Journal of Statistical Physics, Vol. 36, Nos. 1/2, 1984

Diffusion in a Bistable Potential at Intermediate and High Friction

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Received July 25, 1983; revisions received November 14, 1983 and February 3, 1984

We study the motion of a Brownian particle in a bistable potential for intermediate and high-friction γ. Following ideas of Titulaer we perform a high-friction expansion of the distribution function $P(v, x, t)$ in velocity and space. We show (for arbitrary potential) that the expansion coefficients obey simple recursion relations, which allow them to be calculated easily. When terms of order γ^{-5} are neglected the resulting differential equations can be transformed into Hermitian Schrödinger-type equations. Using the WKB technique we solve these equations analytically for the case of the bistable potential and discuss the various time regimes involved in the system, in particular we show that the final approach to equilibrium is governed by the Kramers rate. Our results become exact in the limit of low temperatures.

KEY WORDS: Nonlinear Fokker–Planck–Klein–Kramers equation; inverse friction expansion; diffusion.

1. INTRODUCTION

Brownian particles in external potentials represent model systems for a large number of interesting physical, chemical, and biological systems (for reviews see Refs. 1 and 2). It is generally assumed that the distribution function $P(v, x, t)$ of the velocity (v) and position (x) of a particle with mass m is described by the Fokker–Planck–Klein–Kramers (FPKK) equation

$$\frac{\partial P(v,x,t)}{\partial t} = L(v,x)P(v,x,t) \tag{1.1a}$$

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with the Liouville operator

$$L(v,x) \equiv \gamma\left(\frac{k_B T}{m} \frac{\partial^2}{\partial v^2} + \frac{\partial}{\partial v} v \right) - v \frac{\partial}{\partial x} + \frac{1}{m} \phi'(x) \frac{\partial}{\partial v} \qquad (1.1b)$$

Here, $\phi'(x) \equiv d\phi(x)/dx$ denotes the first derivative of the external potential $\phi(x)$, γ is the friction constant, and T is the temperature of the surrounding heat bath.

In the high-friction limit the distribution function in position space,

$$P_0(x,t) \equiv \int_{-\infty}^{+\infty} P(v,x,t)\, dv \qquad (1.2)$$

satisfies the Smoluchowski equation

$$\frac{\partial P_0(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{\phi'(x)}{m\gamma} P_0(x,t) \right] + \frac{k_B T}{m\gamma} \frac{\partial^2}{\partial x^2} P_0(x,t) \qquad (1.3)$$

Using the transformation

$$P_0(x,t) = \exp\left[-\phi(x)/(2k_B T) \right] \psi(x,t) \qquad (1.4)$$

Equation (1.3) takes the Schrödinger-like form

$$-\frac{k_B T}{m\gamma} \frac{\partial \psi(x,t)}{\partial t} = S(x)\psi(x,t) \qquad (1.5)$$

where

$$S(x) \equiv -\left(\frac{k_B T}{m\gamma} \right)^2 \frac{\partial^2}{\partial x^2} + V(x) \qquad (1.6)$$

and

$$V(x) \equiv \frac{1}{4}\left[\frac{\phi'(x)}{m\gamma} \right]^2 - \frac{1}{2} \frac{k_B T}{m\gamma} \frac{\phi''(x)}{m\gamma} \qquad (1.7)$$

Now the problem of calculating $P_0(x,t)$ is reduced to the problem of finding the eigenvalues λ_n and normalized eigenfunctions $\varphi_n(x)$ of the associated stationary equation

$$S(x)\varphi_n(x) = \lambda_n \varphi_n(x) \qquad (1.8)$$

λ_n and $\varphi_n(x)$ determine $P_0(x,t)$ according to

$$P_0(x,t) = \exp\left[-\phi(x)/(2k_B T) \right] \sum_{n=0}^{\infty} b_n \varphi_n(x) \exp(-\lambda_n t/k_B T) \qquad (1.9)$$

The coefficients b_n are obtained from the initial conditions.

For harmonically bound particles (1.8) is equivalent to the corresponding quantum mechanical problem, which can be solved exactly. For anharmonic potentials standard quantum mechanical methods have been employed. For the case of particles in a bistable potential, for example, perturbational and variational approaches (see, e.g., Refs. 2–6) as well as WKB treatments[7] have been used to study $P_0(x,t)$. In particular the WKB treatment has been applied to calculate φ_n and λ_n analytically; the calculations could be extended also to the case of a time-dependent bistable potential.[8] In both cases, the resulting distribution function was exact up to exponentially small errors for temperatures low compared with the potential barrier. Other nonlinear potentials, e.g., a sinusoidal potential, can be treated analytically in the same manner.

In contrast to the situation described above for the high-friction limit, analytical results are rare for lower friction. Up to now, only the case of harmonically bound particles could be treated analytically[9] in the whole friction regime. It is the purpose of this paper to present analytical results for the bistable potential in the intermediate-friction regime, when the temperature is low compared with the potential barrier.

Following ideas of Titulaer,[10] we first perform a high-friction expansion in the spirit of the Chapman–Enskog procedure and derive recursion relations for the expansion coefficients. We show explicitly, how the resulting differential equations can be transformed into Hermitian Schrödinger-type equations, thereby generalizing (1.4)–(1.8) to the intermediate-friction regime. We solve these equations for the case of the bistable potential using the WKB technique.

2. THEORY

2.1. The Inverse Friction Expansion

For high-friction γ, the term

$$\gamma C(v) \equiv \gamma\left(\frac{k_B T}{m}\frac{\partial^2}{\partial v^2} + \frac{\partial}{\partial v}v\right) \tag{2.1}$$

is dominant in (1.1b). Therefore it is convenient to expand $P(v,x,t)$ in terms of the eigenfunctions $\chi_n(v)$ of $C(v)$. Introducing the operators

$$a^+ = -(m\beta)^{-1/2}\partial/\partial v, \qquad a = (m\beta)^{-1/2}\partial/\partial v + (m\beta)^{1/2}v \tag{2.2}$$

with $\beta \equiv 1/k_B T$ and $[a,a^+]=1$ we find $C(v) \equiv -a^+a$, which has the eigenvalues $-n$ $(n=0,1,2,\ldots)$ and the associated eigenfunctions

$$\chi_n(v) = \frac{H_n\left((m\beta/2)^{1/2}v\right)}{n!\,2(2m\beta)^{(n-1)/2}}\exp\left(-\frac{m\beta}{2}v^2\right) \tag{2.3}$$

H_n are the usual Hermite polynomials. The operators a and a^+ act on $\chi_n(v)$ according to

$$a^+\chi_n(v) = (n+1)\chi_{n+1}(v), \qquad a\chi_n(v) = \chi_{n-1}(v) \tag{2.4}$$

where we have used the convention $\chi_k(v) \equiv 0$ for $k < 0$. Our basis set χ_n is nonorthogonal. It may be associated with the basis set $\tilde{\chi}_n$ of the adjoint[3] operator $C^{\dagger}$, both form a biorthonormal set. The position-dependent part in (1.1b) is conveniently expressed by the operators

$$d^{+} = -(m\beta)^{-1/2}\partial/\partial x, \qquad d = (m\beta)^{-1/2}\partial/\partial x + (\beta/m)^{1/2}\partial\phi(x)/\partial x \tag{2.5}$$

with $[d, d^{+}] = \phi''(x)/m$. a^{+} and a as well as d^{+} and d are adjoint with respect to the scalar product

$$\langle f | g \rangle = \int dv \int dx \exp\left[\beta\left(\frac{m}{2} v^2 + \phi(x) \right) \right] f^*(v,x) g(v,x) \tag{2.6}$$

