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Evaluation of the smallest nonvanishing eigenvalue of the Fokker-Planck equation for Brownian motion in a potential: The continued fraction approach

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An equation for the smallest nonvanishing eigenvalue λ_1 of the Fokker-Planck equation (FPE) for the Brownian motion of a particle in a potential is derived in terms of continued fractions. This equation is directly applicable to the calculation of λ_1 if the solution of the FPE can be reduced to the solution of a scalar three-term recurrence relation for the moments (the expectation values of the dynamic quantities of interest) describing the dynamical behavior of the system under consideration. In contrast to the previously available continued fraction solution for λ_1 [for example, H. Risken, *The Fokker-Planck Equation*, 2nd ed. (Springer, Berlin, 1989)], this equation does not require one to solve numerically a high order polynomial equation, as it is shown that λ_1 may be represented as a sum of products of infinite continued fractions. Besides its advantage for the numerical calculation, the equation so obtained is also very useful for analytical purposes, e.g., for certain problems it may be expressed in terms of known mathematical (special) functions. Another advantage of such an approach is that it can now be applied to systems whose relaxation dynamics is governed by divergent three-term recurrence equations. To test the theory, the smallest eigenvalue λ_1 is evaluated for several double-well potentials, which appear in various applications of the theory of rotational and translational Brownian motion. It is shown that for all ranges of the barrier height parameters the results predicted by the analytical equation so obtained are in agreement with those obtained by independent numerical methods. Moreover, the asymptotic results for λ_1 previously derived for these particular problems by solving the FPE in the high barrier limit are readily recovered from the analytical equations.

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I. INTRODUCTION

The model of Brownian motion of a particle in a potential has a variety of applications. Among the various phenomena to which this model has been applied, one can mention the current-voltage characteristics of the Josephson junction [1], the dielectric and Kerr-effect relaxation of liquids and molecular and liquid crystals [2–5], the mobility of superionic conductors [6], the magnetic relaxation of single-domain ferromagnetic particles (superparamagnetism) [7,8], the escape of particles over potential barriers [9], radio engineering [10], etc. A detailed discussion of this model with many particular applications is given in [11,12].

The dynamics of the Brownian motion of a particle in a potential is described by the Langevin equation for appropriate dynamic variables or the accompanying Fokker-Planck equation (FPE) for the probability density function of these variables [11]. The solution of the Langevin equation or the FPE can be reduced to the solution of an infinite hierarchy of equations for the moments (the expectation values of the dynamic quantities of interest) describing the dynamics of the system under consideration. Various examples can be found in Refs. [11] and [12]. In general, the hierarchies of the moment equations that are generated by the underlying FPE take the form of three- (or higher-order) term differential-recurrence relations between the moments. Thus, the behavior of any selected average is coupled to that of all the others, so forming an infinite system of moment equations. The time behavior of the first-order average, for example, involves that of the second-order average, which in turn involves the third-order average, and so on. If the recurrence relation between the averages is a *scalar* three-term one, the solution may be expressed in terms of ordinary infinite continued fractions [11,12]. A multiterm recurrence relation may be reduced to a *matrix* three-term recurrence relation, which may be solved in terms of matrix continued fractions [11]. In the present paper we confined ourselves to problems that may be reduced to the solution of a scalar three-term recurrence relation only. The problem involving the solution of multiterm recurrence relations will be considered in a forthcoming paper.

A scalar three-term recurrence relation may be written down as [11]

$$\tau_\epsilon \frac{d}{dt} C_n(t) = q_n^- C_{n-1}(t) + q_n C_n(t) + q_n^+ C_{n+1}(t),$$

$$n = 1,2,3, \ldots, \qquad (1)$$

where the $C_n(t)$ are the moments or the appropriate relaxation functions, q_n^-, q_n^+, and q_n are time independent coefficients, and τ_ϵ is a characteristic time constant. Such relations usually arise from solution of the FPE in the high friction (overdamped) limit, when it is possible to neglect the inertia of the Brownian particle [11,12]. A general method of solution of Eq. (1) in terms of continued fractions was described by Risken [11] and later extended by Coffey, Kalmykov, and Waldron [12]. The last approach has the merit of being simpler than the previously available solution. Thus, according to [12], the exact solution of Eq. (1) with $C_0(t) = 0$ for the Laplace transform of $C_1(t)$ is given by

