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Diffusion in a Bistable Potential. General Inverse Friction Expansion

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The derivation of the characteristic times and of the density probability distribution for the motion of a Brownian particle in a bistable potential at intermediate friction was, until now, essentially limited to low orders in the inverse friction γ^{-1}. On the other hand, at least for temperatures low with respect to the barrier height, the Kramers time, which is the lowest nonzero eigenvalue in the bistable potential problem, is known exactly. This paper presents a systematic approach for the determination of the solution of the Fokker–Planck equation in an arbitrary potential in the overdamped regime. This calculation includes anharmonicity corrections up to order γ^{-5}. One feature of this paper is to show that the problem is equivalent to replacing the original potential $\phi(x)$ by a free energy which, for a velocity distribution at equilibrium, simply is $\tilde{\phi}(x) = \phi(x) - k_B T \ln[g(x)]$, where

$$g(x) = \{m\gamma^2/[2\phi''(x)]\}\{1 - [1 - 4\phi''(x)/m\gamma^2]^{1/2}\}$$

For out-of-equilibrium velocity distribution an effective potential is also explicitly given. In every case the function $g(x)$ plays a crucial role. This approach is then applied to the exact determination, in the low-temperature limit, of all the characteristic times and of the probability distribution in bistable potentials. Moreover, from the knowledge of the characteristic times and probability density distribution, it would be easy to determine the general and exact Suzuki scaling law for the relaxation from the instability point at intermediate friction.

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

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1. INTRODUCTION

The relation between the Fokker–Planck–Klein–Kramers (FPKK) description for the distribution function of velocity and position of a Brownian particle in an external field and the Smoluchowski contractd description for the distribution function of position only became evident recently. It was clarified in important contributions by Wilemski[1] in 1976 and Titulaer[2] in 1978. Extensive history may be found in these two papers.

More recently Gouyet and Bunde[3] applied the Titulaer approach to the problem of diffusion in a bistable potential. The method was moreover presented in clearer algebraic form, leading to simpler recursion formulas. In particular, an operator transformation was introduced which makes it possible to write the evolution operator as a simple Hermitian operator valid up to order γ^{-5} at least. In the present paper, a complete solution including the well-known inverse Kramers time[4]

$$\tau_K^{-1} = w_{\mathrm{abs}}\omega_M^{-1}[(\omega_M^2+\gamma^2/2)^{1/2}-\gamma/2]$$

is obtained. The method is as follows.

The distribution function $P(v, x, t)$ of the velocity v and position x of a Brownian particle of mass m in an external potential $\phi(x)$ at time t is described by an FPKK equation,

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

with the Liouville operator L explicitly given by

$$L(v, x) = \gamma C(v) + S(v, x) \tag{1.1a}$$

$$C(v) = (k_B T/m)\, \partial^2/\partial v^2 + (\partial/\partial v) v \tag{1.1b}$$

$$S(v, x) = -v\, \partial/\partial x + (1/m)\, \phi'(x)\, \partial/\partial v \tag{1.1c}$$

where γ is the friction coefficient and T the temperature of the bath. We also define $\beta = 1/k_B T$.

It is useful to introduce the operators a, a^+, d, and d^+ defined by

$$a^+ = -(1/\sqrt{m\beta})\, \partial/\partial v; \qquad a = (1/\sqrt{m\beta})\, \partial/\partial v + \sqrt{m\beta}\, v \tag{1.2a}$$

$$d^+ = -(1/m\beta)\, \partial/\partial x; \qquad d = (1/\sqrt{m\beta})\, \partial/\partial x + \sqrt{(\beta/m)}\phi' \tag{1.3a}$$

giving for the collision or diffusive part γC [see (1.1b)] the simple expression

$$C = -a^+ a \tag{1.2b}$$

and for the streaming part S [see (1.1c)]

$$S = d^{+}a - da^{+} \tag{1.3b}$$

The operators a^{+} and a, and d^{+} and d are adjoints with respect to the scalar product:

$$(f, g) = \int dv \int dx \exp \beta(mv^2/2 + \phi)\, f^{*}(v, x)\, g(v, x) \tag{1.4}$$

Then C is Hermitian and S anti-Hermitian with respect to this scalar product. Moreover, the following commutation relations hold:

$$[a, a^{+}] = 1 \qquad \text{and} \qquad [d, d^{+}] = \phi''/m \tag{1.5}$$

Titulaer's idea,[2] which follows the Chapman–Enskog approach to the Boltzmann equation, is to expand the distribution $P(v, x, t)$ on the basis of the eigenfunctions $\chi_n(v)$ of C (as γC is the leading operator in L). The eigenvalue equation is

$$C\chi_n(v) = -n\chi_n(v) \tag{1.6}$$

with

$$\chi_n(v) = [n!\,(4\pi)^{1/2}(2m\beta)^{(n-1)/2}]^{-1}\, H_n[v\sqrt{(m\beta/2)}] \exp(-m\beta v^2/2) \tag{1.7}$$

in which $H_n(u)$ are the usual Hermite polynomials. Moreover, one has

$$\begin{gathered} a^{+}\chi_n = (n+1)\chi_n; \qquad a\chi_n = \chi_{n-1} \\ \chi_n = 0 \qquad \text{if} \quad n < 0 \end{gathered} \tag{1.8}$$

The χ_n basis is nonorthogonal with respect to the ordinary scalar product $\langle f | g \rangle = \int f^{*}(v)\, g(v)\, dv$ and $\{\tilde{\chi}_n\}$ is the biorthogonal basis associated with the $\{\chi_n\}$ and such that $\langle \tilde{\chi}_m | \chi_n \rangle = \delta_{mn}$.

The Titulaer expansion may then be written in the following way:

$$P(v, x, t) = \sum_n P_{[n]}(v, x, t) \tag{1.9}$$

where

$$P_{[n]}(v, x, t) = c_{[n]}(x, t)\, \chi_n(v) + \sum_{i=1}^{\infty} \gamma^{-i} P_{[n]}^{[i]}(v, x, t) \tag{1.10}$$

We will now use the operator technique recently proposed by Gouyet and Bunde,[3] which is simpler than the original one developed by Titulaer, but is nevertheless directly related to the general formulation showing the parallelism between Bloch and Chapman–Enskog perturbation in degenerate manifolds given in Ref. 2. The $P^{[i]}_{[n]}$ can be expressed as follows:

$$P^{[i]}_{[n]} = \sum_{m=0}^{\infty} \chi_m(v)\, O^{[i]}_{[m][n]}(x)\, c_{[n]}(x, t), \qquad i = 1, 2, 3,... \tag{1.11}$$

Here $c_{[n]}(x, t)$ is the same function as in (1.10). The operators $O^{[i]}_{[m][n]}(x)$ act on x in $c_{[n]}(x, t)$. By definition,

$$O^{[0]}_{[m][n]} = \delta_{mn} \qquad \text{and} \qquad O^{[i]}_{[m][m]} \equiv 0 \quad \text{when} \quad i \neq 0 \tag{1.12}$$

The time evolution of $c_{[n]}(x, t)$ is governed by the expansion (see Refs. 2 and 3)

$$\partial c_{[n]}(x, t)/\partial t = \left[-n\gamma + \sum_{i=0}^{\infty} \gamma^{-i} a^{[i]}_{[n]}(x) \right] c_{[n]}(x, t) \tag{1.13}$$

where $\partial^{[i]}_{[n]}$ are again operators on x in $c_{[n]}(x, t)$.

The operators $O^{[i]}_{[m][n]}$ and $\partial^{[i]}_{[n]}$ are defined by recursions relations and are given in Ref. 3, but they can also be derived from Eqs. (3.17) and (3.15) of Ref. 5.

In the present paper we will not follow the Bloch–Chapman–Enskog–Titulaer (BCET) degenerate perturbation expansion, but try to generalize the Bunde–Gouyet procedure,[3] which consists in searching for a convenient transformation making the evolution operator Hermitian. The different approaches are indeed not independent of one another.

2. BUILDING UP OF A HERMITIAN OPERATOR

This section is devoted to the definition of an operator transformation such that the evolution operator (1.1) becomes Hermitian.

