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Solutions of the Fokker–Planck Equation for a Double-Well Potential in Terms of Matrix Continued Fractions

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Solutions of the Fokker–Planck (Kramers) equation in position-velocity space for the double-well potential $d_2x^2/2 + d_4x^4/4$ in terms of matrix continued fractions are derived. It is shown that the method is also applicable to a Boltzmann equation with a BGK collision operator. Results of eigenvalues and of the Fourier transform of correlation functions are presented explicitly. The lowest nonzero eigenvalue is compared with the escape rate in the weak noise limit for various damping constants and the susceptibility is compared with the zero-friction-limit result.

KEY WORDS: Double-well potential; Fokker–Planck (Kramers) equation; eigenvalues; eigenfunctions; correlation functions; susceptibilities.

1. INTRODUCTION

The problem of Brownian motion of particles in potentials is applied in such different fields as superionic conductors,[1–3] Josephson tunneling junctions,[4–6] rotation of dipoles,[7–9] phase-locked loops,[10–11] charge density waves,[12,13] simple isomerization processes[14–18] like the transition in the NH_3 molecule,[19] chemical reaction theory,[20–28] bistable nonlinear oscillator,[29–31] second-order phase transitions,[32] ligand migration of biomolecules,[33] Lorenz equations.[34] Whereas in Refs. 1–13 the potential is a periodic function of the position, the simplest form in Refs. 14–34 is a double-well potential. In a number of papers[35–40] the Brownian motion in a periodic (e.g., cosine) potential was investigated; see also Chap. 11 of Ref. 41 for a review. In the present paper the Brownian motion in a

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double-well potential is treated. The potential is assumed to have the simple form of a fourth order Taylor expansion with inversion symmetry, i.e., it reads (Landau potential[42])

$$f(x) = d_2 x^2/2 + d_4 x^4/4 \tag{1.1}$$

with positive d_4 and negative d_2. The Brownian motion in a potential is described by an appropriate Fokker–Planck[43,44] or Kramers[20] equation, which is essentially a diffusion equation with first derivatives of the distribution function in position-velocity space, i.e., in phase space. Some of the first derivative terms (streaming terms) describe the reversible motion in the potential without damping; the damping term and the diffusion term (collision term) describe the irreversible motion. The Fokker–Planck equation arises because the noise is assumed to stem from many tiny disturbances. The streaming term also appears in the Boltzmann equation. Here, however, the collision term is nonlinear and it has a complicated form. A simple linearized version of this collision operator is the BGK operator proposed by Bhatnagar, Gross, and Krook.[45] The resulting Boltzmann equation with this BGK collision operator and some generalizations have been investigated in chemical physics.[17,24b] We treat both equations simultaneously, because our method of solution is applicable to both equations.

A large number of special solutions mostly for special parameters for the problem above exist. If for instance the damping constant is large, the Fokker–Planck equation in phase space is reduced to the Fokker–Planck equation in position space, i.e., to the Smoluchowski equation. It has been investigated, e.g., in Refs. 46–48. In the low-temperature limit the transition rate from the left to the right well is especially of interest and can be given analytically for not too low damping constants. The result was first obtained by Kramers[20] and later on by Refs. 49 and 50. A corresponding expression for the BGK case was derived in Ref. 51. For finite temperatures the lowest nonzero eigenvalue, which is twice the escape rate, was obtained in Refs. 17 and 24 by using the high-friction expansion of the eigenvalue and then determining the eigenvalue for intermediate friction by Padé approximants. Fourier transforms of correlation functions have been obtained in Refs. 52 and 53 by a projection method leading to ordinary continued fractions. In the present paper we solve the Kramers equation for the double-well potential (1.1) applying the method developed for arbitrary potentials in Refs. 37–40 (see also Chap. 10 of Ref. 41). In Refs. 35, 36, 39, and 40 the method was applied to a periodic potential. By this method eigenvalues and eigenfunctions of the Kramers equation as well as the Fourier transform of its transition probability can be obtained in terms

of matrix continued fractions. The method consists in the following. First the distribution function is expanded in Hermite functions with respect to the velocity,[54] as first done by Brinkman[21] and additionally also in Hermite functions with respect to position. Next by inserting this distribution function into the Fokker–Planck equation we obtain a recursion relation for the expansion coefficients. By introducing a suitable vector and matrix notation this recurrence relation is then cast into a tridiagonal vector recurrence relation. Finally this vector recurrence relation is solved by matrix continued fractions. As will be shown the method works well down to very low friction constants and up to barrier heights of $\Delta E/(kT) = 10$. In the low-friction limit $\gamma \to 0$, the energy must be introduced as new variable. We will treat this limit case in a further publication[55]; see also the similar method for the periodic potential.[56,58] For the Boltzmann equation with a BGK collision operator the same method can be used as shown in Ref. 39 for the periodic potential.

The present paper is organized as follows. In Section 2 the basic equations and appropriate normalizations are given. In Section 3 the general results of the matrix-continued-fraction method are presented. In Section 4 explicit results for the eigenvalues and eigenfunctions of the Fokker-Planck equation and for the Boltzmann equation with BGK collision operator are given. Finally in Section 5 some susceptibilities, i.e., Fourier transforms of some correlation functions, are shown. Preliminary results for the eigenvalues have already been reported in Ref. 59.

2. BASIC EQUATIONS

The equation of motion for particles of mass m in the potential per mass $f(x)$ defined in (1.1) with a damping force $m\gamma\dot{x}$ and a fluctuating force $m\Gamma(t)$ is given by

$$\ddot{x} + \gamma\dot{x} + d_2 x + d_4 x^3 = \Gamma(t) \tag{2.1}$$

If $d_2 > 0$, $d_4 > 0$, (2.1) without the noise force $\Gamma(t)$ is called a Duffing equation. Though the nonlinearity changes the motion of $x(t)$, many features of the linear equation with $d_4 = 0$ are still present for $d_4 > 0$. In this case the potential (1.1) has only one minimum. For the double-well potential $d_2 < 0$, $d_4 > 0$, however, the motion $x(t)$ strongly deviates from the linear case. The potential (1.1) has now two minima at

$$x_\pm = \pm(-d_2/d_4)^{1/2} \tag{2.2}$$

separated by a maximum at $x = 0$ with the potential difference

$$\Delta f = f(0) - f(x_\pm) = d_2^2/(4d_4) \tag{2.3}$$

Thus for small energies the particle oscillates either in the left or right well, i.e., one has a bistable operation. Introducing the velocity $v = \dot{x}$, (2.1) may be written as a system of first-order equations, i.e.,

$$\begin{aligned} \dot{x} &= v \\ \dot{v} &= -\gamma v - d_2 x - d_4 x^3 + \Gamma(t) \end{aligned} \tag{2.4}$$

The motion of $x(t)$ and $v(t)$ without the noise $\Gamma(t)$ is best discussed by looking at those trajectories in phase space, which go through the saddle point $x = v = 0$; see Fig. 1. The other singular points are $x = x_{\pm}$, $v = 0$. Notice that trajectories not going through the saddle point cannot cross each other. Trajectories starting in the shaded region go to the left well, the others to the right well. The term $\Gamma(t)$ describes the white noise. It is assumed to be Gaussian with zero mean and with the correlation function

$$\langle \Gamma(t)\, \Gamma(t') \rangle = 2\gamma\theta\, \delta(t - t') \tag{2.5}$$

where the noise strength θ is proportional to the temperature T

$$\theta = kT/m \tag{2.6}$$

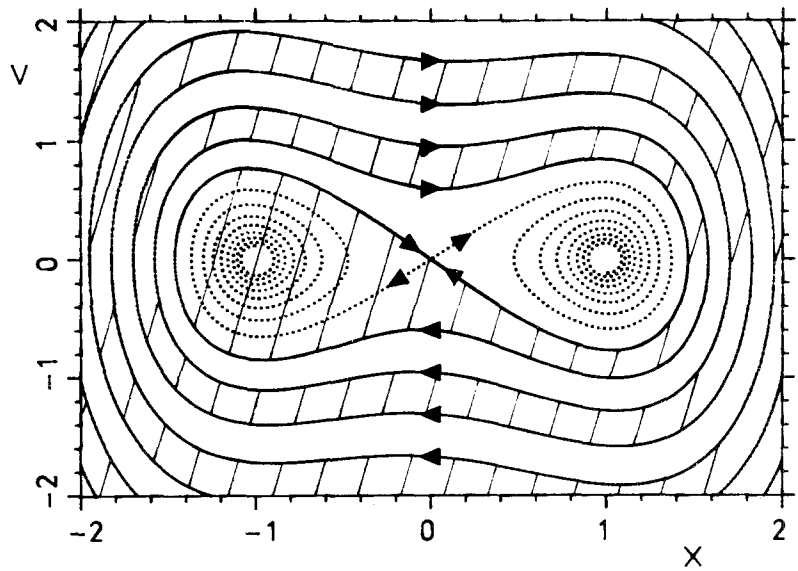

Fig. 1. The trajectories of the noiseless equation (2.4) going through the origin (saddle point) for $d_4 = 1$, $d_2 = -1$, $\gamma = 0.1$.

Even weak noise (low θ) has the effect that the particles do not stay in the same region in Fig. 1, but that they have a chance to go in the opposite direction, so that particles from the left well may finally reach the right well and vice versa. In the following we put the mass $m=1$ for convenience of notation.

The Langevin equations (2.4) are equivalent to the following Fokker–Planck equation for the distribution function $W(x, v, t)$ in phase space[20,43,44]

$$\partial W/\partial t = \mathbf{L}W \tag{2.7}$$

where the operator $\mathbf{L}$ is the Fokker–Planck operator $\mathbf{L}_{\mathrm{FP}}$ given by

$$\mathbf{L}=\mathbf{L}_{\mathrm{FP}}=-\frac{\partial}{\partial x}v+\frac{\partial}{\partial v}(\gamma v+d_2x+d_4x^3)+\gamma\theta\frac{\partial^2}{\partial v^2} \tag{2.8}$$

The Fokker–Planck equation (2.7), (2.8) is valid, if the noise stems from many tiny disturbances, each of which changes the variables in an unpredictable, but small way. In chemical physics one also uses the model, where at each collision the velocities of the particles are changed in such a way that the velocities are distributed according to the Maxwell distribution

$$g_{\mathrm{M}}(v)=(2\pi\theta^{-1/2}\exp[-v^2/(2\theta)] \tag{2.9}$$

The equation of motion for the distribution function is then given by (2.7), where $\mathbf{L}$ is the BGK operator[17,24,45]

$$\begin{aligned}\mathbf{L}_{\mathrm{BGK}}=&-\frac{\partial}{\partial x}v+\frac{\partial}{\partial v}(d_2x+d_4x^3)\\&+\gamma\left[g_{\mathrm{M}}(v)\int_{-\infty}^{\infty}\cdots dv-1\right]\end{aligned} \tag{2.10}$$

The stationary solution in both cases is given by the Boltzmann distribution

$$\begin{aligned}W_{\mathrm{st}}(x, v)&=Ng_{\mathrm{M}}(v)\exp[-f(x)/\theta]\\&=N(2\pi\theta)^{-1/2}\exp(-E/\theta)\end{aligned} \tag{2.11}$$

where we have introduced the energy

$$E=v^2/2+f(x) \tag{2.12}$$

and where the normalization constant N is given by

$$N^{-1} = \int_{-\infty}^{\infty} \exp[-f(x)/\theta]\, dx = \int_0^{\infty} u^{-1/2} \exp[-d_2 u/(2\theta) - d_4 u^2/(4\theta)]\, du$$
$$= \pi^{1/2}(2\theta/d_4)^{1/4} \exp[d_2^2/(8\theta d_4)]\, D_{-1/2}[d_2/(2\theta d_4)^{1/2}] \tag{2.13}$$

Here D_ν is the parabolic cylinder function (Ref. 60, p. 337). We also can express analytically the stationary moments

$$\langle x^{2\mu} \rangle_{\text{st}} = \int_{-\infty}^{\infty} x^{2\mu} \exp[-f(x)/\theta]\, dx \Big/ \int_{-\infty}^{\infty} \exp[-f(x)/\theta]\, dx$$
$$= (2\theta/d_4)^{\mu/2} [\Gamma(\mu + 1/2)/\Gamma(1/2)]$$
$$\times D_{-\mu-1/2}[d_2/(2d_4\theta)^{1/2}]/D_{-1/2}[d_2/(2d_4\theta)^{1/2}] \tag{2.13a}$$

It is much more difficult to obtain time-dependent solutions of (2.7), (2.8), and (2.10). Because $\mathbf{L}$ does not depend on time we can make the separation ansatz

$$W(x, v, t) = \phi(x, v)\, e^{-\lambda t} \tag{2.14}$$

leading to the eigenvalue equation

$$\mathbf{L}\phi(x, v) = -\lambda\phi(x, v) \tag{2.15}$$

For large damping γ the operator $\mathbf{L}$ of the corresponding Smoluchowski equation can be brought to a Hermitian form by multiplying it from the left with the inverse of the square root of the stationary distribution and from the right by the square root itself, i.e.,

$$\bar{\mathbf{L}} = (W_{\text{st}})^{-1/2}\, \mathbf{L} (W_{\text{st}})^{1/2} \tag{2.16}$$

For intermediate or small damping constants, $\bar{\mathbf{L}}$ is neither for the Fokker–Planck nor for the BGK case a Hermitian operator. Thus, in general, the eigenvalues λ are complex. The eigenvalues of (2.16) are the same, i.e.,

$$\bar{\mathbf{L}}\psi(x, v) = -\lambda\psi(x, v) \tag{2.17}$$

and the eigenfunctions are connected by

$$\psi(x, v) = \phi(x, v)(W_{\text{st}})^{-1/2} \tag{2.18}$$

For the Kramers equation the most important time-dependent solution is

the transition probability $P(x, v, t \mid x', v', 0)$, which is a solution of (2.7), (2.8) with the initial condition

$$P(x, v, 0 \mid x', v', 0) = \delta(x - x')\,\delta(v - v') \tag{2.19}$$

With the help of P and W_{st} any two-time correlation functions can be calculated.