In terms of a, a^{+}, d, d^{+} the Liouvillian (1.1b) becomes simply

$$L = -\gamma a^{+} a + d^{+} a - d a^{+} \tag{2.7}$$

$P(v,x,t)$ can be expanded[4] according to[(10)]

$$P(v,x,t) = \sum_n P_{[n]}(v,x,t) \tag{2.8a}$$

where

$$P_{[n]}(v,x,t) = c_{[n]}(x,t)\chi_n(v) + \sum_{i=1}^{\infty} \gamma^{-i} P_{[n]}^{[i]}(v,x,t) \tag{2.8b}$$

are solutions of (1.1a, b). By construction, the coefficients $P_{[n]}^{[i]}$ of the inverse friction expansion (2.8b) are orthogonal to $\tilde{\chi}_n(v)$. The function $c_{[n]}(x,t)$ and $P_{[n]}^{[i]}(v,x,t)$ have to be determined. Following the lines of the Chapman–Enskog–procedure expressions for $c_{[n]}(x,t)$ and $P_{[n]}^{[i]}$ valid up to $\mathscr{O}(\gamma^{-5})$ have been derived by Titulaer.[(10)] The treatment which we give here follows essentially the ideas of Titulaer, but in addition we show explicitly how the various expansion coefficients are related to each other and which are the recursion relations they follow. We expand $P_{[n]}^{[i]}(v,x,t)$ in terms of $\chi_l(v)$ $(l \neq n)$ according to

$$P_{[n]}^{[i]}(v,x,t) = \sum_{l=0}^{\infty} \chi_l(v) \mathscr{O}_{[l][n]}^{[i]}(x) c_{[n]}(x,t), \qquad i = 1,2,3,\ldots \tag{2.9}$$

Here, $c_{[n]}(x,t)$ is the same function as in (2.8); the matrix elements $\mathscr{O}_{[l][n]}^{[i]}(x)$ are operators which act on $c_{[n]}(x,t)$. By definition, for $i \neq 0$, $\mathscr{O}_{[l][l]}^{[i]} \equiv 0$. When $i = 0$ we define $\mathscr{O}_{[l][n]}^{[0]} \equiv \delta_{ln}$. The time evolution of $c_{[n]}(x,t)$ is governed by the expansion

$$\frac{\partial c_{[n]}(x,t)}{\partial t} = \left(-n\gamma + \sum_{i=0}^{\infty} \gamma^{-i} \partial_{[n]}^{[i]}(x) \right) c_{[n]}(x,t) \tag{2.10}$$

[3] Adjoint with respect to the ordinary scalar product $\int f^* g\, dx\, dv$ and noted †.

[4] The notation [ ] marks those indices which refer to the inverse friction expansion.

where $\partial_{[n]}^{[i]}(x)$ are also operators acting on $c_{[n]}(x,t)$. For determining $\mathscr{O}_{[l][n]}^{[i]}$ and $\partial_{[n]}^{[i]}$ we insert (2.8b) with (2.9) and (2.10) into (1.1b) using (2.7) and utilize the relations (2.4) and the biorthonormality between χ_n and $\tilde{\chi}_n$. Then by comparing the coefficients of γ^0 we find

$$\partial_{[n]}^{[0]} = 0, \qquad \mathscr{O}_{[n+l][n]}^{[1]} = -\delta_{l,1}(n+1)d - \delta_{l,-1}d^{+} \tag{2.11}$$

where δ_{ln} denotes the Kronecker symbol.

Comparing the coefficients of γ^{-p}, $p = 1,2,3,\ldots,$ we obtain the recursion relations:

$$\partial_{[n]}^{[p]} = -n\, d\mathscr{O}_{[n-1][n]}^{[p]} + d^{+}\mathscr{O}_{[n+1][n]}^{[p]} \tag{2.12a}$$

$$l\mathscr{O}_{[n+l][n]}^{[p+1]} = -\left(\sum_{i=0}^{p} \mathscr{O}_{[n+l][n]}^{[i]}\partial_{[n]}^{[p-i]}\right) - (n+l)\, d\mathscr{O}_{[n+l-1][n]}^{[p]} + d^{+}\mathscr{O}_{[n+l+1][n]}^{[p]} \tag{2.12b}$$

As $\mathscr{O}_{[n][m]}^{[0]} = \delta_{nm}$, (2, 12a) and (2.11) are particular cases of (2.12b) for $l = 0$ and $p = 0$, respectively. This recursion formula can be equally derived from a general perturbation treatment which has been detailed by Titulaer.[11] The derivation starting from formula (3.17a) in Ref. 11 is straightforward but too lengthy and we do not give it here. From the recursion relation $\partial_{n}^{[p]}$ and $\mathscr{O}_{[n+l][n]}^{[p]}$ can be obtained easily for arbitrary p, n, l. We find

$$p = 1: \quad \partial_{[n]}^{[1]} = -d^{+}d + n\frac{\phi''}{m} \equiv \frac{\partial^2}{\partial x^2} + \frac{\phi'}{m}\frac{\partial}{\partial x} + (n+1)\frac{\phi''}{m} \tag{2.13a}$$

$$\mathscr{O}_{[n+l][n]}^{[2]} = \delta_{l,2}\binom{n+2}{2}d^2 + \delta_{l,-2}\frac{1}{2!}(d^{+})^2 \tag{2.13b}$$

$$p = 2: \quad \partial_{[n]}^{[2]} \equiv 0 \tag{2.14a}$$

$$\begin{aligned}\mathscr{O}_{[n+l][n]}^{[3]} = {} & -\delta_{l,3}\binom{n+3}{3}d^3 \\ & + \delta_{l,1}(n+1)\left[nd^2d^{+} - (n+1)dd^{+}d + \frac{n+2}{2}d^{+}d^2\right] \\ & + \delta_{l,-1}\left[(n+1)(d^{+})^2d - nd^{+}dd^{+} - \frac{n-1}{2}d(d^{+})^2\right] \\ & - \delta_{l,-3}\frac{1}{3!}(d^{+})^3\end{aligned} \tag{2.14b}$$

$$\begin{aligned}p = 3: \quad \partial_{[n]}^{[3]} = {} & \frac{(n+1)(n+2)}{2}(d^{+})^2d^2 - (n+1)^2(d^{+}d)^2 \\ & + n(n+1)\left[d^{+}d^2d^{+} - d(d^{+})^2d\right] \\ & + n^2(dd^{+})^2 - \frac{n(n-1)}{2}d^2(d^{+})^2\end{aligned} \tag{2.15}$$

etc. From the general structure of the recursion relations we see that

$$\mathscr{O}^{[p]}_{[n+p-1][n]}, \quad \mathscr{O}^{[p]}_{[n+p-3][n]}, \ldots, \mathscr{O}^{[p]}_{[n-p+3][n]}, \quad \mathscr{O}^{[p]}_{[n-p+1][n]}$$

and $\partial^{[2p]}_{[n]}$ are zero operators.

The operator $\partial^{[1]}_{[n]}$ is Hermitian. For $n = 0$ it is precisely the usual Smoluchowski operator [see the right-hand side of (1.3)]. In contrast, $\partial^{[3]}_{[n]}$ is non-Hermitian, but is reducible to the quadratic form in d and d^+ as will be shown below [formula (2.25)].

2.2. Treatment of the Initial Value Problem

In the inverse friction expansion the problem to solve the complicated FPKK equation is reduced to the problem of solving the equation (2.10) for $c_{[n]}(x, t)$. The initial values $c_{[n]}(x, 0)$ are determined by the initial distribution $P(v, x, 0)$. Titulaer has given an explicit expression for $c_{[0]}(x, 0)$. We will show here that a compact straightforward derivation of all $c_{[n]}(x, 0)$ is possible in the frame of the $\mathscr{O}$ operators. A general initial condition can be written in the form

$$P(v, x, 0) = \sum_{l=0}^{\infty} a_{[l]}(x)\chi_l(v) \tag{2.16}$$

On the other hand, within the inverse friction expansion, $P(v, x, 0)$ is given by

$$P(v, x, 0) = \sum_{i=0}^{\infty} \gamma^{-i} \sum_{l,n} \chi_l(v)\mathscr{O}^{[i]}_{[l][n]}(x)c_{[n]}(x, 0) \tag{2.17}$$

Following Titulaer we expand $c_{[n]}(x, 0)$ according to

$$c_{[n]}(x, 0) = a_{[n]}(x) + \sum_{i=1}^{\infty} \gamma^{-i} c^{[i]}_{[n]}(x) \tag{2.18}$$

Inserting (2.18) into (2.17) and using the biorthonormality between $\{\chi_n\}$ and $\{\tilde{\chi}_n\}$ we obtain by comparing the coefficients of γ^{-p} in (2.17) and (2.16)

$$c^{[p]}_{[m]}(x) = -\mathscr{O}^{[p]}_{[m][n]} a_{[n]}(x) - \sum_{i=1}^{p-1} \mathscr{O}^{[i]}_{[m][n]} c^{[p-i]}_{[n]}(x), \qquad p = 1, 2, 3, \ldots \tag{2.19}$$

where the summation convention (on n) has been used. Equation (2.19) represents a recursion relation for $c^{[p]}_{[m]}(x)$. For $p = 1, 2, 3$ we obtain simply

$$\begin{aligned}
c^{[1]}_{[m]}(x) &= -\mathscr{O}^{[1]}_{[m][n]} a_{[n]}(x) \\
c^{[2]}_{[m]}(x) &= \left(-\mathscr{O}^{[2]}_{[m][n]} + \mathscr{O}^{[1]}_{[m][l]} \mathscr{O}^{[1]}_{[l][n]}\right) a_{[n]}(x) \\
c^{[3]}_{[m]}(x) &= \left(-\mathscr{O}^{[3]}_{[m][n]} + \mathscr{O}^{[1]}_{[m][l]} \mathscr{O}^{[2]}_{[l][n]} + \mathscr{O}^{[2]}_{[m][l]} \mathscr{O}^{[1]}_{[l][n]}\right. \\
&\quad \left. - \mathscr{O}^{[1]}_{[m][l]} \mathscr{O}^{[1]}_{[l][l']} \mathscr{O}^{[1]}_{[l'][n]}\right) a_{[n]}(x)
\end{aligned} \tag{2.20}$$

where again the summation convention for the lower indices has been employed.