$$\tilde{C}_1(s) = \frac{\tau_\epsilon}{\tau_\epsilon s - q_1 - q_1^+ S_2(s)} \left[C_1(0) + \sum_{n=2}^{\infty} \left(\prod_{k=2}^{n} \frac{q_{k-1}^+ S_k(s)}{q_k^-} \right) C_n(0) \right], \tag{2}$$

where the infinite continued fractions $S_n(s)$ are defined as

$$S_n(s) = \cfrac{q_n^-}{\tau_\epsilon s - q_n - \cfrac{q_n^+ q_{n+1}^-}{\tau_\epsilon s - q_{n+1} - \cfrac{q_{n+1}^+ q_{n+2}^-}{\tau_\epsilon s - q_{n+2} - \cdots}}}. \tag{3}$$

The initial conditions $C_p(0)$ in Eq. (2) can also be expressed in terms of the matrix continued fraction $S_p(0)$ from Eq. (3) (see Refs. [11] and [12]).

Having determined $\tilde{C}_1(s)$ from Eq. (2), one is able to calculate the relaxation (or correlation) time τ of the dynamic quantity of interest, which is defined as

$$\tau = \frac{1}{C_1(0)} \int_0^\infty C_1(t) dt = \frac{\tilde{C}_1(0)}{C_1(0)}. \tag{4}$$

The relaxation time τ may equivalently be defined in the context of the FPE converted to the Sturm-Liouville problem as

$$\tau = \frac{\Sigma_k c_k / \lambda_k}{\Sigma_k c_k}, \tag{5}$$

where λ_k and c_k are the eigenvalues and their corresponding weight coefficients (amplitudes), as the function $C_1(t)$ is given by

$$C_1(t) = \sum_k c_k e^{-\lambda_k t}.$$

Thus in order to evaluate τ from Eq. (5) knowledge of the eigenvalues λ_k and their amplitudes c_k is required. As has been shown in many examples (e.g., Refs. [11], [13–15]), the results given by Eqs. (4) and (5) are completely equivalent. Other time constants that characterize the dynamics of the system, such as the mean first passage time τ_{MFP} [15]. the effective relaxation time τ_{eff} [16], etc. can also be evaluated in terms of λ_k and c_k.

In general, the eigenvalue problem of the FPE is quite difficult to solve. Various methods of calculating the eigenvalues of the FPE have been discussed in detail in Ref. [11]. In the context of the continued fraction approach, the eigenvalues can be determined by inserting the separation ansatz [11]

$$C_n(t) = \hat{C}_n e^{-\lambda t}, \quad n = 1,2,3, \ldots, \tag{6}$$

into Eq. (1). Thus, one obtains an equation for the eigenvalues, viz.,

$$\tau_\epsilon \lambda + q_1 + q_1^+ S_2(-\lambda) = 0. \tag{7}$$

The disadvantage of Eq. (7) is that in some cases it may be extremely difficult to evaluate the eigenvalues, as it involves finding the roots of a very high order polynomial equation, and it is known that standard mathematical programs fail to determine the roots of such an equation. Moreover, there are some examples where the continued fraction $S_2(-\lambda)$ diverges (e.g., [13]), or Eq. (7) is not applicable at all, because the calculation gives rise to unphysical solutions [11]. In such cases, Eq. (7) cannot be used for the evaluation of λ. It is therefore still worthwhile to seek a more advanced approach, which would be applicable to the solution of Eq. (7). This is especially important if one perceives that standard computational methods such as the numerical solution of Eq. (7) arranged as a first-order matrix differential equation, viz.,

$$\frac{d}{dt}\mathbf{X}(t) = \mathbf{A}\mathbf{X}(t) \tag{8}$$

[$\mathbf{A}$ is a tridiagonal system matrix, $\mathbf{X}(t)$ is an infinite column vector arranged from the moments $C_n(t)$], may also be inapplicable in such cases.