Normalization

For later purposes it is very convenient to use proper normalized parameters. By introducing the new variables and parameters

$$\begin{aligned} &\tilde{\tilde{x}} = x/\tilde{\tilde{x}}_0, \qquad \tilde{\tilde{v}} = v/\tilde{\tilde{v}}_0, \qquad \tilde{\tilde{t}} = t\tilde{\tilde{v}}_0/\tilde{\tilde{x}}_0 \\ &\tilde{\tilde{\gamma}} = \gamma\tilde{\tilde{x}}_0/\tilde{\tilde{v}}_0, \qquad \tilde{\tilde{d}}_2 = d_2\tilde{\tilde{x}}_0^2/\tilde{\tilde{v}}_0^2, \qquad \tilde{\tilde{d}}_4 = d_4\tilde{\tilde{x}}_0^4/\tilde{\tilde{v}}_0^2 \\ &\tilde{\tilde{\theta}} = \theta/\tilde{\tilde{v}}_0^2 \end{aligned} \tag{2.20}$$

it is easy to show that the normalized distribution functions and the eigenvalues for the old and the new variables are connected by

$$W(x, v, t; d_2, d_4\theta, \gamma) = (\tilde{\tilde{x}}_0\tilde{\tilde{v}}_0)^{-1}\, W(\tilde{\tilde{x}}, \tilde{\tilde{v}}, \tilde{\tilde{t}}; \tilde{\tilde{d}}_2, \tilde{\tilde{d}}_4, \tilde{\tilde{\theta}}, \tilde{\tilde{\gamma}}) \tag{2.21}$$

$$\lambda(d_2, d_4, \theta, \gamma) = (\tilde{\tilde{v}}_0/\tilde{\tilde{x}}_0)\,\lambda(\tilde{\tilde{d}}_2, \tilde{\tilde{d}}_4, \tilde{\tilde{\theta}}, \tilde{\tilde{\gamma}}) \tag{2.22}$$

A very important quantity for the process is the energy difference $\Delta E = m\Delta f$ divided by kT. Using (2.3), (2.6) and (2.20) we obtain

$$\frac{\Delta E}{kT} = \frac{\Delta f}{\theta} = \frac{d_2^2}{4d_4\theta} = \frac{\tilde{\tilde{d}}_2^2}{4\tilde{\tilde{d}}_4\tilde{\tilde{\theta}}} \tag{2.23}$$

which shows that the quantities $\Delta E/(kT)$ are invariant under the transformation (2.20). The ratio of the damping to the frequency $(d_2)^{1/2}$ $(d_2 > 0)$ or to the imaginary part of the frequency $(-d_2)^{1/2}$ $(d_2 < 0)$ is also invariant, i.e.,

$$\gamma/|d_2|^{1/2} = \tilde{\tilde{\gamma}}/|\tilde{\tilde{d}}_2|^{1/2} \tag{2.24}$$

More invariants can be found from (2.20). Both scaling factors $\tilde{\tilde{x}}_0$ and $\tilde{\tilde{v}}_0$ are arbitrary. Thus one may normalize two of the four parameters d_2, d_4, θ, γ. Very convenient choices used later on are the following:

$$\begin{aligned} &\text{(a)} \quad \tilde{d}_4 = 1, \qquad \tilde{d}_2 = \pm 1, \qquad \text{for} \quad d_2 \begin{matrix} > 0 \\ < 0 \end{matrix} \\ &\qquad \tilde{x}_0 = [|d_2|/d_4]^{1/2}, \qquad \tilde{v}_0 = |d_2|/(d_4)^{1/2} \\ &\qquad \Delta E/(kT) = 1/(4\tilde{\theta}), \qquad \gamma/|d_2|^{1/2} = \tilde{\gamma} \end{aligned} \tag{2.25}$$

$$\text{(b)}\quad \bar{d}_4 = 1, \qquad \bar{\theta} = 1$$
$$\bar{x}_0 = (\theta/d_4)^{1/4}, \qquad \bar{v}_0 = (\theta)^{1/2} \tag{2.26}$$
$$\Delta E/(kT) = \bar{d}_2^2/4$$

According to (2.20)–(2.22) distribution functions and eigenvalues for not normalized parameters can easily be obtained from those for the normalizations (a) and (b).

3. SOLUTIONS IN TERMS OF MATRIX CONTINUED FRACTIONS

The expressions in this chapter simplify a lot if we use the normalization (2.26), i.e., if we put $\theta = d_4 = 1$ (omitting the bar). We first expand the distribution function $W(x, v, t)$ into orthonormalized Hermite functions[54]

$$\phi_n(\xi) = H_n(\xi/\sqrt{2})\, e^{-\xi^2/4}/[n!\, 2^n (2\pi)^{1/2}]^{1/2} \tag{3.1}$$

in the following way:

$$W(x, v, t) = \sqrt{N}\, \phi_0(v) \exp[-\tfrac{1}{2} f(x)] \alpha^{1/2} \sum_{n=0}^{\infty} \sum_{q=0}^{\infty} c_n^q(t) \times \phi_n(v)\, \phi_q(\alpha x) \tag{3.2}$$

Here α is a proper scaling factor, which will be chosen later on. The function in front of the sum is proportional to the square root of the stationary distribution (2.11). The expansion (3.2) guarantees that the boundary conditions for v and x at $\pm$ infinity are satisfied. The Hermite-function expansion in v is very convenient, because the $\phi_n(v)$ are the eigenfunctions of the irreversible part $\mathbf{L}_{ir}$ of the Fokker–Planck operator (2.8) or of the BGK operator (2.10), i.e., those parts containing γ:

$$\mathbf{L}_{ir} \phi_0(v)\, \phi_n(v) = -\gamma l_n \phi_0(v)\, \phi_n(v) \tag{3.3}$$

Here l_n for the Fokker–Planck and BGK case are given by[24]

$$l_n = l_{\mathrm{FP}n} = n \tag{3.4a}$$
$$l_n = l_{\mathrm{BGK}n} = 1 - \delta_{n0} \tag{3.4b}$$

Insertion of (3.2) into (2.7) and using the recurrence relations for the Hermite functions leads to

$$\dot{c}_n^p = -(n+1)^{1/2} \sum_q D^{p,q} c_{n+1}^q - \gamma l_n c_n^p - \sqrt{n} \sum_q \hat{D}^{p,q} c_{n-1}^q \tag{3.5}$$

where the $D^{p,q}$ and $\hat{D}^{p,q}$ are the matrix elements of the operators $D = \partial/\partial x - \frac{1}{2}f'$, $\hat{D} = \partial/\partial x + \frac{1}{2}f'$ with respect to the eigenfunctions $\phi_n(\alpha x)$, see Refs. 38, 39, and 41. For the potential (1.1) we obtain the following matrix elements (upper signs are valid for D^{pq}, lower signs for $\hat{D}^{pq}$)

$$\begin{aligned}\begin{pmatrix} D^{pq} \\ \hat{D}^{pq} \end{pmatrix} &= (\mp)\,\delta_{p,q-3}\cdot[q(q-1)(q-2)]^{1/2}/(2\alpha^3) \\ &+ \delta_{p,q-1}\cdot\sqrt{q}\,[\alpha/2 + (\mp)\,3q/(2\alpha^3) + (\mp)\,d_2/(2\alpha)] \\ &+ \delta_{p,q+1}\cdot\sqrt{p}[-\alpha/2 + (\mp)\,3p/(2\alpha^3) + (\mp)\,d_2/(2\alpha)] \\ &+ (\mp)\,\delta_{p,q+3}[p(p-1)(p-2)]^{1/2}/(2\alpha^3) \end{aligned} \tag{3.6}$$

Thus only the matrix elements $D^{p,p\pm1}$, $D^{p,p\pm3}$ can be different from zero for the potential (1.1). For other potentials, however, also other matrix elements may be different from zero.

Truncating the expansion (3.2) at the index $q = Q$ and using the column vectors $\mathbf{c}_n$ and the matrices $\mathbf{D}$ (and similarly $\hat{\mathbf{D}}$) defined by

$$\mathbf{c}_n = \begin{pmatrix} c_n^0 \\ \vdots \\ c_n^Q \end{pmatrix}, \qquad \mathbf{D} = \begin{pmatrix} D^{00} & \cdots & D^{0Q} \\ \vdots & & \vdots \\ D^{Q0} & \cdots & D^{QQ} \end{pmatrix} \tag{3.7}$$

the system of differential equation (3.5) may be cast in the form

$$\dot{\mathbf{c}}_n = -(n+1)^{1/2}\,\mathbf{D}\mathbf{c}_{n+1} - \gamma l_n \mathbf{c}_n - \sqrt{n}\,\hat{\mathbf{D}}\mathbf{c}_{n-1} \tag{3.8}$$

As it was explained in Refs. 37, 38, and 41 the eigenvalues as well as the Laplace transform of the Green's function matrix of the tridiagonal vector-recurrence relation (3.8) can be expressed in terms of matrix continued fractions. The eigenvalues and eigenvectors follow from ($\mathbf{I}$ = unit matrix)

$$[\lambda\mathbf{I} + \tilde{\mathbf{K}}_0(-\lambda)]\,\mathbf{c}_0 = \mathbf{0} \tag{3.9}$$

i.e., the eigenvalues λ are determined by the transcendental equation

$$D_0(\lambda) = \mathrm{Det}[\lambda\mathbf{I} + \tilde{\mathbf{K}}_0(-\lambda)] = 0 \tag{3.10}$$

(For some more general forms see Refs. 38 and 41].) In (3.9), (3.10) $\tilde{\mathbf{K}}_0(s)$ is given by the following matrix continued fraction:

$$\tilde{\mathbf{K}}_0(s) = \mathbf{D}[(s+\gamma l_1)\,\mathbf{I} - 2\cdot\mathbf{D}[(s+\gamma l_2)\,\mathbf{I} - \cdots]^{-1}\,\hat{\mathbf{D}}]^{-1}\,\hat{\mathbf{D}} \tag{3.11}$$

[see (10.140) of Ref. 41]. For the Fokker–Planck and the BGK case l_n must of course be replaced by (3.4a) and (3.4b), respectively. To obtain the

eigenfunctions, the other $\mathbf{c}_n$ with $n>0$ must also be determined. This can be done by

$$\mathbf{c}_n = \tilde{\mathbf{S}}^+_{n-1}(-\lambda)\cdots\tilde{\mathbf{S}}^+_0(-\lambda)\,\mathbf{c}_0 \tag{3.12}$$

where the $\tilde{\mathbf{S}}^+_n(s)$ are given by the infinite matrix-continued-fractions

$$\begin{aligned}\tilde{\mathbf{S}}^+_n(s) = &-(n+1)^{1/2}\{(s+l_{n+1}\gamma)\,\mathbf{I}\\ &-(n+2)\,\mathbf{D}[(s+l_{n+2}\gamma)\,\mathbf{I}-\cdots]^{-1}\hat{\mathbf{D}}\}^{-1}\hat{\mathbf{D}}\end{aligned} \tag{3.13}$$

see (10.142) of Ref. 41. To perform the normalization the eigenvectors of the adjoint equation must be used. As shown in Ref. 41 (p. 256), however, they can be expressed in terms of the eigenfunctions of the equation itself.