2.3. Normalization

The distribution function must satisfy the normalization condition

$$\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dv\, P(v, x, t) \equiv 1 \tag{2.21}$$

for all times. Inserting (2.8a, b) and (2.9) into (2.21) and using the relation

$$\int_{-\infty}^{+\infty} dv\, \chi_n(v) = \delta_{n,0} \tag{2.22}$$

we find from (2.21)

$$\int_{-\infty}^{+\infty} dx\, c_{[0]}(x, t) + \sum_{n=1}^{\infty} \sum_{i=1}^{\infty} \gamma^{-i} \int_{-\infty}^{+\infty} dx\, \mathscr{O}^{[i]}_{[0][n]} c_{[n]}(x, t) \tag{2.23}$$

The recursion relation (2.12b) gives

$$\mathscr{O}^{[i]}_{[0][n]} = -\frac{1}{n} d^{+} \mathscr{O}^{[i-1]}_{[1][n]} + \frac{1}{n} \sum_{j=0}^{i-1} \mathscr{O}^{[j]}_{[0][n]} \partial^{[i-j-1]}_{[n]}$$

Since $\mathscr{O}^{[1]}_{[0][n]} = -\delta_{n,1} d^{+}$, the above relation implies that d^{+} is a left factor for every $\mathscr{O}^{[i]}_{[0][n]}$. Consequently, as $d^{+} \equiv -(m\beta)^{-1/2}\partial/\partial x$, the second term of (2.23) vanishes when $c_{[n]}(x, t)$ decreases rapidly enough at infinity. This is the case for the bistable potential. Thus, (2.21) implies the important normalization condition

$$\int_{-\infty}^{+\infty} dx\, c_{[0]}(x, t) \equiv 1 \tag{2.24}$$

2.4. The General Solution

In the previous sections we have detailed the inverse friction expansion and the recursion relations for the expansion coefficients as well as the treatment of the initial conditions and the normalization condition for $c_{[0]}(x,t)$. For finding explicitly the distribution function valid up to a certain order p in $1/\gamma$ one has to perform the following steps:

(1) Using the recursion relations (2.12a, b) the differential equations [up to $O(\gamma^{-p})$] for $c_{[n]}(x,t)$ have to be specified. Instead of calculating $c_{[n]}(x,t)$ subject to certain initial conditions $c_{[n]}(x,0)$ it is convenient to determine the corresponding propagator $c_{[n]}(x,t\,|\,x_s,0)$, which is the solution of (2.10) with the initial conditions $c_{[n]}(x,0\,|\,x_s,0)=\delta(x-x_s)$; $c_{[0]}(x,t\,|\,x_s,0)$ must be normalized for all times.

(2) Then for a given initial condition $P(v,x,0)$ the corresponding values of $c_{[n]}(x,0)$ must be determined from the recursion relations (2.19) up to $O(\gamma^{-p})$. The relations yield the functions $c_{[m]}^{[1]}(x), c_{[m]}^{[2]}(x),\ldots, c_{[m]}^{[p]}(x)$, which give $c_{[n]}(x,0)$ up to order γ^{-p}. Finally, $c_{[n]}(x,t)$ is obtained from the propagator by

$$c_{[n]}(x,t)=\int_{-\infty}^{+\infty}dx_s\,c_{[n]}(x,t\,|\,x_s,0)c_{[n]}(x_s,0)$$

(3) As the final step, $c_{[n]}(x,t)$ has to be inserted in (2.9) with $i=1,2,\ldots,p$ and the corresponding differentiations $\mathscr{O}_{[l][n]}^{[i]}c_{[n]}(x,t)$ must be performed. Using (2.8a, b) we obtain $P(v,x,t)$ up to $O(\gamma^{-p})$.

It is obvious that the main difficulty is to solve the differential equations for $c_{[n]}(x,t)$ up to the given order p in $1/\gamma$, step (1). Steps (2) and (3) are comparatively trivial. Therefore, in this paper we will restrict our attention to step (1) and derive analytical results for the propagators $c_{[n]}(x,t\,|\,x_s,0)$. We will choose $p=5$ which corresponds to a regime ranging from intermediate to high friction.

First we present the general method for solving the differential equations for arbitrary external potential and then we will consider as a particular example the bistable potential.

When terms of order γ^{-5} are neglected, the final equation for $c_{[n]}(x,t)$ becomes

$$\begin{aligned}\frac{\partial c_{[n]}(x,t)}{\partial t}=&\Bigg\{-n\gamma-\frac{1}{\gamma}d^{+}\left(1+\frac{\phi''(x)}{m\gamma^2}\right)d\\&+\frac{n}{m\gamma}\left[\phi''(x)\left(1+\frac{\phi''(x)}{m\gamma^2}\right)-\frac{1}{2}\,\frac{n-1}{m\beta\gamma^2}\,\phi^{\mathrm{IV}}(x)\right]\\&-\frac{n(m\beta)^{-1/2}}{m\gamma^3}\left[-(n+2)d^{+}\phi''(x)+n\phi'''(x)d\right]+\mathscr{O}(\gamma^{-5})\Bigg\}\\&\times c_{[n]}(x,t)\end{aligned}\tag{2.25}$$

Equation (2.25) is quadratic in d and d^+ and is clearly non-hermitian with respect to the scalar product defined in (2.6). Up to the coefficient of $\phi^{IV}(x)$ it agrees with Titulaer's result. By definition we have $c_{[0]}(x,t) \equiv P_0(x,t) + O(e^{-\gamma t})$. Setting $n = 0$ Eq. (2.25) represents an extension of the Smoluchowski equation into the intermediate friction regime; see also refs. 12–15. For $n = 1, 2, \ldots$ the equation looks considerably more complicated than for $n = 0$. However, as we will show in the following, (2.25) can be handled for all n on the same footing without difficulties.

For solving (2.25) we suggest the transformation

$$\psi_{[n]}(x,t) = \exp(\beta G_{[n]}(x))c_{[n]}(x,t) \tag{2.26}$$

which is similar to (1.4), and introduce a new potential function $\tilde{\phi}_{[n]}(x)$. We will choose $G_{[n]}(x)$ and $\tilde{\phi}_{[n]}(x)$ such that $\psi_{[n]}(x,t)$ satisfies a Schrödinger-type equation. To facilitate the derivation we introduce operators A_n and $A_n^\dagger$ which are Hermitian with respect to the ordinary scalar product $(f, g) \equiv \int f^*(x)g(x)\,dx$:

$$A_n^\dagger = -(m\beta)^{-1/2}\partial/\partial x + (m\beta)^{1/2}\tilde{\phi}'_{[n]}(x)/(2m) \tag{2.27a}$$

$$A_n = (m\beta)^{-1/2}\partial/\partial x + (m\beta)^{1/2}\tilde{\phi}'_{[n]}(x)/(2m) \tag{2.27b}$$

Using the identity

$$\partial/\partial x \equiv \exp(-\beta G_{[n]})(\partial/\partial x - \beta G'_{[n]})\exp(\beta G_{[n]})$$

the operators d and d^+ can be conveniently expressed by A_n and $A^\dagger{}_n$:

$$d^+ = \exp(-\beta G_{[n]})\left[A_n^\dagger + (\beta/m)^{1/2}(G'_{[n]} - \tilde{\phi}'_{[n]}/2)\right]\exp(\beta G_{[n]}) \tag{2.28a}$$

$$d = \exp(-\beta G_{[n]})\left[A_n + (\beta/m)^{1/2}(\phi' - G'_{[n]} - \tilde{\phi}'_{[n]}/2)\right]\exp(\beta G_{[n]}) \tag{2.28b}$$

Inserting (2.28a, b) into (2.25) we obtain immediately a differential equation for $\psi_{[n]}(x,t)$ where operators $A^\dagger{}_n A_n$, $A^\dagger{}_n$, and A_n act on $\psi_{[n]}(x,t)$. Now we choose $\phi_{[n]}(x)$ and $G_{[n]}(x)$ such that the coefficients of the terms linear in A and $A^\dagger$ vanish identically. The result is

$$G_{[n]}(x) = \phi(x)/2 - \beta^{-1}(n^2 + n - 1/2)\ln g(x) \tag{2.29a}$$

$$\tilde{\phi}_{[n]}(x) = \phi(x) - \beta^{-1}(2n + 1)\ln g(x) \tag{2.29b}$$

where $g(x) \equiv 1 + \phi''(x)/m\gamma^2$. Irrelevant additive constants have been dropped in (2.29a, b).