2.1. The Recursion Relations

Let us define

$$\partial_{[n]}(s, x) = \sum_{i=0}^{\infty} s^i\, \partial^{[i]}_{[n]}(x) \tag{2.1}$$

and

$$O_{[m][n]}(s, x) = \sum_{i=0}^{\infty} s^i O^{[i]}_{[m][n]} \equiv \sum_{i=|m-n|}^{\infty} s^i O^{[i]}_{[m][n]} \tag{2.2}$$

Then the set of Eqs. (1.10) and (1.13) may be written as

$$P_{[n]}(v, x, t) = \sum_{m=0}^{\infty} \chi_m(v)\, O_{[m][n]}(\gamma^{-1}, x)\, c_{[n]}(x, t) \tag{2.3}$$

and

$$\partial c_{[n]}(x, t)/\partial t = [-n\gamma + \partial_{[n]}(\gamma^{-1})]\, c_{[n]}(x, t) \tag{2.4}$$

The operators $\partial_{[n]}$ and $O_{[m][n]}$ will now be calculated starting from the following recursion relation, which is easily obtained after a derivation of (2.3) with respect to time and by using (2.4) and the basic Eq. (1.1) (see Appendix A):

$$O_{[n+p][n]}(\partial_{[n]} + p\gamma) \equiv -(n+p)\, d O_{[n+p-1][n]} + d^{+} O_{[n+p+1][n]} \tag{2.5}$$

Since $O_{[n][n]} \equiv 1$, the relation (2.5) defines $\partial_{[n]}$ as a function of $O_{[m][n]}$ when $p = 0$:

$$\partial_{[n]} \equiv -nd O_{[n-1][n]} + d^{+} O_{[n+1][n]} \tag{2.6}$$

It will be important to notice when comparing the different orders in γ^{-1} that $O_{[m][n]}(\gamma^{-1}, x)$ is proportional to $\gamma^{-|m-n|}$ as γ goes to infinity.

2.2. Search for a Hermitian Operator $\boldsymbol{\partial}_{[n]}$

Titulaer showed[2] that $\partial_{[n]}^{[i]}$ for $i \geqslant 5$ was no longer Hermitian with respect to the scalar product (f, g), so that it would be of great interest to look for a transformation $\partial_{[n]} \Rightarrow \boldsymbol{\partial}_{[n]}$ such that the new operator $\boldsymbol{\partial}_{[n]}$ is Hermitian with respect to some given scalar product $\langle f \mid g \rangle$ ($\int f^{*} g\, dx$, for instance).

For this purpose, let us define $\psi_{[n]}$ with an arbitrary $G_{[n]}$ such that

$$\psi_{[n]} = c_{[n]} \exp(\beta G_{[n]}) \tag{2.7}$$

Then

$$\partial \psi_{[n]}/\partial t = (-n\gamma + \boldsymbol{\partial}_{[n]})\, \psi_{[n]} \tag{2.8}$$

with

$$\boldsymbol{\partial}_{[n]} = e^{\beta G_{[n]}}\, \partial_{[n]} e^{-\beta G_{[n]}} \tag{2.9}$$

and we will try to find two functions $G_{[n]}$ and $\tilde{\phi}_{[n]}$ (defined below) that make $\boldsymbol{\partial}_{[n]}$ Hermitian.

Notations. To simplify the reading, the index $[n]$ will be omitted in the following except when necessary. Moreover, we will use the compact notation $O_p \equiv O_{[n+p][n]}$ and in general a boldface operator for any conjugate transformation of the type $X = \exp(\beta G) X \exp(-\beta G)$.

With this last transformation the basic recursion formulas (2.5) and (2.6) become

$$\mathbf{O}_p(\partial + \gamma p) = -(n+p)\,\mathbf{d}\mathbf{O}_{p-1} + \mathbf{d}^+\mathbf{O}_{p+1} \tag{2.10}$$

$$\partial = -n\mathbf{d}\mathbf{O}_{-1} + \mathbf{d}^+\mathbf{O}_1 \tag{2.11}$$

and

$$\mathbf{O}_0 = O_0 = 1 \tag{2.12}$$

As in the preceding paper,[3] let us now indicate with a "dagger" operators that are mutually adjoint with respect to $\langle f \mid g \rangle = \int f^*(x)\, g(x)\, dx$,

$$A^\dagger = -(m\beta)^{-1/2}\, \partial/\partial x + (m\beta)^{1/2}\, \tilde{\phi}'/2m \tag{2.13}$$

$$A = (m\beta)^{-1/2}\, \partial/\partial x + (m\beta)^{1/2}\, \tilde{\phi}'/2m \tag{2.14}$$

Then $[A, A^\dagger] = \tilde{\phi}''/m$ and

$$\mathbf{d}^+ = A^\dagger + \sqrt{(\beta/m)}(G' - \tilde{\phi}'/2) \tag{2.15}$$

$$\mathbf{d} = A + \sqrt{(\beta/m)}(\phi' - G' - \tilde{\phi}'/2) \tag{2.16}$$

If ∂ is Hermitian, it must be reducible to the general expansion

$$\partial = \sum_K \mathscr{G}_K(x)(A^\dagger A)^K \tag{2.17}$$

where $\mathscr{G}_K(x) \equiv \mathscr{G}_{K[n]}(x)$ is a function to be determined using the above recursions. At this point, it is convenient to introduce two new functions $g_n(x)$ and $h_n(x)$ defined by the two relations (the indices n are omitted)

$$G = \phi/2 + (1 - 2n - 2n^2)/2\beta \ln(g/h) \tag{2.18a}$$

$$\tilde{\phi} = \phi - (1 + 2n)/\beta \ln(gh) \tag{2.18b}$$

These relationss generalize Eqs. (2.29a) and (29b) of Ref. 3.[2] We then consider the following structure for $\mathbf{O}_p$:

$$\mathbf{O}_p = \sum_K [\beta_{Kp}(x) A^\dagger + \gamma_{Kp}(x)](A^\dagger A)^K \tag{2.19}$$

[2] $g(x)$ in Ref. 3 is precisely the same as in (2.18a) and (2.18b) when $n = 0$. Compare, for example, (2.18a) and (2.18b) of this paper when $h = 1$ and (2.29a) and (2.29b) of Ref. 3.

and will verify *a posteriori* that this expression is consistent with the recursion relations. This defines new recursions, but now between the β_{Kp}, γ_{Kp}, and $\mathscr{G}_K$.

The initial condition $O_0 = 1$ gives

$$\beta_{K0} \equiv 0 \qquad \text{and} \qquad \gamma_{K0} \equiv \delta_{K0} \tag{2.20}$$

(where δ is the usual Kronecker symbol).

3. THE $n = 0$ CASE

Since this case is equivalent to the corrected Smoluchowski equation, it is the most important. It essentially corresponds to regimes for which the time is much larger than γ^{-1}, that is, for which most of the velocity distribution has reached equilibrium.

When $n = 0$ and γ^{-1} is set to s, the recursion formulas (2.10) and (2.11) reduce to

$$\partial = \mathbf{d}^+ \mathbf{O}_1 \tag{3.1a}$$

$$\mathbf{O}_p(\partial + p/s) = -p\, \mathbf{d}\mathbf{O}_{p-1} + \mathbf{d}^+ \mathbf{O}_{p+1} \tag{3.1b}$$

3.1. Study of Equation (3.1a)

Expression (3.1a) with (2.17) and (2.19) leads to (the index $n(=0)$ remains omitted)

$$\gamma_{K1} = (m\beta)^{1/2}[\beta'_{K1} + (h'/h - \beta\phi')\beta_{K1}] \tag{3.2a}$$

$$\mathscr{G}_K = -(m\beta)^{-1/2}(\gamma'_{K1} - g'/g\gamma_{K1}) - (\tilde{\phi}''/m)\beta_{K1} - \beta_{K-1,1} \tag{3.2b}$$

The function $g_{(n=0)}$ which appears here is exactly the function g calculated in Ref. 3 up to order γ^{-4}. Explicitly in formulas (2.29a) and (2.29b) of Ref. 3

$$g_0 = g = 1 + \phi''/m\gamma^2 + O(\gamma^{-4})$$

3.2. Study of Equation (3.1b)

The equalities (3.2a) and (3.2b) correspond to the value $p = 0$ in (3.1b). The general case is more complicated to handle. We have the following equation:

$$\left[\sum_K (\beta_{Kp}A^\dagger + \gamma_{Kp})(A^\dagger A)^K\right]\left[\sum_H \mathscr{G}_H(A^\dagger A)^H + p/s\right]$$
$$- p[A^\dagger - (\beta/m)^{1/2}\phi' + (m\beta)^{-1/2}g'/g]\left[\sum_K (\beta_{Kp-1}A^\dagger + \gamma_{Kp-1})(A^\dagger A)^K\right]$$
$$- [A^\dagger + (m\beta)^{-1/2}g'/g]\left[\sum_K (\beta_{Kp+1}A^\dagger + \gamma_{Kp+1})(A^\dagger A)^K\right] \equiv 0 \qquad (3.3)$$

The main problem in the above expression is to put the product

$$(A^\dagger A)^K \mathscr{G}_H(A^\dagger A)^H$$

in a canonical manner

$$\sum_{J=0}^{K} (u_J^{KH}A^\dagger + v_J^{KH})(A^\dagger A)^{J+H}$$

in such a way as to identify the coefficients of $(A^\dagger A)^K$ and $A^\dagger(A^\dagger A)^K$ to zero.