The Laplace transform of the transition probability matrix of (3.5), i.e., $\mathbf{G}_{nm}(t)=(G^{pq}_{nm}(t))$ and therefore also the Laplace transform of the transition probability of (2.7), (2.8) can also be expressed in terms of matrix continued fractions (Ref. 41, Chapter 10.3.1). The general result for the stationary joint distribution reads (see (10.146) of Ref. 41)

$$\begin{aligned}W_2(x,v,t;x',v',0) = &N\phi_0(v)\exp[-f(x)/2]\,\phi_0(v')\exp[-f(x')/2]\\ &\times\sum_{n,m=0}^{\infty}\sum_{p,q}\alpha G^{pq}_{nm}(t)\,\phi_p(\alpha x)\,\phi_q(\alpha x')\,\phi_n(v)\,\phi_m(v')\end{aligned} \tag{3.14}$$

As will be shown in Section 5 the velocity correlation functions $\langle v(t)\,v(0)\rangle$ and $\langle v(t)\,x(0)\rangle$ can be expressed in terms of suitable correlation functions of position only, i.e., of the type $\langle g(x(t))\,g(x(0))\rangle$. Because of the orthonormality of the $\phi_n(v)$ we obtain

$$\begin{aligned}&\langle g(x(t))\,g(x(0))\rangle\\ &\quad=\iiiint g(x)\,g(x')\,W_2(x,v,t;x',v',0)\,dxdvdx'dv'\\ &\quad=N\sum_{p,q}\alpha G^{pq}_{00}(t)\int g(x)\,\phi_p(\alpha x)\exp[-f(x)/2]\,dx\\ &\qquad\times\int g(x')\,\phi_q(\alpha x')\exp[-f(x')/2]\,dx'\end{aligned} \tag{3.15}$$

Thus we only need to know the matrix elements $G^{pq}_{00}(t)$ of the Green's function matrix $\mathbf{G}_{00}(t)$. The Laplace transform of this matrix, i.e.,

$$\tilde{\mathbf{G}}_{00}(s)=\int_0^\infty \mathbf{G}_{00}(t)\,e^{-st}\,dt \tag{3.16}$$

can be expressed by the matrix continued fractions (3.11) (Ref. 41, p. 251), i.e.,

$$\tilde{\mathbf{G}}(s) = (\tilde{G}_{00}^{pq}(s)) = [s\mathbf{I} - \tilde{\mathbf{K}}_0(s)]^{-1} \tag{3.17}$$

Obviously at the negative eigenvalues ($s = -\lambda$) poles of $\tilde{\mathbf{G}}(s)$ occur.

4. EIGENVALUES AND EIGENFUNCTIONS

By calculating the matrix continued fraction (3.11) eigenvalues can be found from (3.10) by some root-finding technique. For real eigenvalues an ordinary *regula falsi* method was used, whereas for complex eigenvalues a two-dimensional *regula falsi* method was applied. Here the real part λ_r and the imaginary part λ_i of the complex eigenvalue λ are determined by the real and imaginary parts of (3.10). The dimension $(Q+1)\times(Q+1)$ of the matrices [compare (3.7)] and the number N of inversions for obtaining an approximate value of the infinite continued fraction (3.11) have been determined in such a way that a further increase of N and Q did not change the result of the plots. The final results are independent of the scaling factor α. By choosing a proper scaling factor, however, the truncation indices Q and N can be minimized. For small $\tilde{\gamma}$ and large $\Delta E/(kT)$ values large Q and N have to be used [typical values are $\tilde{\gamma} = 0.1$, $\Delta E/(kT) = 1/(4\tilde{\theta}) = 10$, $Q = 40$, $N = 160$], whereas for large $\tilde{\gamma}$ only few inversions are needed ($\tilde{\gamma} = 5$, $Q = 10$, $N = 10$). Therefore the method does not work in the limit $\tilde{\gamma} \to 0$ or $\tilde{\theta} \to 0$ but the relatively low value $\tilde{\gamma} = 0.1$ and $\tilde{\theta} = 0.025$ can be handled.

Because of the symmetry of the problem, the eigenfunctions are either symmetric or antisymmetric, i.e.,

$$\underset{a}{\phi_s}(x, v) = \pm \underset{a}{\phi_s}(-x, v) \tag{4.1}$$

For symmetric eigenfunctions only c_{2n}^{2q} and c_{2n+1}^{2q+1} can be different from zero, whereas for antisymmetric eigenfunctions only c_{2n}^{2q+1} and c_{2n+1}^{2q} can be different from zero. Therefore the dimension of the vectors $\mathbf{c}_n$ can be reduced by a factor 2 leading to a $\mathbf{c}_n^{\text{red}}$. The matrices $\mathbf{S}_n^{\text{red}}$ connecting $\mathbf{c}_{n+1}^{\text{red}}$ and $\mathbf{c}_n^{\text{red}}$ are thus only $Q/2 \times Q/2$ matrices (Q even). Because the number of computational steps needed to invert a $Q \times Q$ matrix is proportional to Q^3, the computing time is reduced by a factor 8 by using this symmetry property.

In the plots we have used the normalization (2.25). The transformation from the normalization (2.26) used in Section 3 to the normalization (2.25) is easily obtained from (2.22). In Figs. 2 and 4 the real and complex eigenvalues of the Kramers operator are plotted as a function

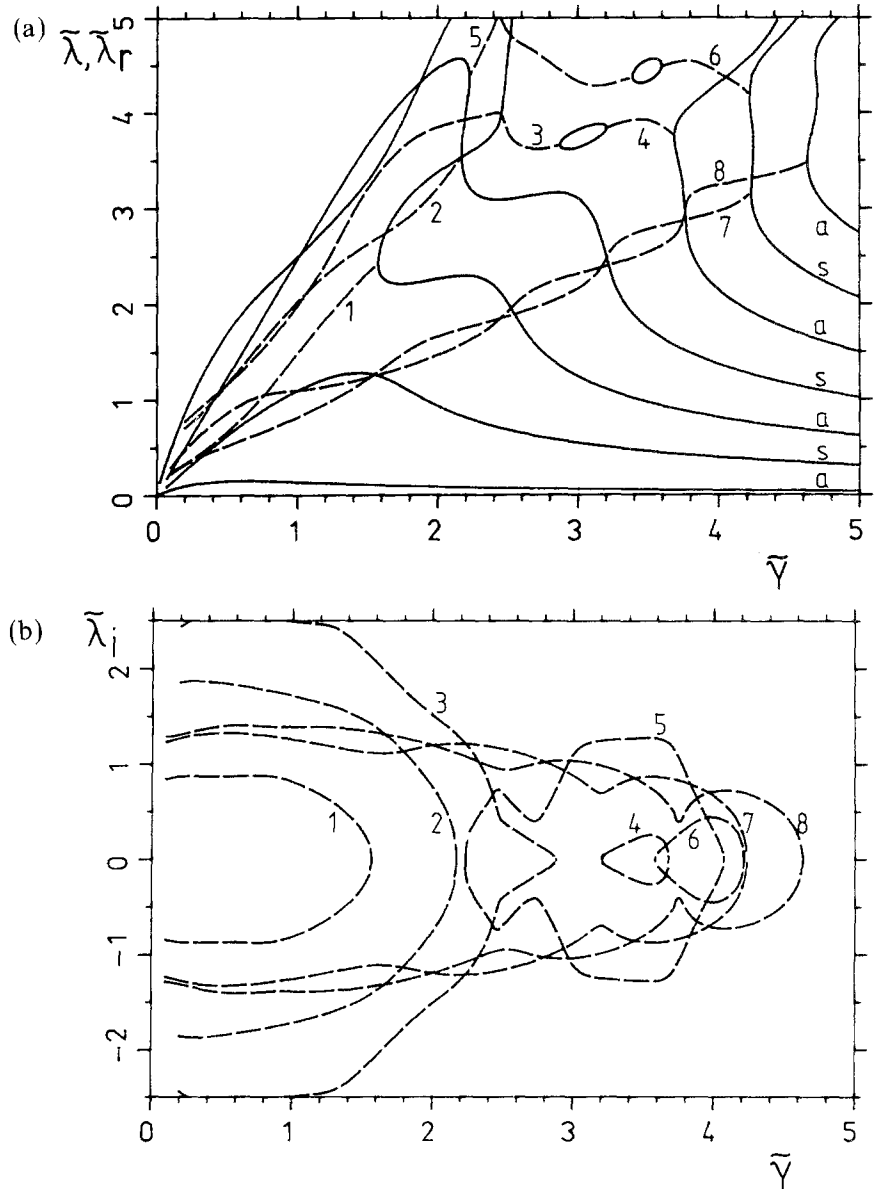

Fig. 2. The eigenvalues normalized according to (2.25) ($\tilde{d}_2 = -1$, $\tilde{d}_4 = 1$) as a function of $\tilde{\gamma}$ for $\Delta E = kT$ for the Kramers equation of the bistable potential. The real eigenvalues are shown by solid lines, the complex eigenvalues by broken lines. Real parts of the complex eigenvalues are shown in (a) and imaginary parts in (b). Same numbers correspond to the same complex eigenvalue. The indices s and a denote symmetric and antisymmetric eigenfunctions.

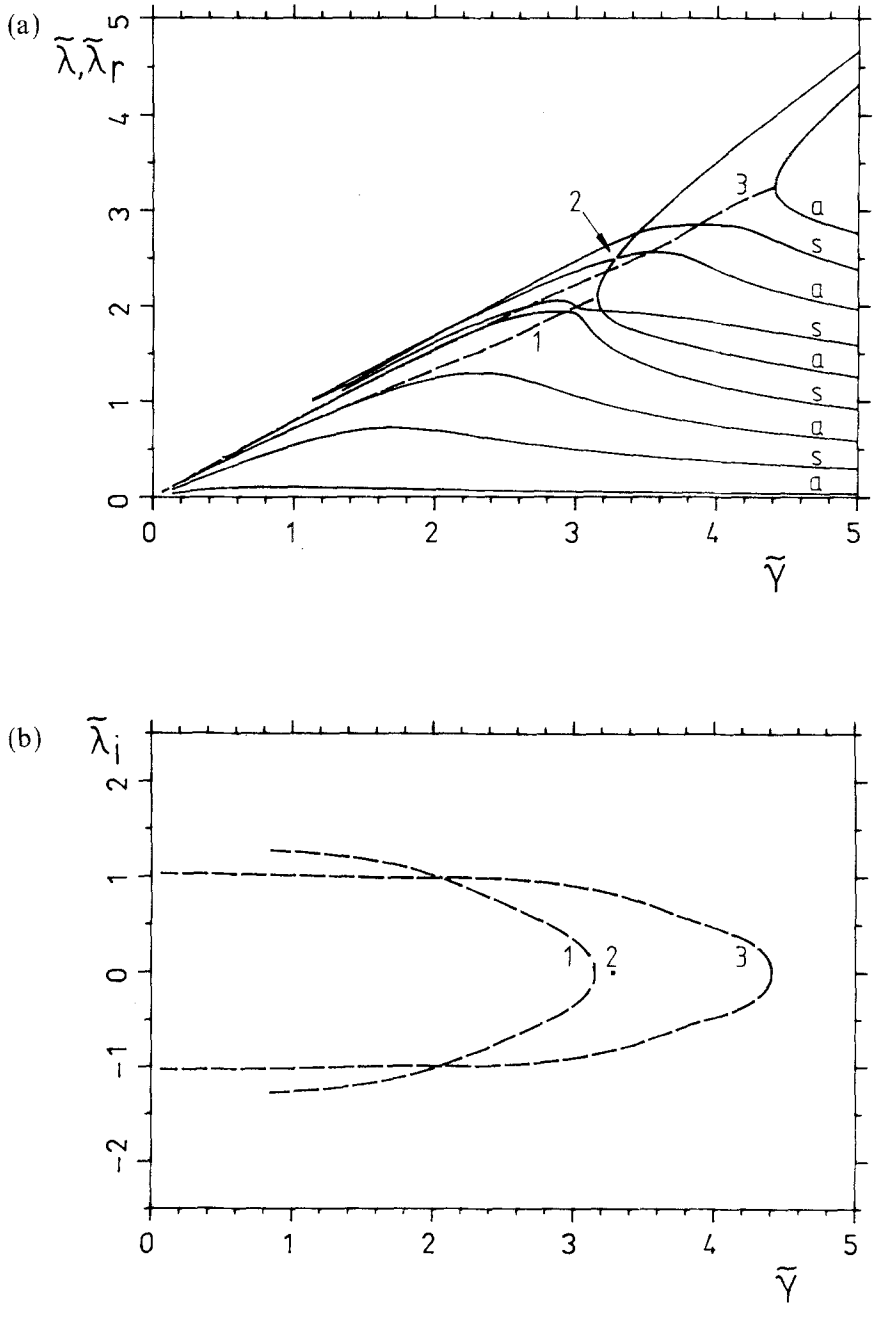

Fig. 3. Same as Fig. 2, but for the BGK case.

of the normalized damping constant $\tilde{\gamma}$ for the bistable potential for $\Delta E = kT$ and for $\Delta E = 5kT$, whereas in Fig. 3 the real and complex eigenvalues are shown for the BGK case for $\Delta E = kT$. As seen in these figures the eigenvalues are always real for large damping constants. (As was already mentioned in the introduction for large $\tilde{\gamma}$ the Kramers equation reduces to the Smoluchowski equation, which has only real eigenvalues.) If the damping constant decreases, some eigenvalues remain real down to very low damping constants, whereas for some other eigenvalues two real eigenvalues come together for decreasing $\tilde{\gamma}$ and then, at the vertical slope, two complex conjugate eigenvalues appear if $\tilde{\gamma}$ is decreased further. This feature was also found for the eigenvalues of the Kramers equation describing the motion in a periodic potential[39,61] and for the eigenvalues of the laser Fokker–Planck operator for intensity and inversion.[62] Figure 2 shows the interesting feature that some of the complex conjugate eigenvalues form, for a small interval of $\tilde{\gamma}$ values, again two real eigenvalues (see the two bubbles in the upper part of Fig. 2a). By comparing Figs. 2 and 4 it is seen that for larger $\Delta E/(kT)$ ratios the eigenvalues have a simpler structure, especially the imaginary parts. By comparing Figs. 2 and 3 it is seen that for the same $\Delta E/(kT)$ value the eigenvalues have a simpler structure for the BGK case than for the Kramers case.