This derivation supposes here $g(x)$ to be positive definite so that the friction coefficient must satisfy,

$$\gamma^2 \geqslant -\inf\left(\frac{\phi''}{m}\right) \tag{2.29c}$$

Finally we obtain

$$\frac{\partial\psi_{[n]}(x,t)}{\partial t}=\left[-n\gamma+\frac{n}{m\gamma}\phi''(x)g(x)+\frac{n(1-n)}{2m^2\beta\gamma^3}\phi^{\mathrm{IV}}(x)\right.$$
$$\left.-\frac{1}{\gamma}g(x)A_n^\dagger A_n+\mathscr{O}(\gamma^{-5})\right]\psi_{[n]}(x,t) \tag{2.30}$$

To simplify (2.30) further we multiply both sides from left with $(1-\phi''(x)/m\gamma^2)$ and express A_n and $A^\dagger{}_n$ by (2.27a, b) with (2.29a, b). Then we introduce the reduced quantities

$$U(x)\equiv\phi(x)/m\gamma,\qquad \tilde{U}_{[n]}(x)\equiv\tilde{\phi}_{[n]}(x)/m\gamma,\qquad \theta\equiv k_BT/m\gamma \tag{2.31}$$

and obtain from (2.30) in the intermediate-friction regime, neglecting $O(\gamma^{-5})$ terms:

$$-\left[1-\frac{1}{\gamma}U''(x)\right]\theta\frac{\partial\psi_{[n]}(x,t)}{\partial t}=\{n\gamma\theta+S_{[n]}(x)\}\psi_{[n]}(x,t) \tag{2.32a}$$

where $S_{[n]}(x)$ is a Schrödinger-type operator,

$$S_{[n]}(x)=-\theta^2\frac{\partial^2}{\partial x^2}+V_{[n]}(x) \tag{2.32b}$$

with an effective potential $V_{[n]}(x)$, given by

$$V_{[n]}(x)=(\tilde{U}'_{[n]}(x))^2/4-(\theta/2)\tilde{U}''_{[n]}(x)-2n\theta U''(x)$$
$$+\frac{1}{2\gamma}n(1-n)\theta^2U^{\mathrm{IV}}(x) \tag{2.32c}$$

Equations (2.32a–c) generalize (1.5)–(1.7) in a straightforward manner. For $n=0$ the operator $S_{[0]}(x)$ becomes identical to $S(x)$, when $\tilde{U}_{[0]}(x)\equiv\tilde{\phi}_{[0]}(x)/m\gamma$ is substituted by $U(x)$. Therefore the eigenfunctions $\varphi_{[0]p}(x)$ and eigenvalues $\lambda_{[0]p}$ of the eigenvalue equation

$$S_{[n]}(x)\varphi_{[n]p}(x)=\lambda_{[n]p}\varphi_{[n]p}(x) \tag{2.33}$$

with $n=0$ can be directly obtained from those of (1.8) when the potential function $U(x)$ is substituted by $\tilde{U}_{[0]}(x)$ from (2.29b). Consequently, $\lambda_{[0]0}=0$ and $\varphi_{[0]0}(x)\sim\exp(-\tilde{U}_{[0]}(x)/2\theta)$ solve (2.33), and (2.32a) has the time-independent solution $\psi_{[0]}(x,t)=\varphi_{[0]0}(x)$, leading to the correct equilibrium state $P_0(x,t)\sim\exp[-U(x)/\theta]$ for $t\to\infty$.

For solving (2.32a–c) in general we expand $\psi_{[n]}(x,t)$ in terms of the eigenvalues $\lambda_{[n]p}$ and eigenfunctions $\varphi_{[n]p}(x)$ of (2.33):

$$\psi_{[n]}(x,t)=\sum_p\varphi_{[n]p}(x)\kappa_{[n]p}(t)\exp\left[-(n\gamma+\lambda_{[n]p}/\theta)t\right] \tag{2.34}$$

and determine the expansion coefficients $\kappa_{[n]p}(t)$ from (2.32a). We obtain

$$\dot{\kappa}_{[n]p}(t) = \sum_p \frac{F_{[n]pq}}{\gamma} e^{(\lambda_{[n]p} - \lambda_{[n]q})t/\theta} \left[\dot{\kappa}_{[n]q}(t) - \left(n\gamma + \frac{\lambda_{[n]q}}{\theta} \right) \kappa_{[n]q}(t) \right] \tag{2.35a}$$

where

$$F_{[n]pq} \equiv \int_{-\infty}^{+\infty} dx\, \varphi^*_{[n]p}(x)\, U''(x) \varphi_{[n]q}(x) \tag{2.35b}$$

In the high-friction limit the right-hand side of (2.35a) vanishes for $n = 0$ and we obtain $\kappa_{[0]p}(t) \equiv \kappa_{[0]p}(0)$.

For the particular case that the matrix elements $F_{[n]pq}$ are diagonal in p and q Eq. (2.35a) simplifies considerably. [See below, formulas (3.7), (3.8), and (3.20).] Then (2.35a) is solved by

$$\kappa_{[n]q}(t) = \kappa_{[n]q}(0) \exp\left[- \frac{F_{[n]q}/\gamma}{1 - F_{[n]q}/\gamma} (n\gamma + \lambda_{[n]q}/\theta) t \right] \tag{2.36}$$

The initial values $\kappa_{[n]q}(0)$ have to be determined from the initial conditions for $P(v, x, t)$. Inserting (2.36) into (2.34) we obtain

$$\psi_{[n]}(x, t) = \sum_p \varphi_{[n]p}(x) \kappa_{[n]p}(0) \exp(-t/\tau_{[n]p}) \tag{2.37a}$$

where

$$\tau_{[n]p} = \left[(n\gamma + \lambda_{[n]p}/\theta)/(1 - F_{[n]p}/\gamma) \right]^{-1} \tag{2.37b}$$

are the characteristic times for the evolution of $P(v, x, t)$ in the intermediate friction regime if F is diagonal. To be consistent with (2.25) the terms of $O(\gamma^{-5})$ have to be neglected in (2.37b).

$\tau_{[n]p}$ must be positive, which implies $F_{[n]p} < \gamma$. This condition is always fulfilled when

$$\sup(U''(x)) < \gamma. \tag{2.37c}$$

Inequalities (2.29c) and (2.37c) represent bounds to the intermediate friction regime.

3. THE BISTABLE POTENTIAL

As a nontrivial application of the formalism developed in the preceding section we consider the motion of a Brownian particle in a bistable potential. The potential $U(x)$ consists of two wells at x_1 and x_2 with depths

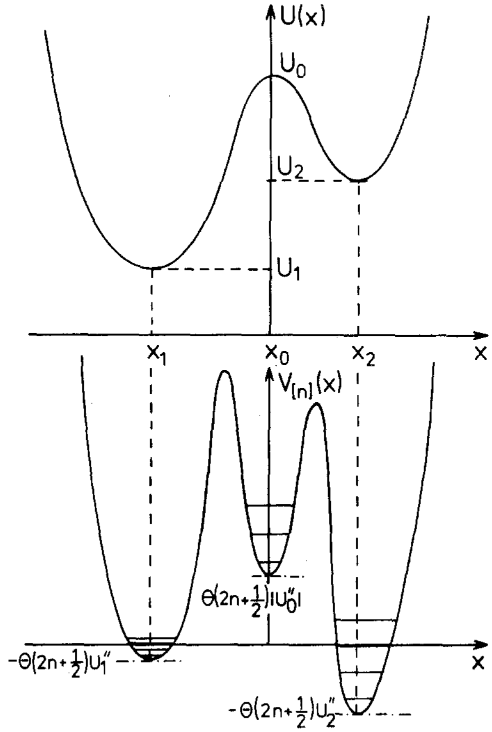

Fig. 1. $U(x)$ and $V(x)$ versus x. For illustration, the energy levels given in (3.3a–c) are drawn into $V_{[n]}(x)$ for $n = 1$.