3.3. The Harmonic Approximation

3.3.1. The Harmonic Approximation. This consists in assuming that $g' = h' = 0$. It will be shown below that under these conditions, $\mathscr{G}_H$ commutes with $A^\dagger$ and A:

$$[A^\dagger, \mathscr{G}_H] = [A, \mathscr{G}_H] = [A^\dagger A, \mathscr{G}_H] = 0$$

This considerably simplifies expression (3.3). Moreover, since the commutator of $A^\dagger A$ with any function f is given by

$$[A^\dagger A, f] = -f''/m\beta + f'/\sqrt{(m\beta)}\{A^\dagger - A\} \qquad (3.4)$$

the commutation $[A^\dagger A, \mathscr{G}_H] = 0$ supposes that

$$\mathscr{G}'_H \equiv 0 \qquad (3.5)$$

In the harmonic approximation, the two basic relations connecting p and $p \pm 1$ are, using (2.18b),

$$\sum_K \beta_{Kp}\mathscr{G}_{L-K} + (p/s)\beta_{Lp} + (m\beta)^{-1/2}(p\beta'_{Lp-1} + \beta'_{Lp+1})$$
$$- (\beta/m)^{1/2}\phi'\beta_{Lp+1} - (p\gamma_{Lp-1} + \gamma_{Lp+1}) = 0 \qquad (3.6a)$$

$$\sum_K \gamma_{Kp}\mathscr{G}_{L-K} + (p/s)\gamma_{Lp} + (m\beta)^{-1/2}(p\gamma'_{Lp-1} + \gamma'_{Lp+1}) + (p\beta_{L-1p-1} + \beta_{L-p+1})$$
$$+ (\beta/m)^{/2}\phi' p\gamma_{Lp-1} + (\phi''/m)(p\beta_{Lp-1} + \beta_{Lp+1}) = 0 \qquad (3.6b)$$

The harmonicity condition $g' = h' = 0$ gives $\tilde{\phi}'' \equiv \phi''$ in the last recursion [see (2.18b)]; moreover, in this case $\mathbf{d} \equiv A$, $\mathbf{d}^+ \equiv A^\dagger$.

3.3.2. Solution of the Recursions (3.6a, b). We can set $p \geqslant 0$ in the case $n = 0$, since then [see (2.3)] negative values for p are not relevant. It is possible to put β_{Kp} and γ_{Kp} in the following form: If one introduces the function

$$\Gamma(z) = (1/2z)[1 - \sqrt{(1-4z)}] \tag{3.7}$$

and uses (3.6a), and (3.2b) with $p \geqslant 0$, one obtains

$$\beta_{Kp} = (1/\gamma)\, p\Gamma(\phi''/m\gamma^2)^p\, b_{Kp} \tag{3.8a}$$

$$\gamma_{Kp} = (1/\gamma)\, p\Gamma(\phi''/m\gamma^2)^p\, c_{Kp} \tag{3.8b}$$

$$\mathscr{G}_K\,(\equiv \mathscr{G}_{K[0]}) = -\delta_{K1}(1/\gamma)\,\Gamma(\phi''/m\gamma^2) \tag{3.8c}$$

where b_{Kp} and c_{Kp} do not depend on γ.

We now understand the reasons for the name "harmonic approximation": The relations (3.8c) and (3.5) imply $\phi'''(x) \equiv 0$ and the potential ϕ is harmonic. Indeed, the above approach is not the best way to study the pure harmonic potential,[6] but it presents the great advantage of making a bridge with the approaches for more general potentials.

The b_{Kp} and c_{Kp} are again obtained through recursion relations obtained from (3.6a) and (3.6b) using the fact that $z\Gamma^2 - \Gamma + 1 \equiv 0$,

$$b_{Kp} = -(m\beta)^{-1/2} b'_{Kp-1} + c_{Kp-1} \tag{3.9a}$$

$$c_{Kp} = -(m\beta)^{-1/2} c'_{Kp-1} - (\beta/m)^{1/2}\phi' c_{Kp-1} - (\phi''/m) b_{Kp-1} - b_{K-1p-1} \tag{3.9b}$$

or equivalently as recursions on K,

$$b_{K-1p} = p(\phi''/m) b_{Kp} - (\beta/m)^{1/2}\phi' b_{Kp+1} - b_{Kp+2} \tag{3.10a}$$

$$c_{K-1p} = p(\phi''/m) c_{Kp} - (\beta/m)^{1/2}\phi' c_{Kp+1} - c_{Kp+2} \tag{3.10b}$$

the solutions of which are, starting from the initial conditions $b_{K0} \equiv 0$ and $c_{K0} \equiv \delta_{K0}$, for $m = 0, 1, 2, \ldots$ ($E[m/2]$ designates the integer part of $m/2$ and $\binom{p}{n}$ are the binomial coefficients):

$$\begin{aligned} b_{Kp}(x) &\equiv b_{K,2K+1+m} \\ &= \sum_{q,r,s=0}^{E[m/2]} (-1)^{K+m+r} A(q,r,s) \binom{m-r}{2q} \binom{K+m-s}{m-r} \\ &\quad \times (\{\beta/m)^{1/2}\phi'\}^{m-2q} \{\phi''/m\}^q \end{aligned} \tag{3.11a}$$

$$
\begin{aligned}
c_{Kp}(x) &\equiv c_{K,2K+1+m} \\
&= \sum_{q,r,s=0}^{E[m/2]} (-1)^{K+m+r} \left\{ (m+2-2q)\, A(q-1, r, s) \binom{m-r}{2q-2} \right. \\
&\quad \left. - (K+m+1-s)/(m+1-r)\, A(q, r, s) \binom{m+1-r}{2q} \right\} \binom{K+m-s}{m-r} \\
&\quad \times \{(\beta/m)^{1/2}\phi'\}^{m-2q+1} \{\phi''/m\}^q
\end{aligned}
\tag{3.11b}
$$

The coefficients $A(q, r, s)$ are pure numbers independent of γ, K, p, or m, but they are too complicated to be explicitly calculated. The first values from $q = 0$–4 are given in Appendix B as well as their recursion relation.

One can also use the recursion relations (3.10a) and (3.10b) starting from the initial conditions

$$
b_{K,2K+1} = (-1)^K; \qquad c_{K,2K+1} = (-1)^{K+1}(K+1)[(\beta/m)^{1/2}\phi']
$$

The first coefficients b_{Kp} and c_{Kp} are

$$
\begin{aligned}
&b_{K0} = 0, && c_{K0} = \delta_{K0} \\
&b_{K1} = \delta_{K0}, && c_{K1} = -[(\beta/m)^{1/2}\phi']\,\delta_{K0} \\
&b_{K2} = -[(\beta/m)^{1/2}\phi']\,\delta_{K0}, && c_{K2} = [(\beta/m)^{1/2}\phi']^2\,\delta_{K0} \\
&b_{K3} = \{[(\beta/m)^{1/2}\phi']^2 + \phi''/m\}\,\delta_{K0} - \delta_{K1} \\
&c_{K3} = -[(\beta/m)^{1/2}\phi']\{[(\beta/m)^{1/2}\phi']^2 \\
&\qquad + \phi''/m\}\,\delta_{K0} + 2[(\beta/m)^{1/2}\phi']\,\delta_{K1} \\
&b_{K4} = -[(\beta/m)^{1/2}\phi']\{[(\beta/m)^{1/2}\phi']^2 \\
&\qquad + 3\phi''/m\}\,\delta_{K0} + [(\beta/m)^{1/2}\phi']\,\delta_{K1} \\
&c_{K4} = [(\beta/m)^{1/2}\phi']^2\{[(\beta/m)^{1/2}\phi']^2 \\
&\qquad + 3\phi''/m\}\,\delta_{K0} - 3[(\beta/m)^{1/2}\phi']^2\,\delta_{K1}
\end{aligned}
$$

and so on.

3.4. The Semianharmonic Approximation

Since the general solution of Eq. (3.3) when ϕ is anharmonic is too difficult to be extracted directly, we will use results obtained by continuity between the GB calculation[3] and the general harmonic formula from Section 3.3. We will first suppose that *the second derivatives of ϕ are now spatially dependent.*

For clarity the index $n=0$ is reintroduced. From (2.8) and (3.8c), we derive the basic equation for $\psi_{[0]}$,

$$\partial\psi_{[0]}/\partial t = \partial_{[0]}\psi_{[0]} \tag{3.12a}$$

where

$$\partial_{[0]} = \mathscr{G}_{1[0]} A^{\dagger}_{[0]} A_{[0]} = -(1/\gamma)\,\Gamma(\Phi''/m\gamma^2) A^{\dagger}_{[0]} A_{[0]} \tag{3.12b}$$

The operator $\partial_{[0]}$ is indeed Hermitian, and the eigenfunctions of $A^{\dagger}_{[0]} A_{[0]}$ are well known:

$$S_{[0]}(x) = \theta/\gamma A^{\dagger}_{[0]} A_{[0]} = \theta^2\,\partial^2/\partial x^2 + V_{[0]}(x) \tag{3.13a}$$

with

$$V_{[0]}(x) = [\tilde{u}_{[0]}(x)/2]^2 - (\theta/2)\,\tilde{u}''_{[0]}(x) \tag{3.13b}$$

and the reduced quantities

$$u(x) \equiv \phi(x)/m\gamma; \qquad \tilde{u}_{[n]}(x) \equiv \tilde{\phi}_{[n]}(x)/m\gamma; \qquad \theta = (m\beta\gamma)^{-1} \tag{3.14}$$

Comparing with formula (2.30) of Ref. 3 when $n=0$, we can see that the two approaches are complementary: Equation (3.12) is

$$-\theta\,\partial\psi_{[0]}/\partial t = \Gamma S_{[0]}\psi_{[0]} \tag{3.15}$$

with

$$\Gamma(\phi''/m\gamma^2) = 1 + (u''/\gamma) + 2(u''/\gamma)^2 + \cdots \equiv g(x) + O(\gamma^{-4})$$

and is valid to any order in γ^{-1} but is *a priori* restricted to harmonic potentials, while the first one corresponds to an arbitrary potential but is limited to order γ^{-3} in $g(x)$.