The goal of the present paper is to extend the continued fraction approach of Ref. [11] for evaluation of the eigenvalues of the FPE for Brownian motion in a potential. Here, a usable method for evaluating the smallest nonvanishing eigenvalue λ_1 is presented. A knowledge of λ_1 is of importance because various time constants such as the relaxation time τ, the mean first passage time, and the escape rate, are mainly determined by the slowest low frequency relaxation mode, which governs transitions over the barriers from one potential well into another. The characteristic frequency of this overbarrier relaxation mode is given by the inverse of λ_1. Moreover, in many cases the influence of other relaxation modes in the low frequency region may be ignored and, thus, knowledge of λ_1 provides sufficient information about the low frequency dynamics of the system under consideration [11,12].

The paper is arranged as follows. In Sec. II, an equation for the smallest eigenvalue λ_1 is derived in terms of continued fractions. Verification of the validity of this equation is given in Secs. III and IV by evaluating λ_1 for symmetric bistable potentials, which appear in various applications of the theory of rotational Brownian motion. Furthermore, the approach developed is used in Sec. V for the calculation of λ_1 for the problem of translational Brownian motion in a quartic double-well potential, where the relaxation dynamics is governed by a divergent three-term recurrence equation.

II. CONTINUED FRACTION SOLUTION FOR λ_1

In general, Eq. (7) allows one to evaluate all the eigenvalues numerically [11]. However, if one is interested in the calculation of λ_1 only, Eq. (7) can be simplified as follows. On supposing that the continued fraction S_2 may be expanded in Taylor series, viz.,

$$S_2(-\lambda_1) = S_2(0) - S_2'(0)\tau_\epsilon\lambda_1 + S_2''(0)\frac{(\tau_\epsilon\lambda_1)^2}{2} + O((\tau_\epsilon\lambda_1)^3), \tag{9}$$

which is subject to the condition

$$|\tau_\epsilon \lambda_1 S_2''(0)/2S_2'(0)| \ll 1 \tag{10}$$

that allows one to take into account only the first two terms in Eq. (9), one has from Eq. (7)

$$\tau_\epsilon\lambda_1[1-q_1^+S_2'(0)]+q_1+q_1^+S_2(0)=0$$

or

$$\tau_\epsilon\lambda_1=-\frac{q_1+q_1^+S_2(0)}{1-q_1^+S_2'(0)}, \tag{11}$$

where $S_2'(0)$ and $S_2''(0)$ are the first and second derivatives of the continued fraction $S_2(s)$ with respect to $s\tau_\epsilon$, respectively. The condition (10) of the applicability of Eq. (11) is evidently valid in the high barrier (or low temperature) limit, where $\tau_\epsilon\lambda_1 \ll 1$ [11,12]. However, Eq. (11) also provides sufficient accuracy for intermediate and small barrier heights, where $\tau_\epsilon\lambda_1 \leqslant 1$, but the condition (10) still remains fulfilled, as $S_2''(0)/2S_2'(0) \ll 1$ (see Secs. III and IV).

In order to calculate λ_1 from Eq. (11), one needs to derive an equation for $S_2'(0)$. This can be accomplished by noting that the continued fraction $S_n(s)$ defined by Eq. (3) and the derivative of $S_n(s)$ with respect to $s\tau_\epsilon$ satisfy the following recurrence relations:

$$S_n(s)=\frac{q_n^-}{\tau_\epsilon s-q_n-q_n^+S_{n+1}(s)} \tag{12}$$

and

$$S_n'(s)=-S_n^2(s)[1-q_n^+S_{n+1}'(s)]/q_n^-, \tag{13}$$

respectively. [Equation (13) can be readily obtained by direct differentiation of Eq. (12).] The solution of the recurrence Eq. (13) may be obtained by iteration and is given by

$$S_n'(s)=-\frac{1}{q_{n-1}^+}\sum_{k=0}^{\infty}\left(\prod_{m=0}^{k}S_{n+m}^2(s)q_{n+m-1}^+/q_{n+m}^-\right),$$

which yields for $s=0$ and $n=2$

$$S_2'(0)=-\frac{1}{q_1^+}\sum_{k=1}^{\infty}\left(\prod_{m=1}^{k}S_{m+1}^2(0)q_m^+/q_{m+1}^-\right). \tag{14}$$