U_1 and U_2 and curvatures U_1'' and U_2''. Both wells are separated by a barrier at $x_0 = 0$ with altitude U_0 and curvature U_0''. Inequalities (2.29c) and (2.37c) imply $|U_\alpha''| < \gamma$, $\alpha = 0, 1, 2$. In the following we will restrict ourselves to temperatures θ low compared with the barrier heights $\Delta U_1 \equiv U_0 - U_1$ and $\Delta U_2 \equiv U_0 - U_2$. Then $V_{[n]}(x)$ is mainly determined by the term $(\tilde{U}_{[n]}'(x)/2)^2$ and shows three minima which are located close to the three extrema of $U(x)$ (see Fig. 1). For calculating the eigenvalues and eigenfunctions of $V_{[n]}(x)$ we shall use the WKB approximation. We follow essentially the treatment which has been elaborated by Caroli et al.[7] when considering the diffusion in a bistable potential in the high friction limit but limit ourselves in this paper to initial distributions located close to the minima of wells 1 and 2, where $V_{[n]}(x)$ can be approximated by harmonic potential wells. In order to be consistent with the WKB approximation we need to know the characteristic parameters of $V_{[n]}$ (position $\tilde{x}_\alpha$ of the minima, values of $V_{[n]}$ and of its curvatures at the minima) to lowest order in $\theta/\Delta U_\alpha$. We find

$$\tilde{x}_\alpha = x_\alpha + O\left(\frac{\theta}{\Delta U_\alpha}\right) \tag{3.1a}$$

$$V_{[n]}(x_\alpha) = -\frac{4n+1}{2}\theta U_\alpha'' + O\left(\left(\frac{\theta}{\Delta U_\alpha}\right)^2\right) \tag{3.1b}$$

$$V_{[n]}''(x_\alpha) = \frac{1}{2}(U_\alpha'')^2 + O\left(\frac{\theta}{\Delta U_\alpha}\right) \tag{3.1c}$$

which yields for x in the vicinity of the minima

$$V_{[n]}(x) \simeq -\frac{4n+1}{2}\theta U_\alpha'' + \frac{1}{4}(U_\alpha'')^2(x-x_\alpha)^2 \tag{3.2}$$

We are interested only in the low lying eigenvalues of $S_{[n]}$ for which $|\lambda_{[n]} - V_{[n]}(x_\alpha)|$ is the order of $\theta|U_\alpha''|$. Then for low temperatures, i.e., $k_B T/\Delta\phi_\alpha \equiv \theta/\Delta U_\alpha \ll 1$, the three wells of $V_{[n]}$ can safely be approximated by harmonic potentials (3.2) *irrespective of the considered friction.*

In addition, in (3.1b, c) the anharmonic part of $V(x)$ does not appear to lowest order in $\theta/\Delta U_\alpha$. It will turn out that, as long as the initial distribution is located in the quasiharmonic region of wells 1 and 2, and as long as the temperature is low enough, the bistable potential can be approximated by piecewise harmonic potentials.

For estimating the time scales involved in the relaxational processes we consider the "energy" levels $\Lambda_{[n]p}^\alpha$ in the three valleys of $V_{[n]}$.

$$\Lambda_{[n]p}^{(\alpha)} = -\frac{4n+1}{2}\theta U_\alpha'' + \theta|U_\alpha''|(p+\tfrac{1}{2}), \qquad p = 0, 1, 2, \ldots \tag{3.3a}$$

which yields for $\alpha = 1, 2$

$$\Lambda_{[n]p}^{(\alpha)} = \theta(p-2n)U_\alpha'' \tag{3.3b}$$

while for $\alpha = 0$ we have

$$\Lambda_{[n]p}^{(\alpha)} = \theta(p+2n+1)|U_0''| \tag{3.3c}$$

For $n \neq 0$ the lowest eigenvalues are $\Lambda_{[n]0}^{(\alpha)} = -2\theta n U_\alpha''$, $\alpha = 1, 2$. These values can be taken as a good approximation for the lowest eigenvalues of $S_{[n]}$. Tunneling between wells 1 and 2 only can give exponential small corrections $\sim\exp(-\Delta U_{1,2}/\theta)$ which can be neglected at low temperatures. The corresponding eigenfunctions are the usual oscillator functions. In contrast, for $n = 0$, the two lowest eigenvalues are $\Lambda_{[0]0}^{(1)} = \Lambda_{[0]0}^{(2)} = 0$ and tunneling between the two states must be considered explicitly. Therefore, both cases $n = 0$ and $n = 1, 2, 3 \ldots$ have to be treated differently. We start with $n = 0$.

3.1. Calculation of $c_{[0]}(x,t)$

For $n=0$ Eqs. (2.33) and (1.8) become formally identical, when $U(x)$ in (1.8) is substituted by $\tilde{U}_{[0]}(x)$. The eigenvalue problem (1.8) has been studied in [7] within the WKB approximation which becomes exact in the low-temperature limit. Performing the same approximation for (2.33) and limiting ourselves to initial distributions essentially located inside the wells instead on the top of the barrier we find the following result: The eigenstates $\varphi_{[0]p}(x)$ are linear combinations of Weber functions $D_l(y)$ with integer l, centered at the bottoms of the wells. The two lowest eigenstates $\varphi_{[0]0}(x)$ and $\varphi_{[0]1}(x)$ are represented by Gaussians centered at x_1 and x_2, while the higher eigenfunctions $\varphi_{[0]p}$ with $p=2,3,4,\ldots$ are described by the pure "oscillatory" states inside the wells. In detail we have for $p=0,1$

$$\varphi_{[0]0}(x)=\varphi_0^{(1)}(x)\left(1+\tilde{d}_{12}^2\right)^{-1/2}+\varphi_0^{(2)}(x)\left(1+\tilde{d}_{21}^2\right)^{-1/2} \tag{3.4a}$$

$$\varphi_{[0]1}(x)=-\varphi_0^{(1)}(x)\left(1+d_{21}^2\right)^{-1/2}+\varphi_0^{(2)}(x)\left(1+\tilde{d}_{12}^2\right)^{-1/2} \tag{3.4b}$$

where

$$\varphi_0^{(\alpha)}(x)\equiv\left(\frac{U_\alpha''}{2\pi\theta}\right)^{1/4}\exp\left[-\frac{(x-x_\alpha)^2U_\alpha''}{4\theta}\right] \tag{3.4c}$$

and

$$\tilde{d}_{12}=\left(U_1''/U_2''\right)^{1/4}\exp\left\{\left[\tilde{U}_{[0]}(x_1)-\tilde{U}_{[0]}(x_2)\right]/2\theta\right\} \tag{3.4d}$$

For $p=2,3,4,\ldots$ [p now corresponds to a couple of indices $l,(\alpha)$] we find

$$\varphi_{[0]p}(x)\equiv\varphi_{[0]l}^{(\alpha)}(x)=(l!)^{-1/2}\left(\frac{U_\alpha''}{2\pi\theta}\right)^{1/4}\cdot D_l\left[(x-x_\alpha)\left(\frac{U_\alpha''}{\theta}\right)^{1/2}\right] \tag{3.5a}$$

where $l=1,2,3,\ldots,\quad\alpha=1,2,$ and

$$D_l(y)=(-1)^l\exp\left(\frac{y^2}{4}\right)\frac{d^l}{dy^l}\exp\left(-\frac{y^2}{2}\right) \tag{3.5b}$$