In Fig. 5 the eigenvalues are shown for the Duffing equation. They have, at least for small $\tilde{\gamma}$, a similar behavior as the eigenvalues for the parabolic potential $f(x) = d_2 x^2/2$ $(d_2 > 0)$, which for the Kramers case are given by [see for instance (10.83) of Ref. 41]

$$\begin{aligned} &\lambda_{n_1,n_2} = \tfrac{1}{2}\gamma(n_1 + n_2) + i(d_2 - \gamma^2/4)^{1/2}\,(n_1 - n_2) \\ &n_1, n_2 = 0, 1, 2,... \end{aligned} \tag{4.2}$$

The main difference of the eigenvalues in Fig. 5a to the eigenvalues (4.2) is the connection between the eigenvalues. This net-like structure is also seen in Figs. 2a–4a. Obviously only eigenvalues belonging to symmetric (or antisymmetric) eigenfunctions are connected.

4.1. Lowest Nonzero Eigenvalue

For the bistable potential the lowest nonzero eigenvalue is very important, because it describes for $\Delta E \gg kT$ the transition rate from the left to the right well and vice versa. Because of the symmetry this transition rate r is given by

$$r = \lambda_1/2 \tag{4.3}$$

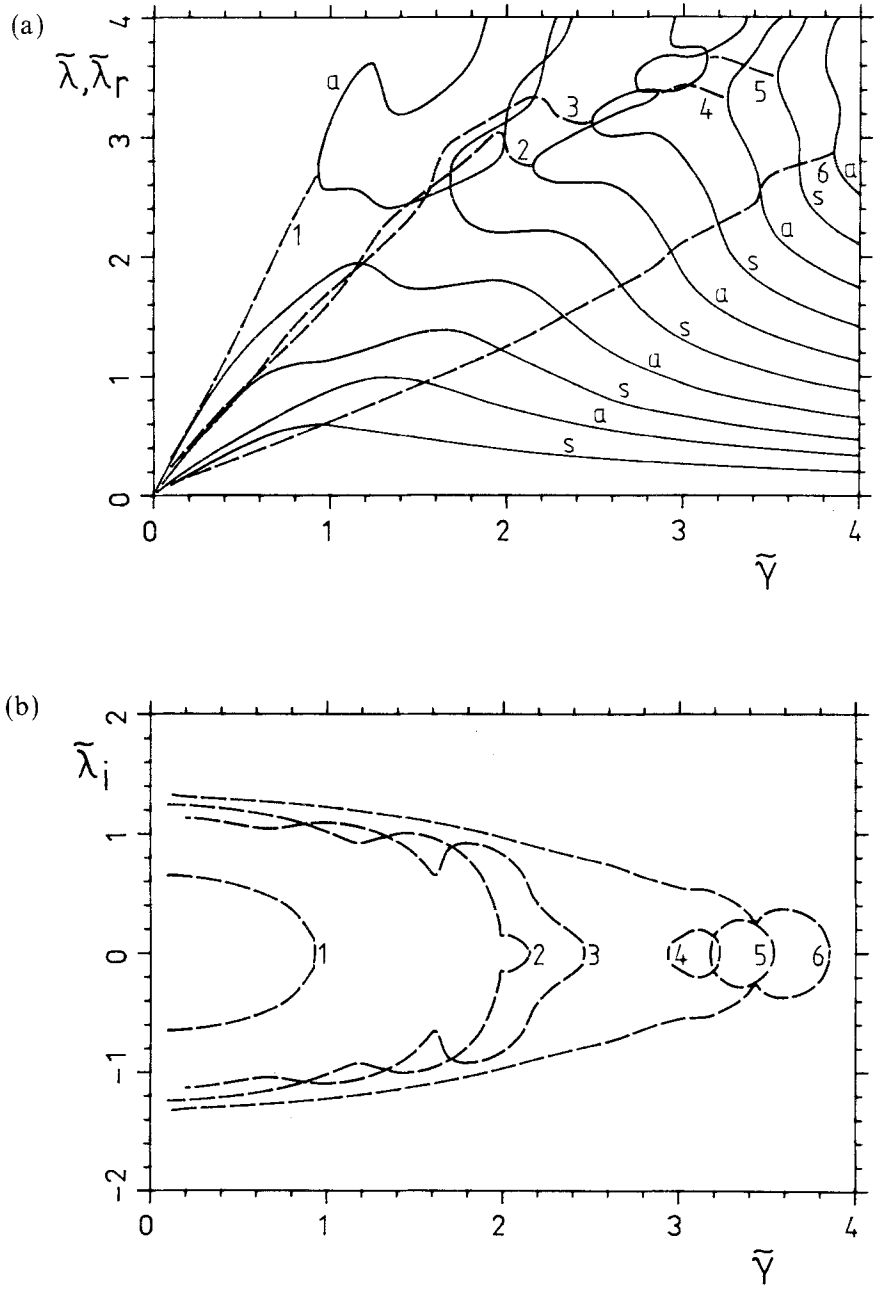

Fig. 4. Same as Fig. 2, but for $\Delta E = 5kT$. Because of its smallness the lowest nonzero real eigenvalue coincides with the $\tilde{\lambda} = 0$ line and is therefore not seen.

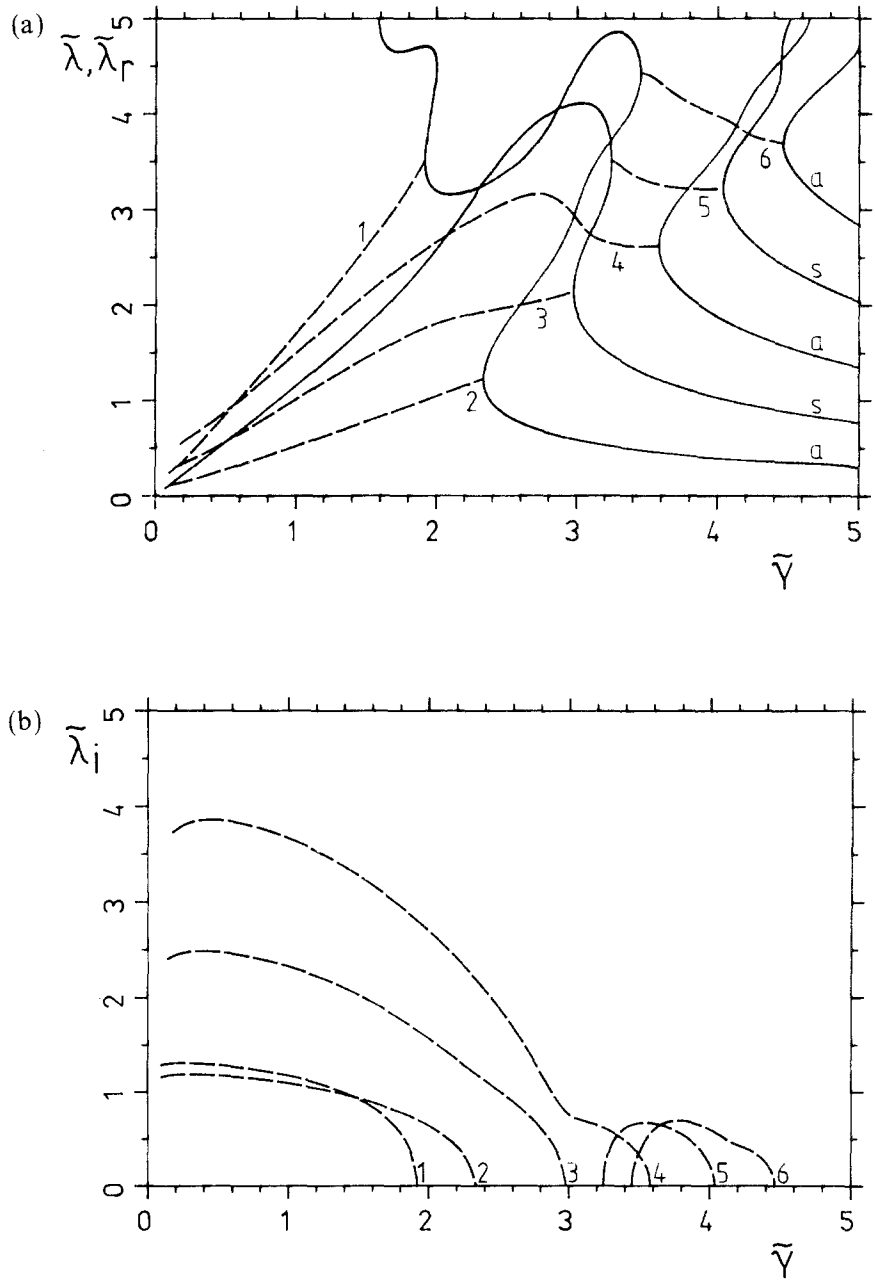

Fig. 5. Same as Fig. 2, but for the Duffing equation ($\tilde{d}_2 = 1$, $\tilde{d}_4 = 1$, $\tilde{\theta} = 0.25$). In Fig. 5b only the positive imaginary parts are shown.

(see also the discussion in Section 2 of Ref. 61). For the bistable potential this eigenvalue is always real, if the temperature is low enough. (No such eigenvalue exists for the Duffing equation.) For high barrier heights transition rates $r = \lambda_1/2$ have been derived for the Fokker–Planck[20,49,50] and the BGK case.[51] In the normalization (2.25) these expressions take the following form:

Fokker–Planck:

$$\tilde{\lambda}_1 = (\sqrt{2}/\pi)[(1+\tilde{\gamma}^2/4)^{1/2} - \tilde{\gamma}/2] \exp[-1/(4\tilde{\theta})] \tag{4.4a}$$

BGK:

$$\tilde{\lambda}_1 = (4\sqrt{2}/\pi) \int_0^1 u^{\tilde{\gamma}+1}(1+u^2)^{-2}\, du \exp[-1/(4\tilde{\theta})] \tag{4.4b}$$

[In the last expression we have used the substitution $u = \exp(-\omega_b t)$ in Eq. (14) of Ref. 51.] Because of the exponential factor we have plotted in Fig. 6 the first nonzero eigenvalue multiplied by the inverse exponential in (4.4), i.e., we have plotted

$$\tilde{\lambda}^+ = \tilde{\lambda}_1 \exp[1/(4\tilde{\theta})] = \tilde{\lambda}_1 \exp[\Delta E/(kT)] \tag{4.5}$$

As seen in Fig. 6 the value obtained by the matrix-continued-fraction method agrees fairly well with the asymptotic expression (4.4), if $\tilde{\gamma}$ is not too small. For very small $\tilde{\gamma}$ and in the low-temperature limit $\tilde{\theta}$ with $\tilde{\gamma}/\tilde{\theta} \ll 1$ one may derive the expression[55,59]

$$\tilde{\lambda}_1 = (\tilde{\gamma}/\tilde{\theta})[2^{3/2}/(3\pi)]\{1 - \kappa[4\tilde{\gamma}/(3\pi\tilde{\theta})]^{1/2}\} \exp[-1/(4\tilde{\theta})] \tag{4.6}$$

with $\kappa = 0.85544$. An expression similar to (4.6), but without the additional term $\sim\tilde{\gamma}^{3/2}$ was obtained by Garrity and Skinner for the BGK case.[17] As seen in Fig. 6 these low-friction-limit results also agree fairly well with the results obtained by the matrix-continued-fraction method.

4.2. Eigenfunctions

The eigenfunctions are obtained by calculating the coefficients $\mathbf{c}_n$ according to (3.12) and then performing the summation in (3.2). [The normalization is explained in (2.22) of Ref. 39]. The matrices $\mathbf{S}_n^+(-\lambda)$ occurring in (3.12) need not be calculated separately. They appear in intermediate steps in the calculation of (3.11). These matrices, however, must now be stored. The altitude chart of a typical real antisymmetric eigenfunction belonging to the lowest nonzero real eigenvalue is shown in Fig. 7.