The harmonic result for $\mathscr{G}_K$ is (3.8c),

$$\mathscr{G}_K = -\delta_{K1}(1/\gamma)\,\Gamma(\phi''/m\gamma^2) = -\delta_{K1}(1/\gamma)(1 + \phi''/m\gamma^2 + \cdots)$$

with $\phi''' \equiv 0$, while the anharmonic GB result is [formula (2.30) in Ref. 3 with $n=0$],

$$\mathscr{G}_K = -\delta_{K1}(1/\gamma)(1 + \phi''/m\gamma^2 + \cdots)$$

but now with $\phi''' \neq 0$. It is clear that expression (3.8c) extends the GB result to any order in γ in the harmonic regions.[3] Let us examine the other quan-

[3] The expansion scheme proposed here can only work when all derivatives stay finite: Therefore, the treatment does not apply strictly for piecewise harmonic potentials. However, the smootheness of the potential $\phi(x)$ in the anharmonic regions is less crucial close to equilibrium than when considering very out-of-equilibrium systems.

tities. In all generality, formulas (3.2a) and (3.2b) relate $\mathscr{G}_K$, γ_{K1}, and β_{K1}. Moreover, $\mathbf{O}_1 = \sum_K (\beta_{K1} A^\dagger + \gamma_{K1})(A^\dagger A)^K$ and the harmonic results for β_{K1} and γ_{K1} are

$$\beta_{K1} = (1/\gamma)\, \Gamma(\phi''/m\gamma^2)\delta_{K0}$$

$$\gamma_{K1} = (1/\gamma)\, \Gamma(\phi''/m\gamma^2)[-(\beta/m)^{1/2}\phi']\delta_{K0}$$

The anharmonic GB results give (Ref. [3], formulas (2.11) and (2.14b) with $n=0$, $p=1$]

$$\mathbf{O}_1 = -\gamma^{-1}\mathbf{d} + \gamma^{-3}(\mathbf{d}^+\mathbf{d}^2 - \mathbf{d}\mathbf{d}^+\mathbf{d}) + \cdots$$

Also, by using $\mathbf{d}^+ = A^\dagger + (m\beta)^{-1/2} g'/g$ and $\mathbf{d} = A + (m\beta)^{-1/2} h'/h$ with (2.15), (2.16), (2.18a), and (2.18b) we obtain

$$\mathbf{O}_1 = (1/\gamma)(1 + \phi''/m\gamma^2 + \cdots)[A^\dagger - (\beta/m)^{1/2}\phi' + (m\beta)^{-1/2} g'/g]$$

For the semianharmonic approximation we can then try

$$\mathbf{O}_1 = (1/\gamma)\, \Gamma(\phi''/m\gamma^2)[A^\dagger - (\beta/m)^{1/2}\phi' + (m\beta)^{-1/2} g'/g]$$

that is,

$$\beta_{K1} = (1/\gamma)\, \Gamma(\phi''/m\gamma 2)\delta_{K0} \tag{3.15a}$$

$$\gamma_{K1} = -(1/\gamma)\, \Gamma(\phi''/m\gamma^2)(m\beta)^{-1/2}(\beta\phi' - g'/g)\delta_{K0} \tag{3.15b}$$

Inserting this into the exact Eqs. (3.2a) and (3.2b), and with Γ'_x denoting the derivative of $\Gamma(\phi''/m\gamma^2)$ with respect to x, gives

$$\Gamma'_x/\Gamma = g'/g - h'/h, \qquad (\Gamma'_x/\Gamma - g'/g)(\beta\phi' - g/g) + (h'/h)' = 0$$

which agree *by continuity* with the choice

$$g(x) = \Gamma(\phi''/m\gamma^2) = (m\gamma^2/2\phi'')[1 - (1 - 4\phi''/m\gamma^2)^{1/2}] \tag{3.16a}$$

$$h(x) = 1 \tag{3.16b}$$

With this choice,

$$\mathbf{O}_1 \equiv \mathbf{O}_{[1][0]} = (\Gamma/\gamma)[A^\dagger - (\beta/m)^{1/2}\tilde{\phi}'] = -(\Gamma/\gamma)\mathbf{d} \tag{3.17}$$

This expression is exact in the harmonic regions and at least to order γ^{-5} for the contributions in ϕ''', ϕ^{IV},..., in the anharmonic region; it is simply obtained by replacing ϕ by $\tilde{\phi}$ in the harmonic results.

To summarize the $n=0$ case, in the semianharmonic approximation, $P_{[0]}(v, x, t)$ is given by formula (2.3),

$$P_{[0]}(v, x, t) = \sum_{p=0}^{\infty} \chi_p(v)\, O_{[p][0]}\, c_{[0]}(x, t)$$

with

$$c_{[0]}(x, t) = \exp(-\beta G_{[0]})\, \psi_{[0]}(x, t)$$

$\psi_{[0]}(x, t)$ itself is a solution of (3.12a), i.e.,

$$-\theta\, \partial\psi_{[0]}/\partial t = \Gamma(\phi''(x)/m\gamma^2)[\theta^2\, \partial^2/\partial x^2 + V_{[0]}(x)]\,\psi_{[0]}$$

In the above expressions, the modified potential $V_{[0]}$ and the function $G_{[0]}$ are simply related to the initial potential $\phi(x)$ [via (3.13b), (2.18a), and (2.18b)]

$$\begin{aligned} V_{[0]}(x) &= [\tilde{u}'_{[0]}(x)/2]^2 - (\theta/2)\, \tilde{u}''_{[0]}(x) \\ G_{[0]}(x) &= \phi(x)/2 + (2\beta)^{-1} \ln \Gamma(\phi''(x)/m\gamma^2) \\ \tilde{u}_{[0]}(x) &\equiv \tilde{\phi}_{[0]}(x)/m\gamma \\ \tilde{\phi}_{[0]}(x) &\equiv \phi(x) - \beta^{-1} \ln \Gamma(\phi''(x)/m\gamma^2) \end{aligned}$$

The modified potential $\tilde{\phi}_{[0]}(x)$ has the structure of an effective free energy, $\ln \Gamma$ playing the role of an oscillation entropy.

It is possible to calculate $P_{[0]}$ up to the term in $\chi_1(v)$, since $O_{[1][0]}$ is known:

$$\begin{aligned} O_{[1][0]} &= (1/\gamma)\, \Gamma(\phi''(x)/m\gamma^2)[(m\beta)^{-1/2}\, \partial/\partial x + (\beta/m)^{1/2}\, \phi'(x)] \\ &= -(\Gamma/\gamma) d \end{aligned}$$

For $p > 1$ the $O_{[p][0]}$ are known in the harmonic approximation, e.g.,

$$O_{[2][0]} = (\Gamma/\gamma)^2 (\beta/m)^{1/2} \phi' d$$

4. THE ARBITRARY n CASE

Expressions (2.10)–(2.12) must now be used, and (3.3) then becomes

$$\begin{aligned} &\left[\sum_K (\beta_{Kp} A^\dagger + \gamma_{Kp})(A^\dagger A)^K\right]\left[\sum_H \mathcal{G}_H (A^\dagger A)^H + p/s\right] \\ &\quad - (n+p)[A^\dagger - (\beta/m)^{1/2}\phi' + (m\beta)^{-1/2} g'/g] \\ &\quad \times \left[\sum_K (\beta_{Kp-1} A^\dagger + \gamma_{Kp-1})(A^\dagger A)^K\right] \\ &\quad - [A^\dagger + (m\beta)^{-1/2} g'/g]\left[\sum_K (\beta_{Kp+1} A^\dagger + \gamma_{Kp+1})(A^\dagger A)^K\right] \equiv 0 \quad (4.1) \end{aligned}$$

We see that except for a factor $(n+p)$, Eqs. (3.3) and (4.1) are identical. But this slight difference is capital, since it is now possible to reach negative values for p. Equation (4.1) gives rise to three recursion relations when expanding β_{Kp}, γ_{Kp}, and $\mathscr{G}_K$ into γ^{-1} power series.