The corresponding eigenvalues are given by

$$\lambda_{[0]0}=0 \tag{3.6a}$$

$$\lambda_{[0]1}=\frac{\theta}{2\pi}\left\{\left(U_1''|U_0''|\right)^{1/2}\exp\left[\left(\tilde{U}_{[0]}(x_1)-\tilde{U}_{[0]}(x_0)\right)/\theta\right]\right.$$
$$\left.+\left(U_2''|U_0''|\right)^{1/2}\exp\left[\left(\tilde{U}_{[0]}(x_2)-\tilde{U}_{[0]}(x_0)\right)/\theta\right]\right\} \tag{3.6b}$$

and

$$\lambda_{[0]p}\equiv\lambda_{[0]l}^{(\alpha)}=\theta l U_\alpha'',\qquad p\geqq 2,\quad l=1,2,3,\ldots,\qquad\alpha=1,2 \tag{3.6c}$$

In the high-friction limit $\tilde{U}_{[0]}(x_\alpha)$ tends to U_α. As a consequence, $\varphi_{[0]0}(x)$ and $\varphi_{[0]1}(x)$ tend to $\varphi_0(x)$ and $\varphi_1(x)$, respectively, which are the solutions of

(1.8), and $\lambda_{[0]1}$ tends to λ_1. For $p \geqq 2$ the eigenfunctions $\varphi_{[0]p}(x)$ and eigenvalues $\lambda_{[0]p}$ are independent on γ and are identical to the corresponding $\varphi_p(x)$ and λ_p from (1.8). To determine $c_{[0]}(x,t)$ we have to calculate first the matrix elements $F_{[0]pq}$ from (2.35b). Then the determine $\kappa_{[0]p}(t)$ from (2.35a) and $c_{[0]}(x,t)$ from (2.26) with (2.29a) and (2.34). Using Eqs. (3.4a)–(3.5) it is a simple matter to calculate the matrix $F_{[0]pq}$. We find

$$F_{[0]00} = \frac{U_1''}{1+\tilde{d}_{12}^2} + \frac{U_2''}{1+\tilde{d}_{21}^2} \tag{3.7a}$$

$$F_{[0]01} = F_{[0]10} = \frac{U_2''-U_1''}{\tilde{d}_{21}+\tilde{d}_{12}} \tag{3.7b}$$

$$F_{[0]11} = \frac{U_1''}{1+\tilde{d}_{21}^2} + \frac{U_2''}{1+\tilde{d}_{12}^2} \tag{3.7c}$$

while for q, $q \geqq 2$ we have

$$F_{[0]pq} \equiv F_{[0]ll'}^{\alpha\beta} = U_\alpha'' \cdot \delta_{\alpha\beta}\delta_{ll'}, \qquad l,l' = 1,2,\ldots, \qquad \alpha,\beta = 1,2 \tag{3.8a}$$

and

$$F_{[0]0p} \equiv F_{[0]p0} \equiv F_{[0]p1} \equiv F_{[0]1p} \equiv 0 \tag{3.8b}$$

Except $p,q = 0,1$ the F matrix is diagonal in p and q. Therefore, for $p \geqq 2$ $\kappa_{[0]p}(t)$ is given by (2.36). When $U_1'' = U_2''$ we have $F_{[0]01} \equiv 0$ and then (2.36) holds for all p. In the general case $\kappa_{[0]0}(t)$ and $\kappa_{[0]1}(t)$ are coupled by (3.8b). Neglecting expressions of order γ^{-5} in $\dot{\kappa}_{[0]0}$ and $\dot{\kappa}_{[0]1}$ we finally obtain from (2.35a) and (3.7a)–(3.8b):

$$\kappa_{[0]0}(t) = \kappa_{[0]0}(0) + \kappa_{[0]1}(0) \cdot \frac{F_{[0]01}}{\gamma} \exp\left[-\frac{\lambda_{[0]1}}{\theta}\left(1+\frac{F_{[0]11}}{\gamma}\right)t\right] \tag{3.9a}$$

$$\kappa_{[0]1}(t) = \kappa_{[0]1}(0) \exp\left[-\frac{\lambda_{[0]1}}{\theta}\frac{F_{[0]11}}{\gamma}t\right] \tag{3.9b}$$

and $c_{[0]}(x,t)$ becomes

$$\begin{aligned} c_{[0]}(x,t) = {} & g(x)^{-1/2} e^{-U(x)/2\theta} \\ & \times \Bigg\{ \varphi_{[0]0}(x)\kappa_{[0]0}(0) + \kappa_{[0]1}(0)\left[\frac{F_{[0]01}}{\gamma}\varphi_{[0]0}(x) + \varphi_{[0]1}(x)\right] \\ & \times \exp\left[-\frac{\lambda_{[0]1}}{\theta}\left(1+\frac{F_{[0]11}}{\gamma}\right)t\right] \\ & + \sum_{\alpha=1}^{2}\sum_{l}\kappa_{[0]l}^{(\alpha)}(0)\varphi_{[0]l}^{(\alpha)}(x)\exp\left[-\frac{\lambda_{[0]l}^{(\alpha)}}{\theta}\left(1+\frac{U_\alpha''}{\gamma}\right)t\right]\Bigg\} \end{aligned} \tag{3.10}$$

For $t \to \infty$ $c_{[0]}(x,t)$ must tend to the stationary equilibrium distribution $P_{\text{eq}}(x)$, i.e.,

$$\lim_{t\to\infty} c_{[0]}(x,t) = P_{\text{eq}}(x) = c\exp\left[-U(x)/\theta\right] \tag{3.11a}$$

where

$$c = \left\{\int_{-\infty}^{+\infty} dx \exp\left[-U(x)/\theta\right]\right\}^{-1} \tag{3.11b}$$

irrespective of the initial conditions. Furthermore, $c_{[0]}(x,t)$ must be normalized for all times. We will show now, that these conditions are satisfied by (3.10) for arbitrary initial conditions. To be consistent with the WKB approximation made above we expand $U(x)$ in the prefactor of (3.10) around x_1, x_2, and x_0 and neglect third- and higher-order derivatives. This yields

$$\kappa_{[0]0}(0)\, g(x)^{-1/2}\exp(-U(x)/2\theta)\varphi_{[0]0}(x) \simeq \kappa_{[0]0}(0)\tilde{c}^{1/2}\exp(-U(x)/\theta) \tag{3.12}$$

with $\tilde{c} = \{\int_{-\infty}^{+\infty} dx\ g(x)\exp[-U(x)/\theta]\}^{-1}$. Inserting this result into (3.10) and performing the limit $t \to \infty$ we find

$$\kappa_{[0]0}(0)\tilde{c}^{1/2} = c \tag{3.13}$$

which determines $\kappa_{[0]0}(0)$.

For the following it is convenient to consider the propagator of $c_{[0]}(x,t)$, $c_{[0]}(x,t \mid x_s, 0)$, which is subject to the initial condition $c_{[0]}(x,0 \mid x_s, 0) = \delta(x - x_s)$ with x_s located inside one of the wells. We expand $\varphi_{[0]0}(x)$ as well as $\varphi_{[0]1}(x)$ in terms of $1/\gamma$ and neglect those terms which lead to contributions of $O(\gamma^{-5})$ in $\dot{c}_{[0]}(x,t)$. Noting that $\lambda_{[0]1}/\theta$ is of order γ^{-1} we obtain finally

$$c_{[0]}(x,t \mid x_s, 0) = \frac{\varphi_0(x)}{\varphi_0(x_s)} \sum_{p=0}^{\infty} \varphi_p(x)\varphi_p(x_s)e^{-t/\tau_{[0]p}} \tag{3.14}$$

where $\varphi_p(x) = \lim_{\gamma\to\infty}\varphi_{[0]p}(x)$ are the WKB eigenfunctions of (1.8). The relaxation times $\tau_{[0]p}$ are given by

$$\tau_{[0]0}^{-1} = 0 \tag{3.15a}$$

$$\tau_{[0]1}^{-1} = \frac{\lambda_{[0]1}}{\theta}\left(1 + \frac{F_{[0]11}}{\gamma}\right) + O(\gamma^{-5}) \tag{3.15b}$$

while for $p \geqq 2$ we have

$$\tau_{[0]p}^{-1} = \left(\tau_{[0]l}^{(\alpha)}\right)^{-1} = lU_\alpha''(1 + U_\alpha''/\gamma) + O(\gamma^{-5}) \tag{3.15c}$$

($\alpha = 1,2,\ l = 1,2,3,\ldots$). Equations (3.14) and (3.15a, b, c) are our *final* result for the propagator $c_{[0]}(x,t \mid x_s, 0)$. The result is valid in the intermediate-friction regime and for temperatures θ low compared with the barrier heights ΔU_1 and ΔU_2. It becomes exact in the limit $\theta/\Delta U_{1,2} \to 0$.