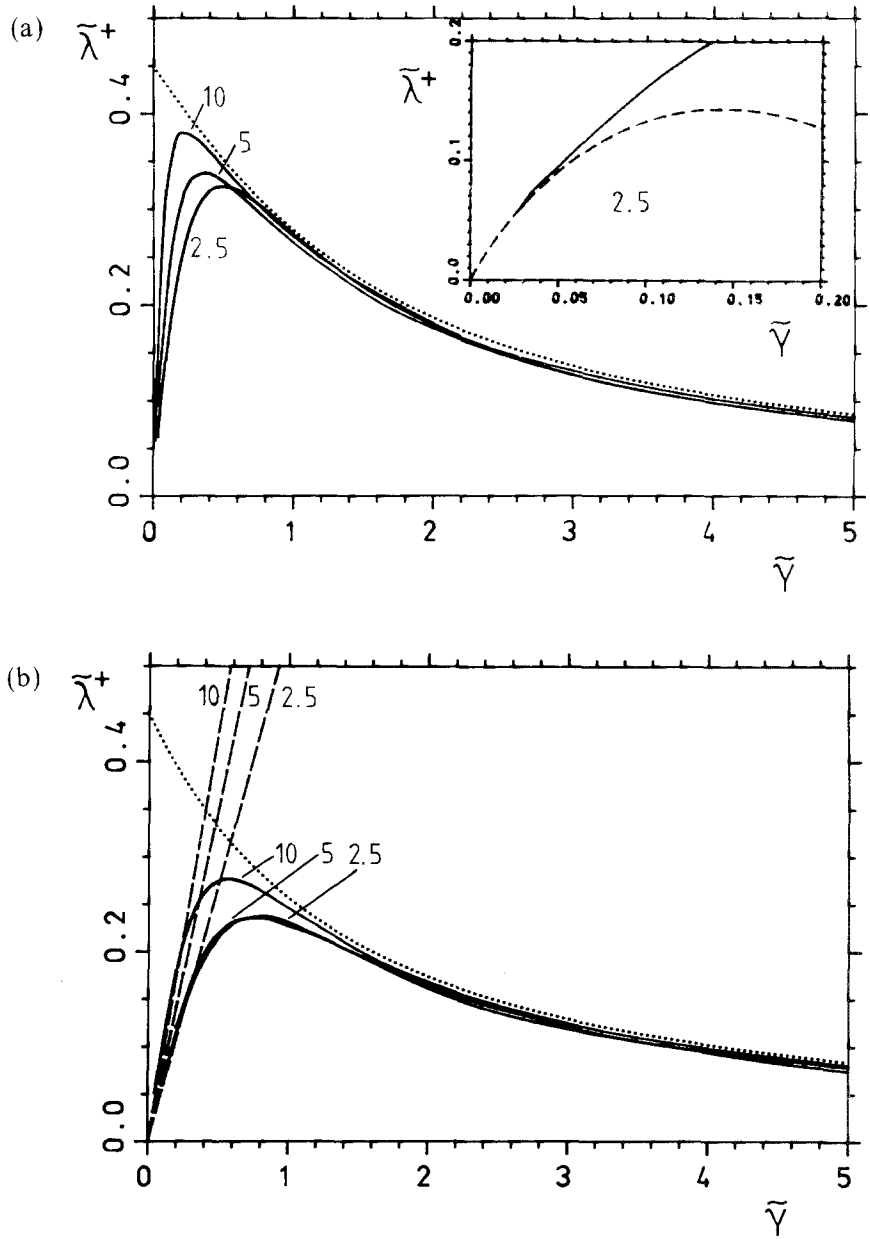

Fig. 6. The lowest nonzero real eigenvalue (4.5) for the normalization (2.25) ($\tilde{d}_2 = -1$, $\tilde{d}_4 = 1$) as a function of $\tilde{\gamma}$ for the (a) Kramers (b) and BGK case. The asymptotic expressions (4.4) are shown by the dotted line, the zero friction limit (4.6) in (a) and the corresponding one of Garrity and Skinner in (b) by a broken line.

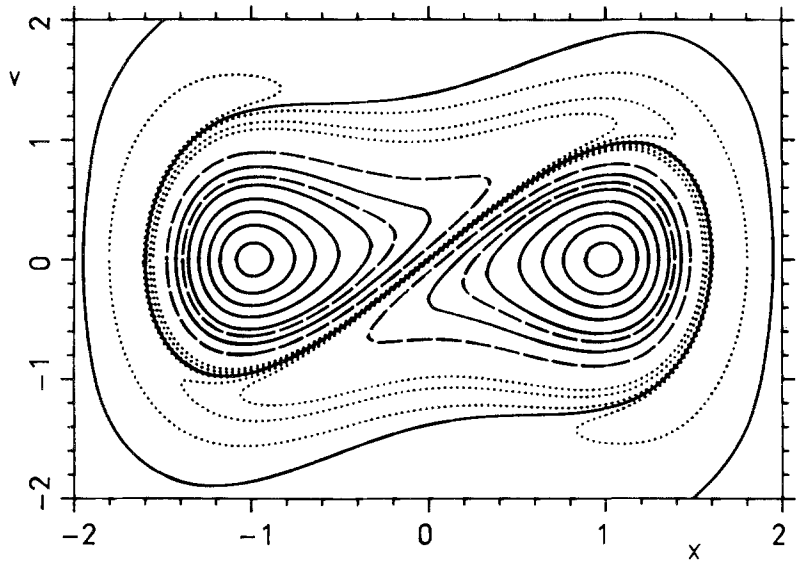

Fig. 7. Altitude chart of the antisymmetric eigenfunction ϕ_1 belonging to the lowest nonzero eigenvalue $\tilde{\lambda}$ of the Kramers equation for the bistable potential in the normalization (2.25). The parameters are $\tilde{\gamma}=0.25$, $\tilde{\theta}=0.25$. The lines $\phi_1=c=\text{const}$ are shown for $c=0$, ± 0.1, ± 0.2, ± 0.3, ± 0.4, ± 0.5, ± 0.6 (solid lines) $c=\pm 0.05$, ± 0.15 (broken lines), $c=\pm 0.001$, ± 0.005, ± 0.01 (dotted lines).

For energies in the vicinity of the energy of the potential minima the lines of constant ϕ_1 approximately agree with the lines of constant energy. For larger energies the lines starting in one of the wells twist somewhat around the other well. The picture has some similarity to Fig. 1. Whereas in Fig. 1 the trajectory going through the origin spirals inwards in clockwise direction, the line $\phi_1=0$ in Fig. 7 spirals outwards in clockwise direction. The nodal line $\phi_1=0$ was approximately obtained in Ref. 25b. Near the origin it agrees very well with our result. Outside the origin, however, we have only qualitative agreement. For times large compared to the inverse of the real parts of the other eigenvalues the solution of the Fokker–Planck equation is given by

$$W(x, v, t)=W_{\text{st}}(x, v)+C\phi_1(x, v)\exp(-\lambda_1 t) \quad \text{for } t\gg 1/\text{Re}\{\lambda_2\} \tag{4.7}$$

where C is a proper constant determined by the initial condition. Thus the first eigenfunction $\phi_1(x, v)$ is important for the transition to the stationary distribution.

5. SUSCEPTIBILITIES

The susceptibility describes the response of the system to a small external field of frequency ω. For the response of the position x and velocity v these susceptibilities are denoted by $\chi_x(\omega)$ and $\chi_v(\omega)$, respectively. They are connected to the half-sided Fourier transform of the correlation functions

$$\tilde{K}_{\substack{xx \\ xv \\ vv}}(\omega) = \int_0^\infty \left\langle \begin{matrix} x(t)\,x(0) \\ x(t)\,v(0) \\ v(t)\,v(0) \end{matrix} \right\rangle e^{-i\omega t}\,dt \tag{5.1}$$

according to (see for instance Ref. 41, Chapter 7)

$$\chi_x(\omega) = \frac{1}{\theta}\tilde{K}_{xv}(\omega) = \frac{1}{\theta}\left[\langle x^2(0)\rangle - i\omega\tilde{K}_{xx}(\omega)\right] \tag{5.2}$$

$$\begin{aligned}\chi_v(\omega) &= \frac{1}{\theta}\tilde{K}_{vv}(\omega) = \frac{i\omega}{\theta}\tilde{K}_{xv}(\omega) \\ &= \frac{1}{\theta}\left[i\omega\langle x^2(0)\rangle + \omega^2\tilde{K}_{xx}(\omega)\right]\end{aligned} \tag{5.3}$$

Thus the susceptibilities $\chi_x(\omega)$ and $\chi_v(\omega)$ can be expressed by the half-sided Fourier transform of the correlation function $K_{xx}(t) = \langle x(t)\,x(0)\rangle$, which can be expressed by

$$\begin{aligned}\tilde{K}_{xx}(\omega) &= \tilde{K}'_{xx}(\omega) - i\tilde{K}''_{xx}(\omega) \\ &= N\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\alpha\tilde{G}_{00}^{pq}(s=i\omega) \\ &\quad\times\int_{-\infty}^{\infty} x\exp[-f(x)/(2\theta)]\,\phi_p(\alpha x)\,dx \\ &\quad\times\int_{-\infty}^{\infty} x'\exp[-f(x')/(2\theta)]\,\phi_q(\alpha x')\,dx'\end{aligned} \tag{5.4}$$

according to (3.15)–(3.17). Here we use the unnormalized variables of Section 2, but we will present our result in the normalization (2.25). In order to calculate $\chi_x(\omega)$ and $\chi_v(\omega)$ we therefore need to calculate the matrix continued fraction (3.17) with $s = i\omega$ and the integrals occurring in (5.4). Because of the symmetry of the potential (1.1) only terms with odd p and q appear in the final sum of (5.4). Therefore we can reduce our matrices to the half, similary as done in Section 4. (For a review article about susceptibility properties see Ref. 63.)

5.1. Zero-Friction Limit

In the zero-friction limit ($\gamma \to 0$) and for bistable operation ($d_2 < 0$), we now give analytical expressions for the Fourier transform of the correlation function

$$\begin{aligned}\tilde{K}'_{xx}(\omega) &= \mathrm{Re}\left\{\int_0^\infty \langle x(t)\, x(0)\rangle\, e^{-i\omega t}\, dt\right\} \\ &= \frac{1}{2}\int_{-\infty}^{\infty} \langle x(t)\, x(0)\rangle\, e^{-i\omega t}\, dt \\ &= \sum_{n=0}^{\infty} S_1^{(n)}(\omega) + S_2^{(0)}(\omega) + \sum_{n=1}^{\infty} S_2^{(n)}(\omega)\end{aligned} \tag{5.5}$$

If we introduce the energy E, the parameter $\alpha(E)$, the nome q, and the oscillator frequencies ω_0 and ω_1

$$E = v^2/2 + d_2 x^2/2 + d_4 x^4/4 \tag{5.6}$$

$$\alpha(E) = \frac{|d_2| + (d_2^2 + 4d_4 E)^{1/2}}{2(d_2^2 + 4d_4 E)^{1/2}} = \frac{\omega_1^2}{\omega_0^2} \tag{5.7}$$

$$q(\alpha) = \exp\left[-\pi \frac{\mathbf{K}'(\alpha)}{\mathbf{K}(\alpha)}\right] = \exp\left[-\pi \frac{\mathbf{K}(1-\alpha)}{\mathbf{K}(\alpha)}\right] \tag{5.8}$$

$$\omega_0^2 = (d_2^2 + 4d_4 E)^{1/2} \tag{5.9}$$

$$\omega_1^2 = \tfrac{1}{2}[|d_2| + (d_2^2 + 4d_4 E)^{1/2}] \tag{5.10}$$

where $\mathbf{K}(m)$ and $\mathbf{E}(m)$ are the complete elliptic integrals of the first and second kind,[64] we can express $S_1^{(n)}$, $S_2^{(n)}$, and ω in parameter representation (E is the running parameter) and $S_2^{(0)}(\omega)$ as follows:

$$\begin{aligned}S_1^{(n)}(\omega) = N \cdot 16\pi^2 \alpha \omega_0^4 \exp\left(\frac{-E}{\theta}\right) \\ \times \left\{(2\pi\theta)^{1/2}\, d_4^2 \left(n + \frac{1}{2}\right)[q(\alpha)^{n+1/2} + q(\alpha)^{-(n+1/2)}]^2\right. \\ \left. \times \left[1 + \frac{|d_2|}{\omega_0^2} \frac{\mathbf{E}(\alpha)}{(1-\alpha)\,\mathbf{K}(\alpha)}\right]\right\}^{-1}\end{aligned} \tag{5.11}$$

$$\omega = \left(n + \frac{1}{2}\right) \cdot \pi\omega_0 / \mathbf{K}(\alpha) \tag{5.12}$$

for $0 < E < \infty$ and $n = 0, 1, 2, \ldots,$

$$S_2^{(0)}(\omega) = \frac{N \cdot 2\pi^3}{(2\pi\theta)^{1/2} d_4} \int_{-d_2^2/(4d_4)}^{0} \frac{\omega_1 \exp(-E/\theta)}{\mathbf{K}(1/\alpha)} dE \cdot \delta(\omega) \tag{5.13}$$

$$S_2^{(n)}(\omega) = N \cdot 16\pi^2 \alpha \omega_0^4 \exp(-E/\theta)$$
$$\times \left((2\pi\theta)^{1/2} d_4^2 n[q(1/\alpha)^n + q(1/\alpha)^{-n}]^2 \right.$$
$$\left. \times \left| \left\{ 1 + \frac{|d_2|}{\omega_0^2} \left[1 - \frac{\alpha \cdot \mathbf{E}(1/\alpha)}{(\alpha - 1) \cdot \mathbf{K}(1/\alpha)} \right] \right\} \right| \right)^{-1} \tag{5.14}$$

$$\omega = n \cdot \pi \omega_1 / \mathbf{K}(1/\alpha) \tag{5.15}$$

for $-d_2^2/(4d_4) \leqslant E < 0$ and $n = 1, 2, 3, \ldots$.