4.1. The Harmonic Approximation

Again, we first limit ourselves to a harmonic potential, but now the index p may take on negative values. The operators $\mathscr{G}_K$ take a very simple form:

$$\mathscr{G}_0 = n\phi''/(m\gamma)\, \Gamma(\phi''/m\gamma^2) \tag{4.2a}$$

$$\mathscr{G}_1 = -1/\gamma\Gamma(\phi''/m\gamma 2) \tag{4.2b}$$

$$\mathscr{G}_{K>1} \equiv 0 \tag{4.2c}$$

On the other hand, the coefficients β_{Kp} and γ_{Kp} necessary to build the O_p and subsequently the different components of $P(v, x, t)$ through (1.9) and (2.3) have much more complicated expressions, which are given at least for the first values of K and p in Appendix D. But let us first consider the equation defining $\psi_{[n]}(x, t)$.

4.2. The Semianharmonic Approximation

From the above results (4.2) and the basic Eqs. (2.7) and (2.17), in which the index n is reintroduced, we obtain an equation of motion for $\psi_{[n]}(x, t)$:

$$\begin{aligned} \partial\psi_{[n]}(x, t)/\partial t = [&-n\gamma + n\phi''/(m\gamma)\, \Gamma(\phi''/m\gamma^2) \\ &- \Gamma(\phi''/m\gamma^2)/\gamma A^\dagger_{[n]} A_{[n]}]\, \psi_{[n]}(x, t) \end{aligned}$$

Using the relation $z\Gamma^2 - \Gamma + 1 = 0$, satisfied by $\Gamma(z)$ [see (3.7)], and introducing again (3.16a)

$$g(x) = \Gamma(\phi''(x)/m\gamma^2) \equiv \Gamma(u''(x)/\gamma) \equiv \gamma/(2u'')\{1 - [1 - (4u'')/\gamma]^{1/2}\}$$

one finds that

$$\partial\psi_{[n]}(x, t)/\partial t = -[n\gamma/g + (g/\gamma)\, A^\dagger_{[n]} A_{[n]}]\, \psi_{[n]}(x, t) \tag{4.3}$$

This expression has the usual Schrödinger-like structure found in this kind of problem with a convenient potential, i.e.,

$$-[\theta/g(x)]\, \partial\psi_{[n]}(x, t)/\partial t = [n\gamma\theta + S_{[n]}(x)]\, \psi_{[n]}(x, t) \tag{4.4a}$$

where

$$S_{[n]}(x) \equiv \theta/\gamma A^{\dagger}_{[n]} A_{[n]} + n\gamma\theta[g(x)^{-2} - 1]$$
$$= \theta^2\, \partial^2/\partial x^2 + V_{[n]}(x) \tag{4.4b}$$

and

$$V_{[n]}(x) = \tilde{u}'_{[n]})^2/4 - (\theta/2)\tilde{u}''_{[n]} + n\gamma\theta[\Gamma(u''/\gamma)^{-2} - 1] \tag{4.4c}$$

Again comparing these results with those of Ref. 3, one observes that one is exact in harmonic regions, while the other is valid up to order γ^{-5} in anharmonic regions. Then, *in the semianharmonic approximation, we will take*

$$V_{[n]}(x) = (\tilde{u}'_{[n]})^2/4 - (\theta/2)\tilde{u}''_{[n]} + n\gamma\theta[\Gamma(u''/\gamma)^{-2} - 1]$$
$$+ (\theta^2/2\gamma)\, n(1-n) u^{\mathrm{IV}} \tag{4.4d}$$

in which the fourth derivative appears as an anharmonic correction and in which also $\phi''(x)$ [or $u''(x)$] is now spatially dependent.

The general solution $\psi_{[n]}$ is then constructed in the usual manner as an expansion on the basis of the eigenfunctions of $S_{[n]}$,

$$S_{[n]}(x)\, \varphi_{[n]\,p}(x) = \lambda_{[n]\,p}\, \varphi_{[n]\,p}(x) \tag{4.5}$$

analogous to Eq. (2.33) in Ref. 2. Hence,

$$\psi_{[n]}(x, t) = \sum_p \varphi_{[n]\,p}(x)\;\; K_{[n]\,p}(t) \exp[-(n\gamma + \lambda_{[n]\,p}/\theta)t] \tag{4.6}$$

in which the time-dependent coefficients $K_{[n]\,p}(t)$ are determined by

$$\partial K_{[n]\,p}(t)/\partial t = -\sum_q (F_{[n]\,pq}/\gamma)(n\gamma + \lambda_{[n]\,q}/\theta)\, K_{[n]\,q}(t)$$
$$\times \exp[(\lambda_{[n]\,p} - \lambda_{[n]\,q})t/\theta] \tag{4.7a}$$

The coefficients $F_{[n]\,pq}$ play a very important role in the calculation of the characteristic times of the problem. Their expression is simply given by

$$F_{[n]\,pq} = \gamma \int_{-\infty}^{+\infty} dx\, \varphi^*_{[n]\,p}(x)[g(x) - 1]\, \varphi_{[n]\,q}(x)$$
$$= \gamma J_{[n]\,pq} - \gamma\delta_{pq} \tag{4.7b}$$

This definition for $F_{[n]pq}$ is similar to that in our earlier paper when γ is taken very large, since then $g-1 \simeq u''/\gamma$; but the introduction of $J_{[n]pq}$,

$$J_{[n]pq} = \int_{-\infty}^{+\infty} dx\, \varphi^*_{[n]p}(x)\, g(x)\, \varphi_{[n]q}(x) \tag{4.7c}$$

will appear as a more natural matrix element.

In the harmonic regions, $J_{[n]pq}$ and $F_{[n]pq}$ are diagonal in p and q, and Eq. (4.7a) simplifies considerably: Let $F_{[n]p} \equiv F_{[n]pp}$,

$$K_{[n]p}(t) = K_{[n]p}(0) \exp[-(F_{[n]p}/\gamma)(n\gamma + \lambda_{[n]p}/\theta)t] \tag{4.8}$$

The initial values $K_{[n]p}(0)$ have to be determined from the initial conditions for $P(v, x, t)$. Inserting (4.8) in (4.6), one obtains

$$\psi_{[n]}(x, t) = \sum_p \varphi_{[n]p}(x)\, K_{[n]p}(0) \exp(-t/\tau_{[n]p}) \tag{4.9a}$$

where

$$1/\tau_{[n]p} = J_{[n]p}(n\gamma + \lambda_{[n]p}/\theta) \tag{4.9b}$$

are the inverse characteristic times for the evolution of $P(v, x, t)$ in the intermediate friction regimes when J is diagonal. In particular, this result is exact in the harmonic regions. It also easy to check that $\tau_{[n]p}$ remains positive in these regimes without any restrictions.

To summarize the arbitrary n case, in the semianharmonic approximation (i.e., valid at any temperature, and up to γ^{-5} in the anharmonic regions), $P_{[n]}(v, x, t)$ is given by formula (2.3),

$$P_{[n]}(v, x, t) = \sum_{p=0}^{\infty} \chi_p(v)\, O_{[p][n]}\, c_{[n]}(x, t)$$

with

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

$\psi_{[n]}(x, t)$ is itself a solution of (4.4), i.e.,

$$-\theta\, \partial\psi_{[n]}/\partial t = g(x)[n\gamma\theta + \theta^2\, \partial^2/\partial x^2 + V_n(x)]\, \psi_{[n]}$$

In the above expressions, the modified potential $V_{[n]}$ and the function $G_{[n]}$ are simply related to the initial potential $\phi(x)$ [via (4.4c), (2.18a), and (2.18b)]

$$V_{[n]}(x)=[\tilde{u}'_{[n]}(x)/2]^2-(\theta/2)\,\tilde{u}''_{[n]}(x)+n\gamma\theta[g(x)^{-2}-1]$$
$$+\ (\theta^2/2\gamma)\,n(1-n)u^{\mathrm{IV}}$$
$$G_{[n]}(x)=\phi(x)/2+(1-2n-2n^2)(2\beta)^{-1}\ln g(x)$$
$$\tilde{u}_{[n]}(x)\equiv\tilde{\phi}_{[n]}(x)/m\gamma$$
$$\tilde{\phi}_{[n]}(x)\equiv\phi(x)-(1+2n)\beta^{-1}\ln g(x)$$

where $g(x)=\Gamma(\phi''(x)/m\gamma^2)$. Once again $\tilde{\phi}_{[n]}$ has the structure of a free energy, the number of available states being $g(x)^{2n+1}$.

The general solution $\psi_{[n]}(x,t)$ is expanded on the eigenstates $\varphi_{[n]p}(x)$ of (4.4) and (4.5):

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

The time-dependent coefficients $K_{[n]p}(t)$, explicitly derived in the harmonic regions [Eq. (4.8)], can be in principle obtained by perturbation via (4.7) in the anharmonic one, but we will not need such corrections in the following application.

5. THE BISTABLE POTENTIAL

We will consider in more detail the important application of the formalism to the Brownian particle in a bistable potential. The potential $u(x)$ [or $\phi(x)$] consists of two wells x_1 and x_2 with depth u_1 and u_2 and curvature u_1'' and u_2''. The wells are separated by a barrier at $x_0=0$ with height u_0 and curvature u_0''. The study is restricted to temperatures θ low compared to the barrier heights $\Delta u_1\equiv u_0-u_1$ and $\Delta u_2\equiv u_0-u_2$. Then $V_{[n]}(x)$ defined by (4.4d) is essentially determined by the term $(\tilde{u}'_{[n]})^2/4$ and shows three minima, which are located close to the extrema of $u(x)$. In fact,

$$V'_{[n]}\simeq u'u''/2-(n+1/2)\,\theta u'''u''/\gamma-(2n+1/2)\,\theta u'''+\cdots$$

in which the contributions $\theta u'''$ may be neglected for n not too large.