Using (3.14) it is easy to verify that $c_{[0]}(x,t)$ satisfies both normalization condition (2.24) and stationary equilibrium condition (3.11a) for arbitrary initial conditions. Equations (3.15b, c) describe the relaxation toward global and local equilibrium. Taking $\lambda_{[0]1}$ from (3.9b) and $F_{[0]11}$ from (3.7c) and employing the convenient definitions

$$\frac{\omega_\alpha^2}{\gamma^2} \equiv \frac{|U_\alpha''|}{\gamma}$$

the relaxation time to global equilibrium, $\tau_{[0]1}$, becomes

$$\tau_{[0]1}^{-1} = \frac{\omega_1\omega_0}{2\pi\gamma}\left(1 - \frac{\omega_0^2}{\gamma^2} + n_{1,\text{eq}}\frac{\omega_2^2 - \omega_1^2}{\gamma^2}\right)e^{-\Delta U_1/\theta} + \frac{\omega_2\omega_0}{2\pi\gamma}\left(1 - \frac{\omega_0^2}{\gamma^2} + n_{2,\text{eq}}\frac{\omega_1^2 - \omega_2^2}{\gamma^2}\right)e^{-\Delta U_2/\theta} \tag{3.16}$$

$n_{1,\text{eq}}$ and $n_{2,\text{eq}}$ denote the equilibrium population of wells 1 and 2, respectively, defined by $n_{1,\text{eq}} \equiv \int_{-\infty}^{0} dx\, P_{\text{eq}}(x) \equiv \int_{-\infty}^{0} dx\, \varphi_0^2(x) = \{1 + (U_1/U_2)\exp[(U_1 - U_2)/\theta]\}^{-1}$ and $n_{2,\text{eq}} \equiv \int_0^\infty dx\, P_{\text{eq}}(x) \equiv 1 - n_{1,\text{eq}}$. It is easy to verify that the terms proportional to $n_{1,\text{eq}}$ and $n_{2,\text{eq}}$ in (3.16) cancel and $\tau_{[0]1}^{-1}$ becomes simply

$$\tau_{[0]1}^{-1} = W_{1\to2} + W_{2\to1} \tag{3.17a}$$

where

$$W_{1\to2} = \frac{\omega_1\omega_0}{2\pi\gamma}\left(1 - \frac{\omega_0^2}{\gamma^2}\right)e^{-\Delta U_1/\theta} \tag{3.17b}$$

and $W_{2\to1}$ results from $W_{1\to2}$ by changing the index 1 into 2. As we show in the appendix, $W_{1\to2}$ and $W_{2\to1}$ can be identified with the escape rates out of the wells 1 and 2, respectively.

The rates are exact up to order γ^{-5} and valid for temperatures small compared with the barrier heights. It is easy to verify that the considered friction regime they agree with the Kramers rates, given by[16]

$$\tau_{K,\alpha\to\beta}^{-1} = \frac{\omega_\alpha}{2\pi\omega_0}\left[\left(\omega_0^2 + \frac{\gamma^2}{4}\right)^{1/2} - \frac{\gamma}{2}\right]\exp\left(-\frac{\Delta U_\alpha}{\theta}\right)$$

3.2. Calculation of $c_{[n]}(x,t)$, $n \neq 0$

When $n \neq 0$, the norm $N_{[n]}(t) \equiv \int_{-\infty}^{+\infty} dx\, c_{[n]}(x,t)$ is no more conserved but decays as

$$N_{[n]}(t) \simeq e^{-n\gamma t} N_{[n]}(0) \tag{3.18}$$

The approximate eigenvalues $\lambda_{[n]p}$ of $S_{[n]}$, $n \neq 0$, are identical to $\Lambda_{[n],p}$ from (3.3a–c). Tunneling between different wells is irrelevant, since it can only lead to exponentially small corrections to the relaxation times. Hence the corresponding eigenfunctions are

$$\varphi_{[n]p}(x) \equiv \varphi^{(\alpha)}_{[n]l}(x) = (l!)^{-1/2}(U''_\alpha/2\pi\theta)^{1/4}D_l\big((x-x_\alpha)(U''_\alpha/\theta)^{1/2}\big) \tag{3.19}$$

and the F matrix reduces to

$$F^{\alpha\alpha'}_{[n]ll'} = U''_\alpha\delta_{\alpha,\alpha'}\delta_{l,l'}, \qquad l,l' = 0,1,2,3,\ldots; \quad \alpha,\alpha' = 0,1,2 \tag{3.20}$$

As a consequence, $\psi_{[n]}(x,t)$ is given by

$$\psi_{[n]}(x,t) = \sum_{l,\alpha}\varphi^{(\alpha)}_{[n]l}(x)\kappa^{(\alpha)}_{[n]l}(0)\exp\big(-t/\tau^{(\alpha)}_{[n]l}\big) \tag{3.21}$$

where for $\alpha = 1,2$

$$\big(\tau^{(\alpha)}_{[n]l}\big)^{-1} = \gamma\left[n\left(1 - \frac{\omega_\alpha^2}{\gamma^2} - \frac{\omega_\alpha^4}{\gamma^4}\right) + l\frac{\omega_\alpha^2}{\gamma^2}\left(1 + \frac{\omega_\alpha^2}{\gamma^2}\right)\right] \tag{3.22}$$

and this is precisely the beginning of the expansion of the eigenvalue $\lambda_{n,l}$ for a harmonic potential obtained by Risken and Vollmer.[17] For $\alpha = 0$,

$$\big(\tau^{(0)}_{[n]l}\big)^{-1} = \gamma\left[n\left(1 + \frac{\omega_0^2}{\gamma^2} - \frac{\omega_0^4}{\gamma^4}\right) + (l+1)\frac{\omega_0^2}{\gamma^2}\left(1 - \frac{\omega_0^2}{\gamma^2}\right)\right] \tag{3.23}$$

The relaxation times are independent on temperature and small compared with the Kramers time. For $\alpha = 1,2$ we have

$$\big(\tau^{(\alpha)}_{[n]l}\big)^{-1} = \big(\tau^{(\alpha)}_{[0]l}\big)^{-1} + n\gamma\left(1 - \frac{\omega_\alpha^2}{\gamma^2} - \frac{\omega_\alpha^4}{\gamma^4}\right) \tag{3.24}$$

and the corresponding eigenfunctions are identical to $\varphi_l^{(\alpha)}$ from (3.5a).

From (3.21) we obtain finally the propagator $c_{[n]}(x,t\,|\,x_s,0)$:

$$\begin{aligned} c_{[n]}(x,t\,|\,x_s,0) = {} & \sum_{\alpha=1,2}\exp\left[-n\gamma\left(1 - \frac{\omega_\alpha^2}{\gamma^2} - \frac{\omega_\alpha^4}{\gamma^4}\right)t\right]\frac{\omega_0^{(\alpha)}(x)}{\omega_0^{(\alpha)}(x_s)} \\ & \times\sum_{l=0}^{\infty}\varphi_l^{(\alpha)}(x)\varphi_l^{(\alpha)}(x_s)\exp\left[-l\frac{\omega_\alpha^2}{\gamma}\left(1 + \frac{\omega_\alpha^2}{\gamma^2}\right)t\right] \\ & + \exp\left[-n\gamma\left(1 + \frac{\omega_0^2}{\gamma^2} - 2\frac{\omega_0^4}{\gamma^4}\right)t\right]\frac{\varphi_0^{(0)}(x)}{\varphi_0^{(0)}(x_s)} \\ & \times\sum_{l=0}^{\infty}\varphi_l^{(0)}(x)\varphi_l^{(0)}(x_s)\exp\left[-(l+1)\frac{\omega_0^2}{\gamma}\left(1 - \frac{\omega_0^2}{\gamma^2}\right)t\right] \end{aligned} \tag{3.25}$$

When the initial distribution is located say in well 1, we have $\varphi_l^{(2)}(x_s) \simeq \varphi_l^{(0)}(x_s) \simeq 0$ and the corresponding sums in (3.25) are zero. From the above expression (3.25) we can calculate more precisely the norm of $c_{[n]}(x,t)$. For x_s close to x_α, $\alpha = 1,2$, we find

$$N_{[n]}(t) = N_{[n]}(0)\exp\left[-n\gamma\left(1 - \frac{\omega_\alpha^2}{\gamma^2} - \frac{\omega_\alpha^4}{\gamma^4}\right)t\right] \tag{3.26a}$$

while for x_s close to x_0 we have

$$N_{[n]}(t) = N_{[n]}(0)\exp\left[-\gamma\left(n + (n+1)\frac{\omega_0^2}{\gamma^2} - (2n+1)\frac{\omega_0^4}{\gamma^4}\right)t\right] \tag{3.26b}$$