It follows from (5.12) that $S_1^{(n)}(\omega)$ is defined in the interval $[0, \infty)$, while (5.15) shows that $S_2^{(n)}(\omega)$ is defined in $[0, n \cdot (2|d_2|)^{1/2}]$. The expressions (5.11)–(5.15) have been derived by Onodera.[65] In this reference, however, the term $S_2^{(0)}(\omega)$ proportional to the δ function is missing. For an alternative derivation see the Appendix. For the Duffing equation ($d_2 > 0$) formulas are simplified to terms containing only $S_1^{(n)}(\omega)$, but they will not be given here (see Ref. 65).

5.2. Results

In Figs. 8 and 9 the real part $\tilde{K}'_{\tilde{x}\tilde{x}}(\tilde{\omega})$ of the half-sided Fourier transform of the correlation function $\langle \tilde{x}(\tilde{t})\, \tilde{x}(0) \rangle$ for the double-well potential $-\tilde{x}^2/2 + \tilde{x}^4/4$ is shown for various damping constants $\tilde{\gamma}$ and in the zero friction limit $\tilde{\gamma} \to 0$. This Fourier transform was obtained by Matsuo[53] for temperatures $\tilde{\Theta} \geqslant 0.25$ and damping constants $\tilde{\gamma} \geqslant 0.5$ using a projection operator method. As seen much lower damping constants and temperatures can be handled by the present method. It is even possible to obtain $\tilde{K}'_{\tilde{x}\tilde{x}}(\omega)$ for the low friction constant $\tilde{\gamma} = 0.01$ so that the connection to the analytical zero-friction limit can be made. As seen in Fig. 8 $\tilde{K}'_{\tilde{x}\tilde{x}}(\tilde{\omega})$ has three maxima for low $\tilde{\gamma}$, one at $\tilde{\omega} = 0$, the other at $\tilde{\omega} \approx 0.6$, and the third at $\tilde{\omega} \approx 1.3$. These structures are explained as follows. The maximum at zero frequency, i.e., the response to a constant force stems from the fact that particles move from the left to the right well if the force is switched on. A closer inspection of the numerical values shows that, near $\tilde{\omega} \approx 0$, $\tilde{K}'_{\tilde{x}\tilde{x}}(\tilde{\omega})$ can be approximated by the Lorentz line

$$\tilde{K}'_{\tilde{x}\tilde{x}}(\tilde{\omega}) = A \frac{\tilde{\lambda}_1}{\tilde{\lambda}_1^2 + \tilde{\omega}^2} \tag{5.16}$$

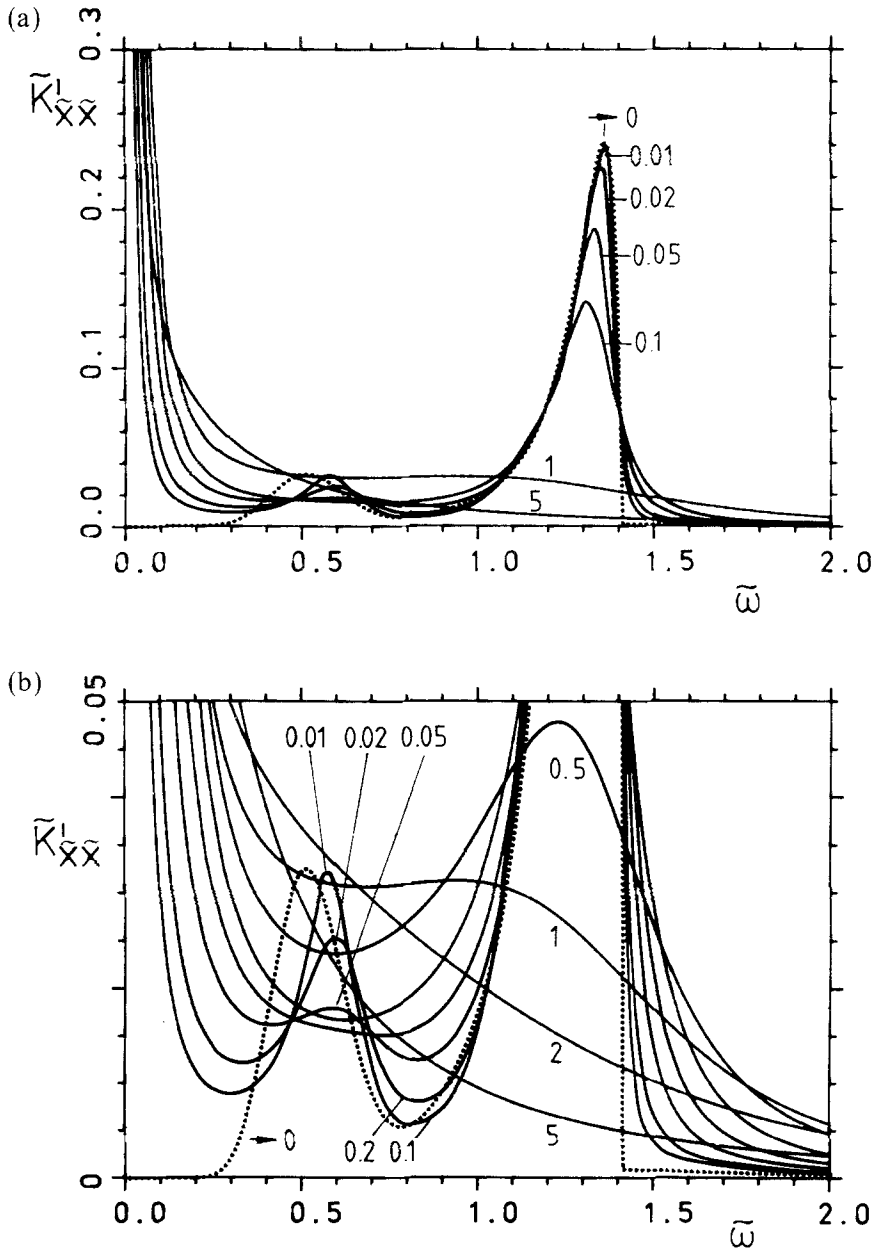

Fig. 8. The real part of the half-sided Fourier transform of $\langle \tilde{x}(\tilde{t})\, \tilde{x}(0) \rangle$ in the normalization of (2.25) for $\tilde{\theta} = 0.05 (\Delta E = 5kT)$ and for various damping constants $\tilde{\gamma}$ (full lines) and for the zero friction limit (dotted line). (a) and (b) differ only in the scale for the ordinate.

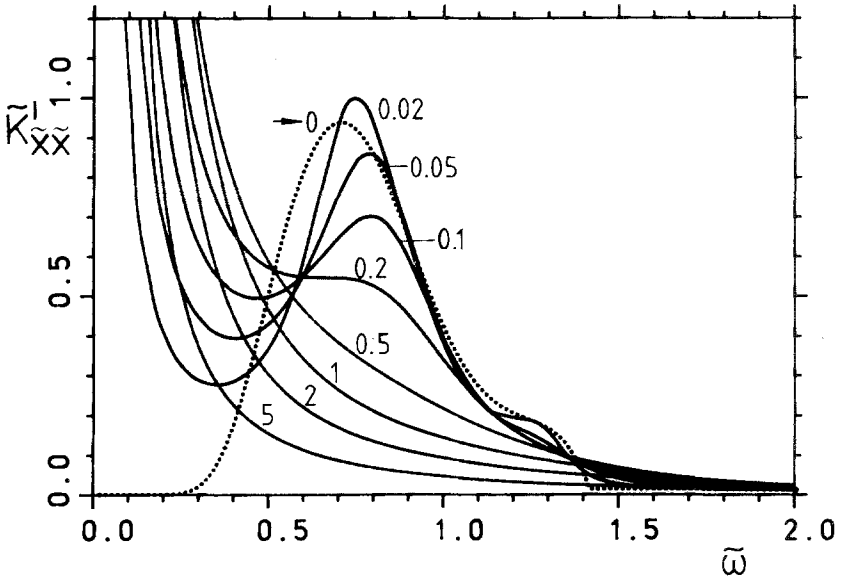

Fig. 9. Same as Fig. 8 but with $\tilde{\theta}=0.25$ ($\Delta E=kT$) and for one ordinate scale only.

where $\tilde{\lambda}_1$ is the first nonzero eigenvalue describing the transition from the left to the right well and vice versa (see Section 4). Eq. (5.16) implies that the correlation function for large times is given by

$$\langle \tilde{x}(\tilde{t})\, \tilde{x}(0)\rangle = Ae^{-\tilde{\lambda}_1 \tilde{t}} \tag{5.17}$$

For low temperatures A is nearly equal to the stationary expectation value $\langle \tilde{x}^2\rangle$, but for larger temperatures it is less than $\langle \tilde{x}^2\rangle$. For $\tilde{\gamma}\to 0$ (5.16) passes over to

$$\tilde{K}'_{\tilde{x}\tilde{x}}(\tilde{\omega}) = A\pi\delta(\tilde{\omega}) \tag{5.18}$$

because $\tilde{\lambda}_1$ goes to zero for $\tilde{\gamma}\to 0$ [see (4.6)]. The comparison with (5.5), (5.13) shows that the constant A for $\tilde{\gamma}\to 0$ is given by

$$\begin{aligned} A &= \frac{N2\pi^2}{(2\pi\theta)^{1/2}\, d_4} \int_{-d_2^2/(4d_4)}^{0} \frac{\omega_1 \exp(-E/\theta)}{\mathbf{K}(1/\alpha)}\, dE \\ &= \frac{N}{(2\pi\theta)^{1/2}} \iint_{-d_2^2/(4d_4)\le E(x,v)\le 0} x^2 \exp[-E(x,v)/\theta]\, dx\, dv \end{aligned} \tag{5.19}$$

where $E(x, v)$ is given by (5.6).

Evaluation of the integral in (5.19) shows, that A for $\tilde{\gamma} \to 0$, and $\langle \tilde{x}^2 \rangle$ agree for small temperatures $\tilde{\theta}$. Up to terms proportional to $\tilde{\theta}$ we have [cf. also (2.13a) for $\mu = 1$]

$$A \approx \langle \tilde{x}^2(0) \rangle \approx (|\tilde{d}_2|/\tilde{d}_4)(1 - \tilde{d}_4\tilde{\theta}/\tilde{d}_2^2) = 1 - \tilde{\theta} \tag{5.20}$$

which agrees very well with the value determined by the matrix continued fraction method for $\tilde{\gamma} = 0.01$ and $\tilde{\theta} = 0.05$.