Again, we will use the WKB method[7] to derive the physical behavior of the double well. We need the characteristic parameters of $V_{[n]}$ at its minima (position $\tilde{x}_\alpha$, curvature, and value of $V_{\alpha[n]}$), which are derived in Appendix C. We find with $\Gamma_\alpha=\Gamma(u_\alpha''/\gamma)$ that

$$\tilde{x}_\alpha=x_\alpha+O(\theta/\Delta u_\alpha) \tag{5.1a}$$

$$V_{[n]}(x_\alpha)=V_{\alpha[n]}=-(1/2)\,\theta u_\alpha''-n\theta u_\alpha''(\Gamma_\alpha+1)+O[(\theta/\Delta u_\alpha)^2] \tag{5.1b}$$

$$V''_{[n]}(x_\alpha)=V''_{\alpha[n]}=(1/2)(u_\alpha'')^2+O(\theta/\Delta u_\alpha) \tag{5.1c}$$

so that in the vicinity of a minimum,

$$V_{[n]}(x) \simeq -\tfrac{1}{2}[2n(\Gamma_\alpha+1)+1]\,\theta u''_\alpha + \tfrac{1}{4}(u''_\alpha)^2(x-x_\alpha)^2 \tag{5.2}$$

Since only the low-lying eigenvalues of $S_{[n]}$, for which $|\lambda_{[n]} - V_{\alpha[n]}|$ is of order $\theta|u''_\alpha|$, are relevant in our problem, and since the temperature is taken to be low with respect to the barrier, an harmonic approximation appears to be justified[3,6] for $V_{[n]}$.

The time scales involved in the relaxation processes are determined starting from the "energy" levels $\Lambda^\alpha_{[n]p}$ in the three valleys of $V_{[n]}$:

$$\Lambda^\alpha_{[n]p} = -(1/2)[2n(\Gamma_\alpha+1)+1]\,\theta u''_\alpha + \theta\,|u''_\alpha|\,(p+1/2), \qquad p=0,2,2,... \tag{5.3a}$$

$$\Lambda^\alpha_{[n]p} = \theta u''_\alpha[p-n(\Gamma_\alpha+1)] \tag{5.3b}$$

and for $\alpha=0$,

$$\Lambda^0_{[n]p} = \theta\,|u''_0|\,[p+n(\Gamma_\alpha+1)+1] \tag{5.3c}$$

and one can verify that the eigenvalues of Ref. 3 are recovered when γ is large enough to give $\Gamma_\alpha \simeq 1$.

For $n\neq 0$, the lowest eigenvalues are $\Lambda^\alpha_{[n]0} = -\theta u_\alpha'' n(\Gamma_\alpha+1)$, $\alpha=1, 2$. These values can be considered to be good approximations for the lowest eigenvalues of $S_{[n]}$. Tunneling between wells 1 and 2 can only introduce exponentially small corrections $\sim\exp(-\Delta u_{1,2}/\theta)$, which can be neglected at low temperature. The eigenfunctions associated with the eigenvalues (5.3b) are the usual oscillator functions. In contrast, for $n=0$ the two lowest eigenvalues are $\Lambda_{1[0]0} = \Lambda_{2[0]0} = 0$ and tunneling between the two states must be explicitly considered. We will start first with the $n=0$ case.

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

The structure of the calculation remains similar to Ref. 3. The new modified potential extracted from (3.13b), (3.14), (2.18b), (3.16a), and (3.16b) is $\tilde{u}_{[0]}(x) = u(x) - \theta \ln g(x)$. The eigenvalue problem (3.15) is studied using the WKB approximation, which becomes exact in the low-temperature limit. If we are concerned with distributions in the vicinity of equilibrium, hence located inside the wells of $u(x)$, the eigenstates $\varphi_{[0]p}(x)$ are linear combinations of Weber functions $D_r(y)$ with integer r, centered at the bottoms of the wells. The two lowest eigenstates $\varphi_{[0]0}(x)$ and $\varphi_{[0]1}(x)$ are linear combinations of Gaussians centered on x_1 and x_2, while the higher eigenfunctions $\varphi_{[0]p}$ with $p=2, 3,...$ are described by pure "oscillatory" states inside the wells:

$$\varphi_{[0]0}(x)=\varphi_0^{(1)}(x)(1+\tilde{d}_{12}^2)^{-1/2}+\varphi_0^{(2)}(x)(1+\tilde{d}_{21}^2)^{-1/2} \tag{5.4a}$$

$$\varphi_{[0]1}(x)=-\varphi_0^{(1)}(x)(1+\tilde{d}_{21}^2)^{-1/2}+\varphi_0^{(2)}(x)(1+\tilde{d}_{12}^2)^{-1/2} \tag{5.4b}$$

where

$$\varphi_0^{(\alpha)}(x)\equiv(u_\alpha''/2\pi\theta)^{1/2}\exp[-(x-x_\alpha)^2 u_\alpha''/4\theta] \tag{5.4c}$$

and

$$\tilde{d}_{12}=(u_1'')^{1/2}\exp\{[\tilde{u}_{[0]}(x_1)-\tilde{u}_{[0]}(x_2)]/2\theta\} \tag{5.4d}$$

For $p=2, 3, 4,...$, where p now corresponds to a pair of indices r, (α), we find

$$\varphi_{[0]p}(x)=\varphi_p(x)\equiv\varphi_r^{(\alpha)}(x)\equiv(r!)^{-1/2}(u_\alpha''/2\pi\theta)^{1/4}D_r([x-x_\alpha](u_\alpha''/\theta)^{1/2}) \tag{5.5a}$$

with $r=1, 2, 3,...$, $\alpha=1, 2$, and

$$D_r(y)=(-1)^r\exp(y^2/4)\,d^r/dy^r\,[\exp(-y^2/4)] \tag{5.5b}$$

The corresponding eigenvalues are also unchanged compared to Ref. 3,

$$\lambda_{[0]0}=0 \tag{5.6a}$$

$$\begin{aligned}\lambda_{[0]1}=\theta/(2\pi)[&(u_1''\,|u_0''|)^{1/2}\exp\{[\tilde{u}_{[0]}(x_1)-\tilde{u}_{[0]}(x_0)]/\theta\}\\&+(u_2''\,|u_0''|)^{1/2}\exp\{[\tilde{u}_{[0]}(x_2)-\tilde{u}_{[0]}(x_0)]/\theta\}]\end{aligned} \tag{5.6b}$$

$$\lambda_{[0]p}\equiv\lambda_{[0]r}^{[\alpha]}=\theta r u_\alpha'',\qquad p\geqslant 2,\quad r=1, 2, 3,...,\quad \alpha=1, 2 \tag{5.6c}$$

We also need the corresponding expressions for $J_{[0]pq}$. Using Eqs. (5.4) and (5.5), we find

$$J_{[0]00}=g_1/(1+\tilde{d}_{12}^2)+g_2/(1+\tilde{d}_{21}^2) \tag{5.7a}$$

$$J_{[0]01}=J_{[0]10}=(g_2-g_1)/(\tilde{d}_{12}+\tilde{d}_{21}) \tag{5.7b}$$

$$J_{[0]11}=g_1/(1+\tilde{d}_{21}^2)+g_2/(1+\tilde{d}_{12}^2) \tag{5.7c}$$

while for $p, q\geqslant 2$ we have

$$J_{[0]pq}\equiv J_{[0]rr'}^{\alpha\beta}=g_\alpha\,\delta_{\alpha\beta}\,\delta_{rr'},\qquad r, r'=1, 2, 3,...,\quad \alpha, \beta=1, 2 \tag{5.8a}$$

and

$$J_{[0]0p}\equiv J_{[0]p0}\equiv J_{[0]1p}\equiv J_{[0]p1}=0 \tag{5.8b}$$

In the above formulas $g_\alpha=g(x_\alpha)$ is given by (3.16a).

