac{d}{dE}\right) + T(E)\, A_0\right] \varphi^{(0)}(E) = 0 \tag{B3}$$

$$(1 + A_0)\, \varphi^{(0)}(E_{\min}) + \Theta \varphi^{(0)'}(E_{\min}) = 0 \tag{B4}$$

$$\varphi^{(0)}(E_0) = 0 \tag{B5}$$

and in the order $(\kappa/\alpha)^1$

$$\left[\frac{d}{dE} I(E) \left(1 + \Theta \frac{d}{dE}\right) + T(E)\, A_0\right] \varphi^{(1)}(E) = T(E)\, A_0 B \varphi^{(0)}(E) \tag{B6}$$

$$(1 + A_0)\, \varphi^{(1)}(E_{\min}) + \Theta \varphi^{(1)'}(E_{\min}) = A_0 B \varphi^{(0)}(E_{\min}) \tag{B7}$$

$$\varphi^{(1)}(E_0) = -\Theta \varphi^{(0)'}(E_0) \tag{B8}$$

Equation (B7) follows from (B6). We assume that we have solved (B3)–(B5). To find B we multiply (B6) with $\exp(E/\Theta)\, \varphi^{(0)}(E)$ and integrate the resulting equation from $E_{\min}$ to E_0

$$\int_{E_{\min}}^{E_0} e^{E/\Theta} \varphi^{(0)}(E) \left[\frac{d}{dE} I(E) \left(1 + \Theta \frac{d}{dE}\right) + T(E)\, A_0\right] \varphi^{(1)}(E)\, dE$$

$$= A_0 B \int_{E_{\min}}^{E_0} T(E)\, e^{E/\Theta} [\varphi^{(0)}(E)]^2\, dE \tag{B9}$$

In the term of the left-hand side containing the derivative of second order we perform two partial integrations, in the term containing the derivative of first order we perform one partial integration. Using $I(E_{\min}) = 0$, (B8) and (B3)–(B5) we arrive at

$$e^{E_0/\Theta} I(E_0 - 0)\, \Theta^2 [\varphi^{(0)'}(E_0 - 0)]^2 = A_0 B \int_{E_{\min}}^{E_0} T(E)\, e^{E/\Theta} [\varphi^{(0)}(E)]^2\, dE \tag{B10}$$

which together with (B1) leads immediately to (4.7), (4.8).

APPENDIX C

The eigenfunctions $\Phi(x, v)$ of the non-Hermitian operator $\mathbf{L}$ in (2.1) are normalized according to

$$\int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dx\, \Phi^{+}(x, v)\, \Phi(x, v) = 1 \tag{C1}$$

Because the eigenfunctions Φ^{+} of the adjoint operator $\mathbf{L}^{+}$ can be expressed by [see (10.164) of Ref. 9], a factor $1/N$ is, however, added here)

$$\begin{aligned} \Phi^{+}(x, v) &= \Phi(x, v)/W_{\mathrm{St}}(x, v) \\ &= (2\pi\Theta)^{1/2} \exp\{[v^2/2 + f(x)]/\Theta\}\, \Phi(x, v)/N \end{aligned} \tag{C2}$$

where N is the normalization

$$N^{-1} = \int_{-\infty}^{\infty} \exp[-f(x)/\Theta]\, dx \tag{C3}$$

Thus we may write instead of (C1)

$$(2\pi\Theta)^{1/2} N^{-1} 2 \int_{0}^{\infty} dv \int_{-\infty}^{\infty} dx \exp(E/\Theta)\, \Phi(x, v)\, \Phi(x, -v) = 1 \tag{C1'}$$

This normalization was also used in Ref. 1.