Thus, on substituting Eq. (14) into Eq. (11), we have an equation for λ_1, viz.,

$$\tau_\epsilon\lambda_1=-\frac{q_1+q_1^+S_2(0)}{1+\sum_{k=1}^{\infty}\left(\prod_{m=1}^{k}S_{m+1}^2(0)q_m^+\Big/q_{m+1}^-\right)}. \tag{15}$$

We shall now show that the calculation of λ_1, unlike the representation of Eq. (7), which always requires one to solve numerically a high order polynomial equation in λ, can now easily be accomplished from Eq. (15). Equation (15) requires only calculation of the continued fractions $S_n(0)$, which can be carried out even on a programmable pocket calculator [11]. Moreover, Eq. (15) can be further simplified by using the method developed by Coffey, Kalmykov, and Waldron [12]. According to this method, the continued fraction $S_n(0)$ for certain problems may be expressed in terms of equilibrium averages as a ratio of known mathematical (hypergeometric) functions. This allows us to derive analytical equations for λ_1. The advantage of such an approach is that it can also be used for the evaluation of λ_1 for those problems where the continued fractions $S_n(0)$ diverge and thus the continued fraction approach based on solving Eq. (7) is no longer applicable (see, e.g., Ref. [13]). Such an example will be considered in Sec. V.

III. TWO-DIMENSIONAL ROTATIONAL BROWNIAN MOTION IN A DOUBLEFOLD COSINE POTENTIAL

Here we shall consider the noninertial rotational Brownian motion of a planar rotator with a dipole moment $\boldsymbol{\mu}$ in a doublefold cosine potential

$$V(\theta)=U\sin^2\theta, \tag{16}$$

where θ is the angle between the dipole vector $\boldsymbol{\mu}$ and the z axis. A comprehensive numerical study of this model has been made by Lauritzen and Zwanzig [17] and Coffey *et al.* [18] in connection with site models of dielectric relaxation in molecular crystals. Here this model is used as a simple example for verification of the continued fraction solution Eq. (15). Furthermore, although this model has already been well documented in Refs. [17] and [18], an equation for λ_1 that would be valid for all ranges of the barrier height parameters has not yet been presented.

In order to study the longitudinal relaxation behavior, it is supposed that a small uniform field **E** applied along the z axis is switched off at $t=0$. Then the noninertial Langevin equation for a dipole $\boldsymbol{\mu}$ rotating about an axis normal to the xz plane is [12]

$$\varsigma\frac{d}{dt}\theta(t)+U\sin^2\theta(t)=\lambda(t)\quad(t>0), \tag{17}$$

where $\varsigma\dot\theta$ and $\lambda(t)$ are the frictional and white noise torques due to the Brownian motion, and ς is the viscous drag coefficient. The relevant noninertial FPE for the probability distribution function W of the angle θ is [17]

$$\tau_D\frac{\partial}{\partial t}W=\frac{1}{kT}\frac{\partial}{\partial\theta}\left(W\frac{\partial}{\partial\theta}V\right)+\frac{\partial^2}{\partial\theta^2}W, \tag{18}$$

where

$$\tau_D=\varsigma/kT \tag{19}$$

is the Debye relaxation time for a planar rotator and kT is the thermal energy with k the Boltzmann constant and T the absolute temperature.

The differential-recurrence equation for the odd statistical moments $f_{2n-1}(t)$ appropriate to dielectric relaxation defined as

$$f_{2n-1}(t)=\langle\cos(2n-1)\theta\rangle \tag{20}$$

(the angular brackets mean a statistical averaging) is given by [18]

$$\frac{d}{dt}f_{2p+1}(t)+\frac{(2p+1)^2}{\tau_D}f_{2p+1}(t)$$
$$=\frac{\sigma(2p+1)}{2\tau_D}[f_{2p-1}(t)-f_{2p+3}(t)]. \tag{21}$$

Here

$$\sigma=\frac{U}{kT} \tag{22}$$

is the barrier height parameter.