An expression for $c_{[0]}(x, t)$ in the semianharmonic approximation is then easily derived:

$$\begin{aligned} c_{[0]}(x,t) = g(x)^{-1/2}\exp[-u(x)/2\theta]\{\varphi_{[0]0}(x)K_{[0]0}(0) \\ + K_{[0]1}(0)[J_{[0]01}\varphi_{[0]0}(x)\exp(-\lambda_{[0]1}J_{[0]11}t/\theta) \\ + \sum_{\alpha=1}^{2}\sum_{r=1}^{\infty} K_{[0]r}^{(\alpha)}(0)\,\varphi_{[0]r}^{(\alpha)}(x)\exp(-\lambda_{[0]r}g_\alpha t/\theta)\} \end{aligned} \tag{5.9}$$

The coefficient $K_{[0]0}(0)$ is determined by the normalization[3] at all times of $c_{[0]}(x, t)$:

$$K_{[0]0}(0) = \left[\int_{-\infty}^{+\infty} dx\, g(x)e^{-u(x)/\theta}\right]^{1/2} \Big/ \left[\int_{-\infty}^{+\infty} dx\ e^{-U(x)/\theta}\right] \tag{5.10}$$

It is interesting to consider the evolution of the distribution $c_{[0]}(x, t)$ located at $x = x_s$ at $t = 0$. Starting from (5.9) and using the boundary conditions at $t = 0$ and $t = \infty$, it is easy to show that

$$c_{[0]}(x, t \mid x_s, 0) = [\varphi_0(x)/\varphi_0(x_s)] \sum_{p=0}^{\infty} \varphi_p(x)\,\varphi_p(x_s)\,e^{-t/\tau_{[0]p}} \tag{5.11}$$

In this expression, we only need the eigenfunctions $\varphi_p(x) = \lim_{\gamma\to\infty}\varphi_{[0]p}(x)$, which correspond to the large damping case and have previously been determined. In the derivation, we use the fact that the distributions are strongly located in the bottoms of the wells, so that $g(x)\,\varphi_r^{(\alpha)}(x) \simeq g(x_\alpha)\,\varphi_r^{(\alpha)}(x)$. The relaxation times are on the contrary stongly dependent on γ:

$$\tau_{[0]0}^{-1} = 0 \tag{5.12a}$$

$$\tau_{[0]1}^{-1} = \theta^{-1}\lambda_{[0]1}J_{[0]11} \tag{5.12b}$$

while for $p \geqslant 2$ ($\alpha = 1.\ 2$; $r = 1, 2, 3,\ldots$),

$$\tau_{[0]p}^{-1} = (\tau_{[0]r}^{(\alpha)})^{-1} = ru_\alpha'' g_\alpha \tag{5.12c}$$

These final results are valid to any order in γ^{-1} as long as the anharmonic parts of the potential are not reached by the distributions $\varphi_p(x)$, i.e., for temperatures low compared with barrier heights Δu_1 and Δu_2.

$c_{[0]}(x, t)$ satisfies both the normalization condition [see formula (2.24) of Ref. 3] and the stationary equilibrium limit

$$\lim_{t\to\infty} c_{[0]}(x, t) = P_{\text{eq}}(x) = \left[\int_{-\infty}^{+\infty} dx\, e^{-u(x)/\theta}\right]^{-1} \exp[-u(x)/\theta]$$

for any arbitrary initial conditions. The slowest relaxation time toward equilibrium $\tau_{[0]1}$ can be found explicitly by taking $\lambda_{[0]1}$ from (5.6b) and $J_{[0]11}$ from (5.7c), and using the convenient definition

$$(\omega_\alpha/\gamma)^2 \equiv |u''_\alpha|/\gamma, \qquad \tau_{[0]1}^{-1} = W_{1\to 2} + W_{2\to 1} \tag{5.13a}$$

where

$$W_{1\to 2} = \omega_1 \omega_0/(2\pi\gamma)\, g(x_0) \exp(-\Delta u_1/\theta)$$
$$W_{2\to 1} = \omega_2 \omega_0/(2\pi\gamma)\, g(x_0) \exp(-\Delta u_2/\theta)$$

This expression for the rate is exact to any order of γ^{-1} and valid for temperatures small compared to the barrier heights. Using the explicit expression for g_0, one finds that

$$W_{\alpha\to\beta} \equiv \tau_{K,\alpha\to\beta}^{-1} = \omega_\alpha/(2\pi\omega_0)[(\omega_0^2+\gamma^2/4)^{1/2}-\gamma/2]\exp(-\Delta u_\alpha/\theta) \tag{5.13b}$$

5.2. Calculation of $c_{[n]}(x, t)$

When $n \neq 0$ the norm $N_{[n]}(t) \equiv \int_{-\infty}^{+\infty} dx\, c_{[n]}(x, t)$ is no longer conserved but decays as $\exp(-n\gamma t)$. The approximate eigenvalues $\lambda_{[n]p}$ of $S_{[n]}$, $n \neq 0$, are identical to $\Lambda_{[n]p}$ from (5.3b) and (5.3c). Tunneling between different wells is irrelevant, since it can only lead to exponentially small corrections to the relaxation times. Hence the corresponding eigenfunctions are

$$\varphi_{[n]p}(x) = \varphi_p(x) \equiv \varphi_r^{(\alpha)}(x) \equiv (r!)^{-1/2}(u''_\alpha/2\pi\theta)^{1/2} D_r(x-x_\alpha)(u''_\alpha/\theta)^{1/2}) \tag{5.14}$$

so that (4.9a) gives

$$\psi_{[n]}(x, t) = \sum_{r,\alpha} \varphi_{[n]r}^{(\alpha)}(x)\, K_{[n]r}^{(\alpha)}(0) \exp(-t|\tau_{[n]r}^{(\alpha)}) \tag{5.15}$$

Using (4.9b) and the relation $(u''_\alpha/\gamma)\, g_\alpha^2 - g_\alpha + 1 = 0$, one obtains for $\alpha = 1, 2$ that

$$\begin{aligned}(\tau_{[n]r}^{(\alpha)})^{-1} &= n\gamma + u''_\alpha(r-n)\, g_\alpha \\ &= (n+r)\gamma/2 + [(\gamma^2/4-\omega_\alpha^2)^{1/2}](n-r)\end{aligned} \tag{5.16a}$$

while for $\alpha = 0$,

$$\begin{aligned}(\tau_{[n]r}^{(0)})^{-1} &= \eta\gamma + |u''_0|\,(r+n+1)\, g_\alpha \\ &= (n-r-1)\gamma/2 + [(\gamma^2/4-\omega_\alpha^2)^{1/2}](n+r+1)\end{aligned} \tag{5.16b}$$

These expression are completely identical to the eigenvalue $\lambda_{n,r}$ for the harmonic potential given by Risken and Vollmer,[6] and this is not surprising since the essential contribution comes from the harmonic regions. From (5.16a) and (5.16b) one sees that for $\alpha = 0, 1, 2$, $(\tau^{(\alpha)}_{[n]r})^{-1}$ has the general structure

$$(\tau^{(\alpha)}_{[n]r})^{-1} = (\tau^{(\alpha)}_{[0]r})^{-1} + (\tau'^{(\alpha)}_{[n]})^{-1} \tag{5.17}$$

with

$$(\tau^{(\alpha)}_{[0]r})^{-1} = r[\gamma/2 - (\gamma^2/4 - \omega_\alpha^2)^{1/2}]$$
$$(\tau'^{(\alpha)}_{[n]})^{-1} = n[\gamma/2 + (\gamma^2/4 - \omega_\alpha^2)^{1/2}]$$

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

In the case of an initial distribution close to the bottom of a well α ($\alpha = 1$ or 2) the propagator $c_{[n]}(x, t \mid x_s, 0)$ has the following expression:

$$\begin{aligned} c_{[n]}(x, t \mid x_s, 0) = {} & P_0^{\text{fin}}\, \delta_{n0} + \exp(-t/\tau_n'^{(\alpha)})\{[\varphi_0^{(\alpha)}(x)]^2(1-\delta_{n0}) \\ & + [\varphi_0^{(\alpha)}(x)/\varphi_0^{(\alpha)}(x_s)] \\ & \times \sum_{r=1}^{\infty} \varphi_r^{(\alpha)}(x)\, \varphi_r^{(\alpha)}(x_s) \exp(-t/\tau^{(\alpha)}_{[0]r})\} \end{aligned} \tag{5.18}$$

The general solution $P(v, x, t)$ is then constructed from (1.9)–(1.11). But one must be aware that the initial value problem needs some caution.[4] This point is detailed in Section 2.2 of Ref. 3.

6. CONCLUSION

In this paper we first derived a general approach to obtain the solutions of the FPKK equation in the overdamped regime. The main results are summarized at the end of the corresponding sections. Moreover, in Section 5, we applied the results to the bistable potential and calculated the characteristic times and the propagator, but when temperature is low with respect to the barrier heght, a case for which the WKB approach can be used.[7] Not only is the usual Kramers time recovered, but also all the characteristic times of the system as well as the propagator, even for velocity and position far from equilibrium. The same technique could also

[4] The equation relating the set $c_{[n]}(x, 0)$ to the initial value coefficients $a_{[n]}(x, 0)$ nevertheless takes a remarkably simple operator form: $c = \{O/(1+O)\}a$, where $c = \|c_{[n]}\|$, $O = \|O_{[n][m]}\|$, and $a = \|a_{[n]}\|$.

be applied to determine the generalized Suzuki scaling law for the evolution from the instability point in overdamped systems governed by a FPKK equation (and not simply by a diffusion equation). This would generalize a previous calculation[8] limited to the lowest orders in γ^{-1}.