For the first odd eigenfunction we have according to (2.7), (2.11), and (3.10) for the x-independent eigenfunctions

$$\begin{aligned} \Phi(x, v) &= \pm\varphi(E), & E < E_0 \\ &= 0, & E > E_0 \end{aligned} \tag{C4}$$

where the upper sign is valid for $x > 0$ and the lower sign for $x < 0$. The boundary-layer region itself can be neglected in the normalization, because it leads to a contribution of the order $\sqrt{\gamma^2} = \gamma$. Inserting (C4) into (C1') introducing the variables E and x instead of v and x and using (2.16), (2.19) we thus arrive at the normalization condition

$$(2\pi\Theta)^{1/2} N^{-1} \int_{E_{\min}}^{E_0} T(E)\, \varphi^2(E) \exp(E/\Theta)\, dE = 1 \tag{C5}$$

REFERENCES

1. K. Voigtlaender and H. Risken, *J. Stat. Phys.* **40**:397 (1985).
2. H. Haken, *Synergetics, An Introduction*, 3rd ed., Springer Series in Synergetics, Vol. 1 (Springer, New York, 1983), Chap. 7.4.

3. H. A. Kramers, *Physica* 7:284 (1940).
4. R. L. Stratonovich, *Topics in the Theory of Random Noise*, Vols. I and II (Gordon & Breach, New York, 1963 and 1967).
5. B. J. Matkowsky, Z. Schuss, and E. Ben-Jacob, *J. Appl. Math.* **42**:835 (1982).
6. (a) B. Carmeli and A. Nitzan, *J. Chem. Phys.* **79**:393 (1983); (b) B. Carmeli and A. Nitzan, *J. Chem. Phys.* **80**:3596 (1984).
7. M. Büttiker, E. Harris, and R. Landauer, *Phys. Rev. B* **28**:1268 (1983).
8. (a) M. Büttiker and R. Landauer, *Phys. Rev. B* **30**:1551 (1984); (b) M. Büttiker, *Proceedings of the 17th International Conference on Low Temperature Physics*, U. Eckern, A. Schmid, W. Weber, and H. Wühl, eds. (North-Holland, Amsterdam, 1984).
9. H. Risken, *The Fokker–Planck Equation*, Springer Series in Synergetics, Vol. 18 (Springer, New York, 1984).
10. K. Voigtlaender and H. Risken, *Chem. Phys. Lett.* **105**:506 (1984).
11. A. Sommerfeld, *Partielle Differentialgleichungen der Physik*, Vol. VI, 6th edition (Akademische Verlagsanstalt, Leipzig, 1966); see also A. Sommerfeld, *Partial Differential Equations in Physics*, Vol. VI, 4th printing, E. G. Straus, transl. (Academic Press, New York, 1967).
12. H. Risken and H. D. Vollmer, *Z. Phys. B* **35**:177 (1979).
13. M. A. Burschka and U. M. Titulaer, *J. Stat. Phys.* **25**:569 (1981); J. V. Selinger and U. M. Titulaer, *J. Stat. Phys.* **36**:293 (1984).
14. A. Zygmund, *Trigonometric Series*, Vol. 1 (Cambridge University Press, Cambridge, 1968).
15. P. Jung and H. Risken, *Z. Phys. B* **54**:357 (1984).
16. I. S. Gradstheyn and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1965), pp. 905, 906.
17. Y. Onodera, *Progr. Theor. Phys.* **44**:1477 (1970).
18. H. Risken and H. D. Vollmer, unpublished calculations.
19. H. D. Vollmer and H. Risken, *Physica* **110A**:106 (1982).
20. W. Renz, *Z. Phys. B* **59**:91 (1985).
21. M. Büttiker and R. Landauer, *Phys. Rev. Lett.* **52**:1250 (1984).
22. B. Carmeli and A. Nitzan, *Phys. Rev. Lett.* **52**:1251 (1984).
23. P. Hänggi, *J. Stat. Phys.* **42**:1 (1986).
24. J. L. Skinner and P. G. Wolynes, *J. Chem. Phys.* **69**:2143 (1978); *J. Chem. Phys.* **72**:4913 (1980).