The set of Eq. (21) may be transformed into the matrix equation (8), where the system matrix $\mathbf{A}$ is given by

$$\mathbf{A}=-\frac{1}{\tau_D}\begin{pmatrix} (1-\sigma/2) & \sigma/2 & 0 & 0 & 0 & \cdots \\ -3\sigma/2 & 9 & 3\sigma/2 & 0 & 0 & \cdots \\ 0 & -5\sigma/2 & 25 & 5\sigma/2 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{23}$$

and

$$\mathbf{X}(t)=\begin{pmatrix} f_1(t) \\ f_3(t) \\ \vdots \\ f_{2p+1}(t) \\ \vdots \end{pmatrix}. \tag{24}$$

The lowest eigenvalue λ_1 is then the smallest root of the characteristic equation

$$\det(\lambda\mathbf{I}-\mathbf{A})=0. \tag{25}$$

For the problem in question, evaluation of the eigenvalues from Eq. (25) creates no difficulties and it is used here only for the purpose of comparison with the results of the continued fraction approach.

In the context of the continued fraction approach, the smallest eigenvalue is given by Eq. (15). For the present problem, where only the odd moments are involved in Eq. (21). Eq. (15) becomes

$$\tau_D\lambda_1=-\frac{q_1+q_1^+S_3(0)}{1+\sum_{k=1}^{\infty}\left(\prod_{m=1}^{k}S_{2m+1}^2(0)q_{2m-1}^+\Big/ q_{2m+1}^-\right)}, \tag{26}$$

where

$$q_{2m+1}=-(2m+1)^2,\quad q_{2m+1}^+=-\frac{\sigma}{2}(2m+1),$$

$$q_{2m+1}^-=\frac{\sigma}{2}(2m+1), \tag{27}$$

and the continued fraction $S_{2k+1}(0)$ is given by [18]

$$S_{2k+1}(0)=\frac{\sigma}{4k+2+\sigma S_{2k+3}(0)}. \tag{28}$$

The $S_{2k+1}(0)$ from Eq. (28) may in turn be expressed in terms of modified Bessel functions of the first kind of half integer order $I_{k+1/2}(z)$ [19] as [18]

$$S_{2k+1}(0)=\frac{I_{k+1/2}(\sigma/2)}{I_{k-1/2}(\sigma/2)}. \tag{29}$$

Equation (26) then becomes after some algebra

$$\lambda_1\tau_D=\left(\frac{\pi}{1-e^{-\sigma}}\sum_{p=0}^{\infty}(-1)^p\frac{I_{p+1/2}^2(\sigma/2)}{2p+1}\right)^{-1}, \tag{30}$$

where we have used [19]

$$I_{1/2}^2(z)=\frac{2}{\pi z}\sinh^2 z,\quad \frac{I_{3/2}(z)}{I_{1/2}(z)}=\coth z-\frac{1}{z}. \tag{31}$$

Equation (30) can be further simplified, on noting that [20]

$$\sum_{p=0}^{\infty}(-1)^p\frac{I_{p+1/2}^2(z)}{2p+1}=\frac{2z}{\pi}\,{}_2F_3(1,1;\tfrac{3}{2},\tfrac{3}{2},\tfrac{3}{2};z^2),$$

where ${}_2F_3(a_1,a_2;b_1,b_2,b_3;z)$ is a hypergeometric function [20]. Thus, Eq. (30) yields

$$\lambda_1\tau_D=\left[\frac{\sigma}{1-e^{-\sigma}}\,{}_2F_3\left(1,1;\tfrac{3}{2},\tfrac{3}{2},\tfrac{3}{2};\frac{\sigma^2}{4}\right)\right]^{-1}. \tag{32}$$

For $\sigma\ll 1$, one can obtain from Eq. (32) the Taylor series expansion of λ_1, viz.,

$$\lambda_1\tau_D=1-\frac{\sigma}{2}+\frac{5}{54}\sigma^2+O(\sigma^3). \tag{33}$$