The maximum at $\tilde{\omega} \approx 0.6$ stems from those particles, which have energies larger than zero and thus oscillate from the left to the right well and vice versa, whereas the maximum at $\tilde{\omega} \approx 1.3$ stems from those particles, which have energies less than zero and oscillate in the wells. The frequencies of the maxima and their widths are approximately given by the imaginary and real parts of the antisymmetric complex eigenvalues (see Fig. 4). In the zero-friction limit the first maximum at $\tilde{\omega} = 0$ passes over to the δ-function term in (5.5), (5.13) (this term was not obtained in Ref. 65), whereas the other maxima have a finite width and finite height for $\tilde{\gamma} \to 0$. Whereas for the low-temperature value $\Delta E = 5kT$ in Fig. 8 the maximum at $\tilde{\omega} = 0.6$ is lower than the one at $\tilde{\omega} = 1.3$, the reverse is true for the higher temperature $\Delta E = kT$ in Fig. 9. Here the second maximum at $\tilde{\omega} \approx 1.3$ is degenerated to a hump. The shift of the maximum at $\tilde{\omega} \approx 0.6$ of the $\tilde{\gamma} = 0.02$ curve and its larger value (larger than the $\tilde{\gamma} \to 0$ curve) may be explained as follows. For finite $\tilde{\gamma}$ the δ-function peak at $\tilde{\omega} = 0$ actually has a finite width. The tail of this peak, which leads to a small but finite value at $\tilde{\omega} \approx 0.6$, has to be added to the dotted curve. It is seen that near $\tilde{\omega} \approx 1.3$ the $\tilde{\gamma} = 0.01$ curve agrees much better with the zero-friction-limit result than near $\tilde{\omega} \approx 0.6$. This larger deviation at $\tilde{\omega} \approx 0.6$ and especially the larger frequency shift of the maximum may be explained by the fact that the motion of the particles just going over the top of the double-well potential is more influenced by the constant than the motion of particles at the bottom of the wells. The finite values in the zero-friction-limit curve for $\tilde{\omega} \geqslant \sqrt{2}$ in Figs. 8, 9, and 11 stem from the terms with $n \geqslant 2$ in (5.11), (5.14). In Figs. 10 and 11 the real and imaginary parts of the susceptibility $\chi_{\tilde{x}}(\tilde{\omega})$ are shown for $\Delta E = 5kT$. This susceptibility describes the response of the coordinate $\tilde{x}$ to an external force. Because it is given by (5.2) the imaginary part is given by $\tilde{K}'_{\tilde{x}\tilde{x}}(\tilde{\omega})$ multiplied by $\tilde{\omega}/\tilde{\theta}$. The discussion is essentially the same as in Fig. 8. The real part $\chi'_{\tilde{x}}(\tilde{\omega})$ in Fig. 10 shows the in-phase response of $\tilde{x}$ to the external force. At the frequencies $\tilde{\omega} \approx 0.6$ and $\tilde{\omega} \approx 1.3$ a typical in-phase response of oscillators is seen for small damping constants. It should be noted that the zero-friction-limit result was obtained by the Hilbert transformation. The δ-function peak was omitted. If it is added an additional $1/\tilde{\omega}$ part has to be added, leading for small $\tilde{\omega}$ to a better agreement between the low- and the zero-friction-limit result.

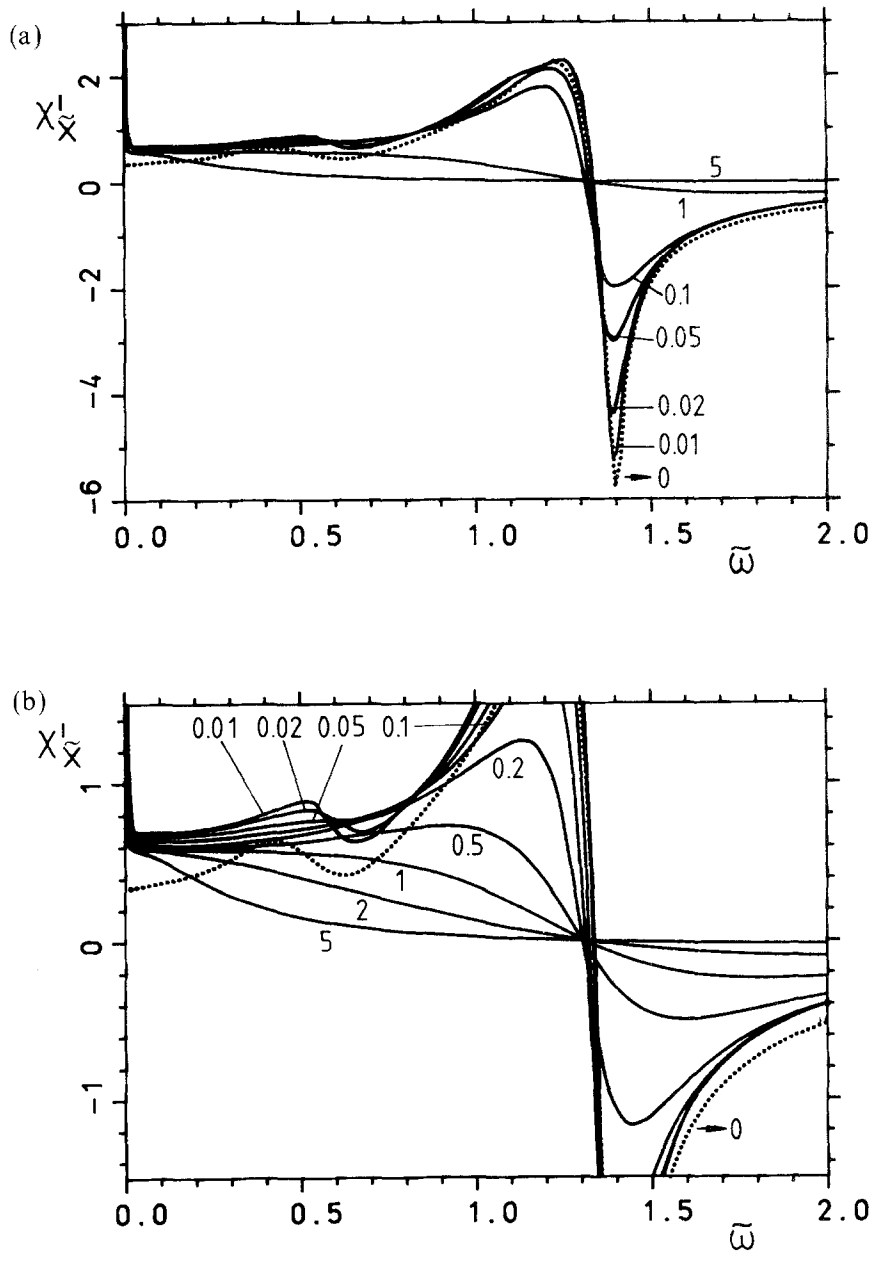

Fig. 10. The real part of the susceptibility $\chi_{\tilde{x}}(\tilde{\omega})$ in the normalization (2.25) for $\tilde{\theta}=0.05(\Delta E=5kT)$ and for various damping constants $\tilde{\gamma}$ (full lines) and zero friction limit (dotted line). (a) and (b) differ only in the scale for the ordinate.

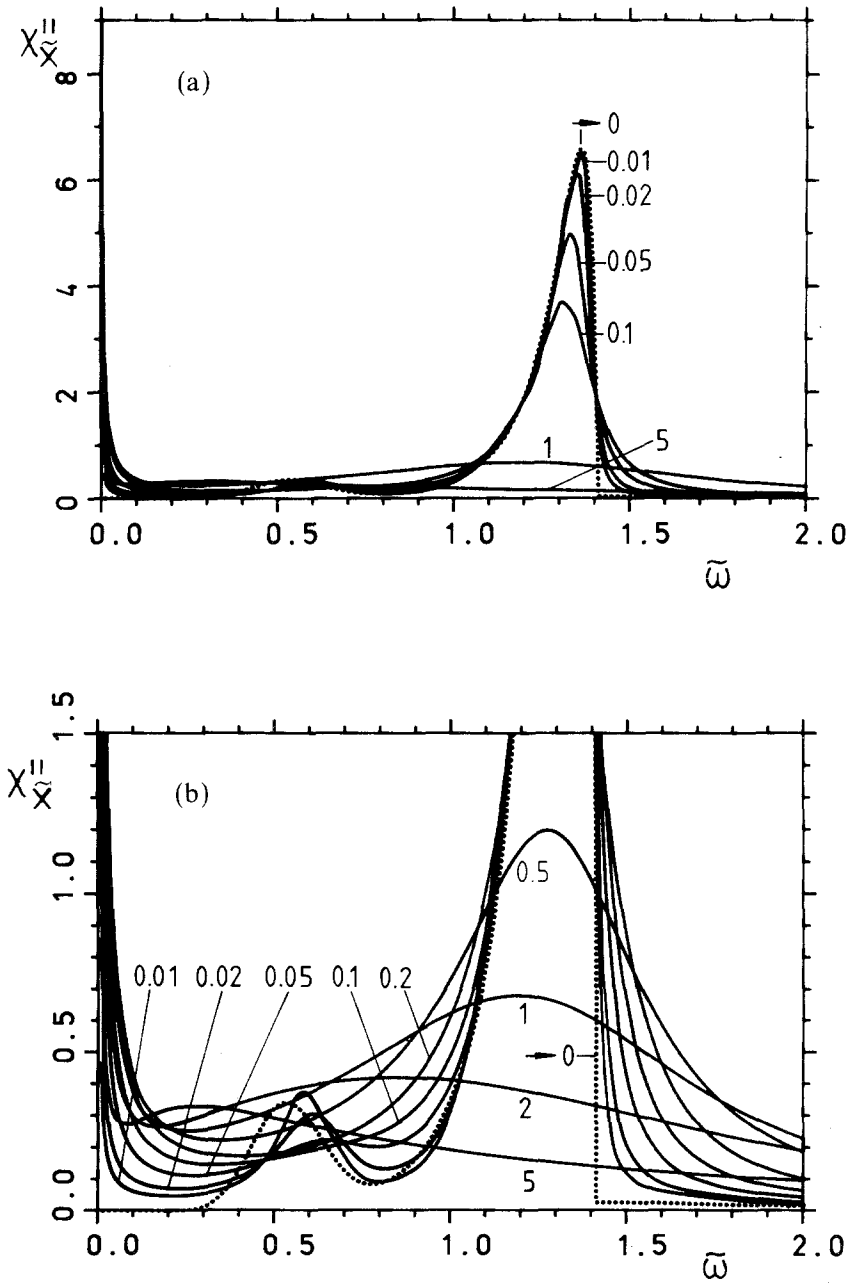

Fig. 11. Same as Fig. 10 but instead of the real part the imaginary part of $\chi_{\tilde{x}}$ is shown.

In the actual calculation the following effect was observed: If the truncation indices Q and N are not chosen large enough, a larger number of artificial peaks occur for small $\tilde{\gamma}$. By increasing the order of Q and N and by choosing a proper scaling factor α, these artificial peaks then disappear. For $\tilde{\gamma}=0.01$ and $\Delta E=5kT$ we have used $Q=40$, $N=160$, $\alpha=5$, leading to the smooth curve shown in Fig. 8.

6. CONCLUSION

It was shown that the calculation of eigenvalues and eigenfunctions as well as correlation functions for the Kramers equation in a double-well potential of the form $d_2x^2/2+d_4x^4/4$ can be obtained very effectively with the same matrix-continued-fraction method. By slight modifications of the matrix continued fraction the BGK case could also be handled. We have seen that the method works very well up to $\Delta E/(kT)$ ratios of 5 and for damping constants down to $\gamma=0.01$, so that the connection to the corresponding asymptotic results could be made. For potentials of the form $d_1x+d_2x^2/2+d_3x^3/3+d_4x^4/4+\cdots+d_{2N}x^{2N}/(2N)$ $(d_{2N}>0)$ the same method is applicable. The matrix elements D^{pq} and $\hat{D}^{pq}$ will then have a more complicated form than (3.6). (For asymmetric potentials, however, no symmetry property can be used.) For more complicated potentials the method may also be applied. In general, however, the matrix elements must then be calculated numerically. In the zero-friction limit, the energy becomes a slow variable and therefore a transformation to the energy variable has to be made and the transformed Fokker–Planck equation has to be solved. This will be investigated in a forthcoming publication.[55]

APPENDIX

Zero-Friction Limit

In the zero-friction limit the stationary solution W_{st} is still given by (2.11), whereas the transition probability (2.19) for finite times t is, owing to the deterministic motion, given by

$$P(x, v, t \mid x', v', 0)=\delta(x-X)\cdot\delta(v-V) \tag{A1}$$

Here $X=X(x', v', t)$ and $V=V(x', v', t)$ are the solutions of the equations of motion (2.4) without damping and fluctuations, i.e., they are solutions of the system

$$\dot{x}=v, \qquad \dot{v}=-d_2x-d_4x^3 \tag{A2}$$

with the initial condition

$$X(x', v', 0) = x', \qquad V(x', v', 0) = v' \tag{A3}$$

The correlation function (3.15) may thus be written in the form

$$\langle g(x(t))\, g(x(0)) \rangle$$

$$= \iiiint g(x)\, \delta(x - X(x', v', t))\, \delta(v - V(x', v', t))\, W_{\mathrm{st}}(x', v')$$

$$\times\, g(x')\, dx dv\, dx' dv' = \iint g(X(x', v', t))\, g(x')\, W_{\mathrm{st}}(x', v')\, dx' dv' \tag{A4}$$

Thus the autocorrelation function $K_{xx}(t)$ is given by

$$K_{xx}(t) = \langle x(t)\, x(0) \rangle = (2\pi\theta)^{-1/2} N \iint X(x', v', t)\, x'$$

$$\cdot \exp[(-v'^2/2 - d_2 x'^2/2 - d_4 x'^4/4)/\theta]\, dx'\, dv' \tag{A5}$$

In the following we use the abbreviations (5.7), (5.9), and (5.10) and

$$a^2 = [|d_2| + (d_2^2 + 4 d_4 E)^{1/2}]/d_4 = 2\omega_1^2/d_4 \tag{A6}$$

Instead of the variables x' and v' we use the energy (5.6) and the angle ψ defined by

$$\psi = \psi(x', v') = \begin{cases} \arccos x'/a, & E > 0 \\ \arcsin\{\alpha[1 - (x'/a)^2]^{1/2}\} & E < 0 \end{cases} \tag{A7}$$