Further developments may be considered in two directions:

The first consists in improving the corrections due to anharmonicity by taking into account the lowest corrections arising from the commutator of $\mathscr{G}_H$ with A and $A^\dagger$ [formula (3.4)]. One remaining issue is whether it is possible to find a Hermitian operator for higher order corrections $\partial^{[i]}_{[n]}$, $i \geqslant 5$. To answer this, the first point needs to be addressed.

The second point is to obtain simpler expressions in particular for the $O_{[m][n]}$ operators. In particular, it is possible that a more convenient approach could be found to solve the operator Eqs. (2.10) and (2.11).

APPENDIX A. DERIVATION OF THE RECURSION RELATIONS (2.5) AND (2.6)

We give here the main leading to the recursion relation (2.5),

$$O_{[n+p][n]}(\partial_{[n]} + p\gamma) \equiv -(n+p)\, dO_{[n+p-1][n]} + d^+ O_{[n+p+1][n]}$$

and the particular relation $(p=0)$ (2.6),

$$\partial_{[n]} \equiv -ndO_{[n-1][n]} + d^+ O_{[n+1][n]}$$

To perform this calculation, it is necessary to compare different orders in γ^{-1}, i.e., to derive first recursion relations between $O^{[i]}_{[p][n]}$ and $\partial^{[i]}_{[n]}$. To do this, we insert (1.10) with (1.11) and (1.13) into (1.1), using (1.2) and (1.3), and then utilize the relations (1.8) and the biorthogonality between χ_n and $\tilde{\chi}_n$. Then, by comparing the coefficients of γ^{-p}, we obtain the recursion relations between the different orders [relations (2.11), (2.12a), and (2.12b) of Ref. 2] and then immediately the relations (2.5) and (2.6) after multiplication of both sides by γ^{-p} and summation on p.

APPENDIX B. DETERMINATION OF $A(q, r, s)$

From the recursions (3.9a) and (3.9b) it is easy to deduce the equation satisfied by $A(q, r, s)$. For and L and p one has

$$\sum_r (-1)^r/(p-2q-r)! \sum_s (L+p-s-2)!/(L+r-s)!$$
$$\times [(L+p-s-1)\, A(q, r, s) - (2q-1)(2L+p-1)\, A(q-1, r, s)] \equiv 0$$

This equation rapidly leads to complicated expressions for $A(q, r, s)$. Some particular cases are nevertheless easily calculated. We only give here tables in the lowest coefficients in q, r, s which correspond to the most interesting values:

$q=0$

$r \backslash s$	0
0	1

$q=1$

$r \backslash s$	0
0	1

$q=2$

$r \backslash s$	0	1	2
0	3	8	1
1	0	0	2

$q=3$

$r \backslash s$	0	1	2	3
0	15	71	33	1
1	0	0	21	8
2	0	0	0	6

$q=4$

$r \backslash s$	0	1	2	3	4
0	105	744	718	112	1
1	0	0	462	356	22
2	0	0	0	162	58
3	0	0	0	0	24

APPENDIX C. TAYLOR EXPANSION OF $V_{[n]}$ POTENTIALS IN THE VICINITY OF THEIR MINIMA

The starting formula is formula (4.4d). Using the explicit expression for $\tilde{u}$, $\tilde{u} = u - (2n+1)\theta \ln g$, and neglecting the θ^2 contributions, we obtain

$$\begin{aligned} V_{[n]}(x) &= (u')^2/4 - (n+1/2)\theta u'g'/g - (\theta/2)u'' - n\theta u''_\alpha(g+1) \\ &\simeq V_{\alpha[n]} + V''_{\alpha[n]}(x - x_\alpha)^2 \end{aligned}$$

where the extrema $\tilde{x}_\alpha$ associated to $V'_{\alpha[n]} = 0$ correspond to (using $g' = \Gamma' u''/\gamma$)

$$u'_\alpha \simeq \theta u'''_\alpha [(2n+1)\, \Gamma'/\gamma\Gamma + (1 + 4n\Gamma'/\Gamma^3)/u'']$$

so that

$$\begin{aligned} V_{\alpha[n]} &= -(1/2)\theta u''_\alpha - n\theta u''_\alpha(\Gamma+1) + O[)\theta/\Delta u_\alpha)^2] \\ V''_{\alpha[n]} &= (1/2)(u''_\alpha)^2 + O(\theta/\Delta u_\alpha) \end{aligned}$$

The equilibrium positions $\tilde{x}_\alpha$ of $V_{[n]}$ only differ by a term of order $\theta u'''_\alpha$ from the original equilibrium x_α of the potential $u(x)$ as $\tilde{x}_\alpha - x_\alpha \simeq 2u'_\alpha/u''_\alpha$. This difference will be considered as negligible.

APPENDIX D. EXPRESSION OF THE FIRST COEFFICIENTS β_{Kp} AND γ_{Kp} FOR GENERAL n

Let $z = \phi''/m\gamma^2$, $F = (\beta/m)^{1/2}\phi'$, and $S = \phi''/m$; then the solution of recursions derived from (4.1) analogous to (3.6a) and (3.6b) gives following results.

(a) For $K = 0$,

$$\begin{aligned} \beta_{01} &= (n+1)\{1 - (n-2)z/2! + (n^2 - 10n + 12)z^2/3! \\ &\quad - (n^3 - 23n^2 + 130n - 120)z^3/4! + \cdots\} \end{aligned}$$

$$\beta_{0-1} = -\Gamma(z); \qquad \gamma_{01} = -F\beta_{01}; \qquad \gamma_{0-1} = 0$$

$$\begin{aligned} \beta_{02} &= -F(n+1)(n+2)\{1/2! - (2n-6)z/3! \\ &\quad + (3n^2 - 35n + 60)z^2/4! \\ &\quad - (4n^3 - 102n^2 + 658n - 840)z^3/5! + \cdots\} \end{aligned}$$

$$\beta_{0-2} = (F/2)\,\Gamma(z)^2; \qquad \gamma_{02} = -F\beta_{02}; \qquad \gamma_{0-2} = -(S/2)\,\Gamma(z)^2$$

$$\beta_{03} = (F^2+S)(n+1)(n+2)(n+3)\{1/3! - (3n-12)\,z/4! + (6n^2-81n+180)z^2/5! - (10n^3-282n^2+2072n-3360)z^3/6! + \cdots\}$$

$$\beta_{0-3} = -(F^2-2S)/3!\,\Gamma(z)^3$$

$$\gamma_{03} = -F\beta_{03}; \qquad \gamma_{0-3} = (FS)/3!\,\Gamma(z)^3$$

$$\beta_{04} = -F(F^2+3S)(n+1)(n+2)\cdots(n+4)\{1/4! - (4n-20)z/5! + (10n^2-154n+420)z^2/6! - (20n^3-620n^2+5136n-10{,}080)z^3/7! + \cdots\}$$

$$\beta_{0-4} = F(F^2-5S)/4!\,\Gamma(z)^4$$

$$\gamma_{04} = -F\beta_{04}; \qquad \gamma_{0-4} = -S(F^2-3S)/4!\,\Gamma(z)^4$$

$$\beta_{05} = (F^4+6F^2S+3S^2)(n+1)(n+2)\cdots(n+5)\{1/5! - (5n-30)z/6! + (15n^2-260n+840)z^2/7! - (35n^3-1185n^2+10{,}950n-25{,}200)z^3/8! + \cdots\}$$

$$\beta_{0-5} = -(F^4-9F^2S+8S^2)\,\Gamma(z)^5$$

$$\gamma_{05} = -F\beta_{05}; \qquad \gamma_{0-5} = FS(F^2-7S)/5!\,\Gamma(z)^5$$

and so on.

(b) *For* $K=1$,

$$\beta_{11} = -n(n+1)\{z/2! - (3n-9)z^2/3! + [(13/2)n^2 - (131/2)n + 107]z^3/4! - \cdots\}$$

$$\beta_{1-1} = (n+1)z/2! - (n^2-9n+10)z^2/3! + (n^3-22n^2+107n+130)z^3/4! - \cdots$$

$$\gamma_{11} = -F\beta_{11}; \qquad \gamma_{1-1} = 0$$

$$\beta_{12} = Fn(n+1)(n+2)\{2z/3! - [(17/2)n - (65/2)]z^2/4! + (24n^2-277n+573)z^3/5! - \cdots$$

$$\beta_{1-2} = -F(n+1)\{2z/3! - [(5/2)n-35]z^2/4! + (9n^2-255n+1974)z^3/5! + \cdots\}$$

$$\gamma_{12} = -F\beta_{12} + S\{(2n+6)z/3! - (3n^2-35n+60)z^2/4! + (4n^3-102n^2+658n-840)z^3/5! + \cdots\}$$

$$\gamma_{1-2} = S\{(2n-4)z/3! - [(5/2)n^2 + (65/2)n - 25]z^2/4! \\ + (3n^3 - 82n^2 + 573n - 182)z^2/5! + \cdots\}$$

and so on. General expressions for β_{Kp} and γ_{Kp} have been obtained at least up to $K = 4$, $p = 6$. They have been derived by solving the recursion relations issuing from (4.1). The AMP symbolic program was of great help in this derivation.

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