3.3. Calculation of $P(v,x,t)$

In the preceding sections we have detailed the propagators $c_{[n]}(x,t \mid x_s, 0)$ for $n = 0,1,2,\ldots$. When considering initial distributions close to the bottom of well α, $\alpha = 1$ or 2, we can combine Eqs. (3.25) and (3.14) to give

$$\begin{aligned} c_{[n]}(x,t \mid x_s,0) = P_0^{\text{fin}}\delta_{n,0} + \exp&\left[-n\gamma\left(1 - \frac{\omega_\alpha^2}{\gamma^2} - \frac{\omega_\alpha^4}{\gamma^4}\right)t\right] \\ &\times\Bigg\{\left[\varphi_0^{(\alpha)}(x)\right]^2(1-\delta_{n,0}) \\ &\quad + \frac{\varphi_0(x)}{\varphi_0(x_s)}\sum_{l=1,2,\ldots}\varphi_l^{(\alpha)}(x)\varphi_l^{(\alpha)}(x_s)\exp(-t/\tau_l^{(\alpha)})\Bigg\} \end{aligned} \tag{3.27}$$

where $\tau_l^{(\alpha)} \equiv \tau_{[0]l}^{(\alpha)}$ and

$$P_0^{\text{fin}} \equiv \varphi_0^2(x) + \frac{\varphi_0(x)}{\varphi_0(x_s)}\varphi_1(x)\varphi_1(x_s)\exp\left(-\frac{t}{\tau_{[0]1}}\right)$$

From (3.25) the distribution function for a given initial distribution is obtained easily. After $c_{[n]}(x,0)$ has been specified we find $c_{[n]}(x,t)$ by a simple integration, as detailed in Section 2.4. The final result for $P(v,x,t)$ is obtained by summing terms like $\mathscr{O}_{[l][n]}^{[i]}c_{[n]}(x,t)$, which are determined by successive application of operators d and d^+ on $c_{[n]}$ and hence on different $\varphi_l^{(\alpha)}(x)$. d and d^+ act on $\varphi_l^{(\alpha)}(x)$ as follows:

$$d^+\varphi_l^{(\alpha)}(x) = \frac{\omega_\alpha}{2}\left[(l+1)^{1/2}\varphi_{l+1}^{(\alpha)}(x) - \sqrt{l}\,\varphi_l^{(\alpha)}(x)\right] \tag{3.28a}$$

$$d\varphi_l^{(\alpha)}(x) = \frac{\omega_\alpha}{2}\left[(l+1)^{1/2}\varphi_{l+1}^{(\alpha)}(x) + 3\sqrt{l}\,\varphi_{l-1}^{(\alpha)}(x)\right] \tag{3.28b}$$

where we have defined $\varphi_l^{(\alpha)} \equiv 0$ for $l < 0$. Using these relations it is easy to calculate $\mathscr{O}^{[i]}_{[l][n]} c_{[n]}$ for given i, l, n and then to obtain the distribution function.

4. CONCLUSION

In this paper we have derived recursion relations for the coefficients of the inverse friction expansion introduced by Titulaer.[10] Using these recursion relations it is an easy matter to calculate the coefficients up to any order one likes. As a by-product we have derived a normalization condition for $c_{[0]}(x, t)$, which reflects the normalization of the spatial distribution function. Our further studies were restricted to the intermediate- and high-friction regime. Using a special transformation we have shown that the problem of finding $P(v, x, t)$ in this regime can be reduced to the simpler problem of solving a set of Schrödinger-type equations.

We have used this method to study analytically the motion of Brownian particles in the bistable potential at intermediate and high friction, in particular the time evolution of initial distributions close to the minima of the potential wells. We have confined the study to temperatures low compared with the barrier height. To solve the Schrödinger-type equations and to calculate propagators $c_{[n]}(x, t \mid x_s, 0)$ we have used the WKB technique, the results become exact in the limit of low temperatures. We have shown that the final approach to equilibrium is governed by a relaxation time, which is precisely the Kramers time in the considered friction regime [up to $O(\gamma^{-5})$].

We have not considered the time evolution of initial distributions close to the top of the potential barrier. It is indeed possible to apply our method to this case also, but the detailed study of the decay of unstable states is nevertheless complicated and is beyond the scope of this paper. It will be subject of a further publication.

ACKNOWLEDGMENT

It is a pleasure for us to thank W. Dieterich for valuable discussions. Financial support by Centre National de la Recherche Scientifique and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

APPENDIX: EVOLUTION EQUATION FOR THE POPULATION OF ONE WELL IN THE VICINITY OF EQUILIBRIUM

The population $n_1(t)$ of well 1 is defined by

$$n_1(t) = \int_{-\infty}^{0} dx\, P_0(x, t) \tag{A1}$$

Replacing $P_0(x,t)$ by its $1/\gamma$ expansion leads to

$$n_1(t) = \int_{-\infty}^{0} dx\, c_{[0]}(x,t) + \int_{-\infty}^{0} dx \sum_{i=1}^{\infty} \gamma^{-i} \sum_{n} \mathscr{O}^{[i]}_{[0][n]}(x) c_{[n]}(x,t) \quad \text{(A2)}$$

From the recursion relations we know that all operators $\mathscr{O}^{[i]}_{[0][n]}$ contain a left factor $\partial/\partial x$ and therefore can be written as $\mathscr{O}^{[i]}_{[0][n]} \equiv (\partial/\partial x) Q^{[i]}_{[0][n]}$ with $Q^{[i]}_{[0][n]}$ again a differential operator. Then the integral in the second term of the right-hand side of (A2) becomes

$$\sum_{i=1}^{\infty} \gamma^{-i} \sum_{n} \{\, Q^{[i]}_{[0][n]}(x) c_{[n]}(x,t) \} |_{x=0}$$

which is exponentially small ($\sim \exp[-\Delta U_{1,2}/\theta]$) for particles being in the vicinity of equilibrium and therefore must be neglected (see Section 3.2). Thus, in the intermediate and high-friction regime $n_1(t)$ is simply given by

$$n_1(t) = \int_{-\infty}^{0} dx\, c_{[0]}(x,t) \quad \text{(A3)}$$

when the initial distribution of the particles is close to the minima of $U(x)$ and the temperature is low compared with the potential barriers. For $t \to \infty$ $n_1(t)$ tends to the equilibrium population $n_{1,\text{eq}}$; $c_{[0]}(x,t)$ is determined by the propagator $c_{[0]}(x,t \mid x_s,0)$ and the initial distribution $c_{[0]}(x_s,0)$. From (3.14) we obtain

$$n_1(t) = \left[\int_{-\infty}^{0} dx\, \varphi_0^2(x)\right]\left[\int_{-\infty}^{+\infty} dx_s\, c_{[0]}(x_s,0)\right]$$
$$+ e^{-t/\tau_{[0]1}} \left[\int_{-\infty}^{0} dx\, \varphi_0(x)\varphi_1(x)\right]\left[\int_{-\infty}^{+\infty} dx_s \frac{\varphi_1(x_s)}{\varphi_0(x_s)} c_{[0]}(x_s,0)\right] \quad \text{(A4)}$$

the higher terms in the sum of (3.14) do not contribute to $n_1(t)$. As $\int_{-\infty}^{0} dx\, \varphi_0^2(x) \equiv n_{1,\text{eq}}$, (A4) is equivalent to the equation of motion

$$\dot{n}_1(t) = -\tau_{[0]1}^{-1}(n_1(t) - n_{1,\text{eq}})$$

which can be written

$$\dot{n}_1(t) = -\frac{n_{2,\text{eq}}}{\tau_{[0]1}} n_1(t) + \frac{n_{1,\text{eq}}}{\tau_{[0]1}} n_2(t) \quad \text{(A5)}$$

Equation (A5) shows that $n_{2,\text{eq}}/\tau_{[0]1} \equiv W_{1\to 2}$ and $n_{1,\text{eq}}/\tau_{[0]1} \equiv W_{2\to 1}$ can be identified as hopping rates $W_{i\to j}$ for a particle to jump from well i to well j. The inverse hopping rate is identical to the mean escape time the particle needs to diffuse from well i over the potential barrier.

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