The solutions of the system (A2) with the initial condition (A3) may then be expressed in terms of the Jacobian elliptic functions (for the elliptic functions we use the notation of Ref. 64) for:

$E > 0$:

$$x(t) = a \cdot \mathrm{cn}(\omega_0 t + \psi, \alpha) \tag{A8}$$

$$v(t) = -a \cdot \omega_0\, \mathrm{sn}(\omega_0 t + \psi, \alpha) \cdot \mathrm{dn}(\omega_0 t + \psi, \alpha) \tag{A9}$$

and for

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

$$x(t) = \pm a \cdot \mathrm{dn}(\omega_1 t + \psi, 1/\alpha) \tag{A10}$$

$$v(t) = -\frac{a}{\alpha}\, \omega_1 \cdot \mathrm{sn}(\omega_1 t + \psi, 1/\alpha) \cdot \mathrm{cn}(\omega_1 t + \psi, 1/\alpha) \tag{A11}$$

The upper sign in (A10) is valid in the right well, the lower in the left well. The period of the functions $\mathrm{sn}(\psi, \alpha)$ and $\mathrm{cn}(\psi, \alpha)$ is $4\mathbf{K}(\alpha)$, whereas the period of the function $\mathrm{dn}(\psi, \alpha)$ is $2\mathbf{K}(\alpha)$, where $\mathbf{K}(\alpha)$ is the complete elliptic integral of the first kind.[64] For $t=0$ we can express x' and v' by (A8)–(A11) as a function of E and ψ. If we use instead of the variables x', v' the variables E and ψ, the double integral (A5) is transformed to

$$K_{xx}(t) = (2\pi\theta)^{-1/2} N \cdot (2\omega_0)^3 \left[\int_0^\infty e^{-E/\theta} I_1(E, t) \frac{dE}{\omega_0} \cdot a^2 + a^2 \cdot 2 \int_{-d_2^2/(4d_4)}^0 e^{-E/\theta} I_2(E, t) \frac{dE}{\omega_1} \right] \tag{A12}$$

$$I_1(E, t) = \int_0^{4\mathbf{K}(\alpha)} \mathrm{cn}(\omega_0 t + \psi, \alpha)\, \mathrm{cn}(\psi, \alpha)\, d\psi \tag{A13}$$

$$I_2(E, t) = \int_0^{2\mathbf{K}(1/\alpha)} \mathrm{dn}(\omega_1 t + \psi, 1/\alpha)\, \mathrm{dn}(\psi, 1/\alpha)\, d\psi \tag{A14}$$

In deriving (A12) we have used that the Jacobian of the transformation from x' and v' to the E and ψ variables is given by

$$J = \frac{\partial(E, \psi)}{\partial(x', v')} = \begin{cases} \omega_0, & E > 0 \\ \omega_1, & E < 0 \end{cases} \tag{A15}$$

The factor 2 in front of the last integral in (A12) stems from the fact that we have two wells for $E<0$. In order to evaluate the integrals in (A13) and (A14) we use the following series expansion of the elliptic functions cn and dn (see 16.23.2, 16.23.3 of Ref. 64)

$$\mathrm{cn}(u, m) = \frac{2\pi}{\sqrt{m}\,\mathbf{K}(m)} \sum_{n=0}^{\infty} \frac{\sqrt{q}\, q^n}{1 + q^{2n+1}} \cos\left[(2n+1) \frac{\pi u}{2\mathbf{K}(m)} \right] \tag{A16}$$

$$\mathrm{dn}(u, m) = \frac{\pi}{2\mathbf{K}(m)} + \frac{2\pi}{\mathbf{K}(m)} \sum_{n=1}^{\infty} \frac{q^n}{1 + q^{2n}} \cos\left[2n \frac{\pi u}{2\mathbf{K}(m)} \right] \tag{A17}$$

where the nome q is given by (5.8). By inserting the appropriate expressions (A16) and (A17) into (A13) and (A14) we can perform the integration over ψ leading to

$$I_1(E, t) = \frac{4\pi^2 q(\alpha)}{\alpha \mathbf{K}(\alpha)} \sum_{n=0}^{\infty} \frac{q^{2n}(\alpha)}{[1 + q^{2n+1}(\alpha)]^2} \times \cos\left[(2n+1) \frac{\pi \omega_0 t}{2\mathbf{K}(\alpha)} \right], \quad \text{for} \quad E > 0 \tag{A18}$$

$$I_2(E, t) = \frac{\pi^2}{2\mathbf{K}(1/\alpha)} \left\{ 1 + 8 \sum_{n=1}^{\infty} \frac{q^{2n}(1/\alpha)}{[1 + q^{2n}(1/\alpha)]^2} \times \cos\left[2n \frac{\pi \omega_1 t}{2\mathbf{K}(1/\alpha)} \right] \right\}, \quad \text{for} \quad \frac{-d_2^2}{4d_4} \leqslant E < 0 \tag{A19}$$

Because we are interested in the susceptibilities we have to make a half-sided Fourier transform of the correlation function (A12). For further treatment we restrict ourselves to the calculation of the real part $\tilde{K}'_{xx}(\omega)$. The imaginary part $\tilde{K}''_{xx}(\omega)$ follows from the Kramers-Kronig relations. Because of

$$\int_0^\infty \cos \alpha t \cos \omega t \, dt = \frac{1}{2} \int_{-\infty}^{\infty} \cos \alpha t \, e^{-i\omega t} \, dt = \frac{\pi}{2} [\delta(\alpha - \omega) + \delta(\alpha + \omega)]$$

we can immediately perform the cos transformation of $I_1(E, t)$ and $I_2(E, t)$. Because of the δ function we can then easily perform the integration over E and finally arrive at (5.5) and (5.11)–(5.15).

REFERENCES

1. P. Fulde, L. Pietronero, W. R. Schneider, and S. Strässler. *Phys. Rev. Lett.* **35**:1776 (1975).
2. T. Geisel, in *Physics of Superionic Conductors*, M. B. Salamon, ed., *Topics in Current Physics*, Vol. 15 (Springer, Berlin, 1979), p. 201.
3. W. Dieterich, P. Fulde, and I. Peschel, *Adv. Phys.* **29**:527 (1980).
4. B. D. Josephson, *Phys. Lett.* **1**:251 (1962).
5. L. Solymar, *Superconductive Tunneling and Applications* (Chapman and Hall, London, 1972).
6. A. Barone, G. Paterno, *Physics and Applications of the Josephson Effect* (Wiley, New York 1982).
7. J. McConnel, *Rotational Brownian Motion and Dielectric Theory* (Academic, London, 1980).
8. W. T. Coffey, *Adv. Mol. Relaxation Interaction Processes* **17**:169 (1982); M. Evans, G. J. Evans, W. T. Coffey, and P. Grigolini, *Molecular Dynamics* (Wiley, New York, 1982).
9. E. Praestgard and N. G. van Kampen, *Molec. Phys.* **43**:33 (1981).
10. A. J. Viterbi, *Principles of Coherent Communication* (McGraw-Hill, New York, 1966).
11. W. C. Lindsey, *Synchronization Systems in Communication and Control* (Prentice-Hall, Englewood Cliffs, New Jersey, 1972).
12. G. A. Toombs, *Phys. Rev.* **40C**:181 (1978).
13. W. Wonneberger and H. J. Breymayer, *Z. Phys.* **B43**:329 (1981).
14. D. Chandler, *J. Chem. Phys.* **68**:2959 (1978).
15. B. J. Berne, J. L. Skinner, and P. G. Wolynes, *J. Chem. Phys.* **73**:4314 (1980).
16. D. L. Hasha, T. Eguchi, and J. Jonas, *J. Chem. Phys.* **73**:1571 (1981); *J. Am. Chem. Soc.* **104**:2290 (1982).
17. D. K. Garrity and J. L. Skinner, *Chem. Phys. Lett.* **95**:46 (1983).
18. B. Carmeli and A. Nitzan, *J. Chem. Phys.* **80**:3596 (1984).
19. H. A. Staab, *Einführung in die theoretische organische Chemie*, 4th ed., 2nd printing (Verlag Chemie, Weinheim, 1970).

20. H. A. Kramers, Physica **7**:284 (1940).
21. H. C. Brinkman, *Physica* **22**:29 (1956); *Physica* **22**:149 (1956).
22. C. Blomberg, *Physica* **86A**:49 (1977).
23. P. B. Visscher, *Phys. Rev. B* **14**:347 (1976).
24. (a) J. L. Skinner and P. G. Wolynes, *J. Chem. Phys.* **69**:2143 (1978); (b) *J. Chem. Phys.* **72**:4913 (1980).
25. (a) R. S. Larson and M. D. Kostin, *J. Chem. Phys.* **69**:4821 (1978); (b) *J. Chem. Phys.* **72**:1392 (1980).
26. S. C. Northrup and J. T. Hynes, *J. Chem. Phys.* **69**:5246 (1978); *J. Chem. Phys.* **69**:5261 (1978); *J. Chem. Phys.* **73**:2700 (1980); R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **73**:2715 (1980).
27. M. Mangel, *J. Chem. Phys.* **72**:6606 (1980).
28. K. Schulten, Z. Schulten, and A. Szabo, *J. Chem. Phys.* **74**:4426 (1981).
29. M. Bixon and R. Zwanzig, *J. Stat. Phys.* **3**:245 (1971).
30. (a) M. I. Dykman and M. A. Krivoglaz, *Synergetics, Proceedings of the International Symposium* (Tallinn, 1983), p. 33; (b) *Sov. Phys.* **50**:30 (1979).
31. P. Hänggi, *Phys. Lett.* **78A**:304 (1980).
32. J. A. Krumhansl and J. R. Schrieffer, *Phys. Rev. B* **11**:3535 (1975).
33. P. Hänggi, *J. Stat. Phys.* **30**:401 (1983).
34. T. Shimizu, *Phys. Lett.* **71A**:319 (1979); K. Takeyama, *Progr. Theor. Phys.* **60**:613 (1978); *Progr. Theor. Phys.* **63**:91 (1980).
35. H. Risken and H. D. Vollmer, *Z. Phys.* **B33**:297 (1979).
36. H. D. Vollmer and H. Risken, *Z. Phys.* **B34**:313 (1979).
37. H. Risken and H. D. Vollmer, *Z. Phys.* **B39**:339 (1980).
38. H. Risken, H. D. Vollmer, and M. Mörsch, *Z. Phys.* **B40**:343 (1981).
39. H. D. Vollmer and H. Risken, *Physica* **110A**:106 (1982).
40. H. Risken and H. D. Vollmer, *Molec. Phys.* **46**:555 (1982).
41. H. Risken, *The Fokker–Planck Equation*, Springer Series in Synergetics, Vol. 18 (Springer, Berlin, 1984).
42. L. D. Landau and E. M. Lifschitz, *Lehrbuch der Theoretischen Physik*, Vol. V, *Statistische Physik* (Akademie-Verlag, Berlin, 1975); L. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon, London, 1968).
43. S. Chandrasekar, *Rev. Mod. Phys.* **15**:1 (1943).
44. M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**:323 (1945).
45. P. L. Bhatnagar, E. P. Gross, and M. Krook, *Phys. Rev.* **94**:511 (1954).
46. L. de Haro, *Physica* **111A**:65 (1982).
47. H. Dekker, *Proefschrift* (Physisch Laboratorium TNO, 's-Gravenhage, 1980).
48. H. Dekker and N. G. van Kampen, *Phys. Lett.* **76A**:101 (1980).
49. B. J. Matkowsky, Z. Schuss, and E. Ben-Jacob, *J. Appl. Math.* **42**:835 (1982).
50. C. W. Gardiner, *J. Stat. Phys.* **30**:157 (1983).
51. J. T. Hynes, *Chem. Phys. Lett.* **79**:344 (1981).
52. J. B. Morton and S. Corrsin, *J. Stat. Phys.* **2**:153 (1970).
53. K. Matsuo, *J. Stat. Phys.* **6**:535 (1978).
54. W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer, New York, 1966).
55. H. Risken and K. Voigtlaender, in preparation.
56. H. Risken and H. D. Vollmer, *Z. Phys.* **B35**:177 (1979).
57. H. D. Vollmer and H. Risken, *Z. Phys.* **B37**:343 (1980).
58. P. Jung and H. Risken, *Z. Phys.* **B54**:357 (1984).
59. K. Voigtlaender and H. Risken, *Chem. Phys. Lett.* **105**:506 (1984).

60. I. S. Gradstheyn and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1965).
61. H. D. Vollmer and H. Risken, *Z. Phys.* **B52**:259 (1983).
62. M. Mörsch, H. Risken, and H. D. Vollmer, *Z. Phys.* **B49**:47 (1982).
63. P. Hänggi and H. Thomas, *Phys. Rep.* **88**:207 (1982).
64. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
65. Y. Onodera, *Progr. Theor. Phys.* **44**:1477 (1970).