In the opposite limit $(\sigma\gg 1)$, on using the asymptotic expansion of $I_p(z)$ for large values of z in Eq. (30), one arrives at

$$\lambda_1^{\rm as}\tau_D\sim\frac{4\sigma e^{-\sigma}}{\pi}. \tag{34}$$

Equation (34) is in agreement with the results of Lauritzen and Zwanzig [17], who obtained an asymptotic expansion for the lowest eigenvalue in the limit of high potential barrier. This is also in accordance with the leading term of the asymptotic expansion for λ_1 obtained in Ref. [21], viz.,

$$\lambda_1^{\rm as}\tau_D\sim\frac{4\sigma e^{-\sigma}}{\pi}\left(1-\frac{1}{2\sigma}\right). \tag{35}$$

Equation (34) is also in accordance with results of the evaluation of the mean first passage time of the model under consideration in the high barrier limit [15].

For the present problem the lowest eigenvalue completely determines the behavior of the correlation time τ from the exact Eq. (4), which yields [18]

$$\tau=\frac{\tau_D(e^{\sigma}-1)}{\sigma I_{1/2}(\sigma/2)}\times\sum_{p=0}^{\infty}\frac{(-1)^p}{(2p+1)}\frac{I_{p+1}(\sigma/2)+I_p(\sigma/2)}{I_1(\sigma/2)+I_0(\sigma/2)}I_{p+1/2}(\sigma/2). \tag{36}$$

Equation (36) may be equivalently presented in an integral form as

$$\tau=\frac{\tau_D}{\pi[I_1(\sigma/2)+I_0(\sigma/2)]}\times\int_0^{2\pi}e^{-(\sigma/2)\cos 2\phi}\left(\int_0^{\phi}\cos x\,e^{(\sigma/2)\cos 2x}dx\right)^2 d\phi. \tag{37}$$

TABLE I. Numerical values for the doublefold cosine potential.

$\sigma/2$	$\tau_D\lambda_1^{\rm num}$ [13]	$\tau_D\lambda_1$ [Eq. (30)]	$\tau_D\lambda_1^{\rm as}$ [Eq. (35)]	τ_D/τ [Eq. (37)]
0	1.0	1.0	$-\infty$	1.0
1	0.323 7	0.323 36	0.258 47	0.325 71
2	0.082 0	0.081 93	0.081 62	0.082 64
3	0.017 2	0.017 15	0.017 36	0.017 25
4	0.003 18	0.003 18	0.003 20	0.003 19
5	5.463×10^{-4}	5.463×10^{-4}	5.491×10^{-4}	5.473×10^{-4}
6	8.966×10^{-5}	8.966×10^{-5}	8.997×10^{-5}	8.965×10^{-5}
7	1.426×10^{-5}	1.426×10^{-5}	1.429×10^{-5}	1.427×10^{-5}
8	2.22×10^{-6}	2.217×10^{-6}	2.221×10^{-6}	2.218×10^{-6}
9	3.389×10^{-7}	3.389×10^{-7}	3.394×10^{-7}	3.390×10^{-7}
10	5.112×10^{-8}	5.112×10^{-8}	5.117×10^{-8}	5.114×10^{-8}

Here we recalled (see, e.g., Ref. [11], Sec. S.9) that for a stochastic system the dynamics of which obeys the one-variable FPE for the distribution function W of a variable x,

$$\frac{\partial}{\partial t}W(x,t)=L_{\rm FP}W(x,t), \tag{38}$$

where

$$L_{\rm FP}(x)=\frac{\partial}{\partial x}\left(D^{(2)}(x)e^{-U(x)}\frac{\partial}{\partial x}e^{U(x)}\right) \tag{39}$$

is the Fokker-Planck operator, $D^{(2)}(x)$ is the diffusion coefficient, and $U(x)$ is a generalized potential [11], the correlation time τ of the equilibrium (stationary) autocorrelation function $C_A(t)=\langle A(x(0))A(x(t))\rangle_0-\langle A\rangle_0^2$ of a dynamic variable $A(x)$ is [11]

$$\tau=\frac{1}{C_A(0)}\int_0^\infty C_A(t)dt=\frac{1}{C_A(0)}\int_{x_1}^{x_2}\frac{f^2(x)dx}{D^{(2)}(x)W_0(x)}. \tag{40}$$

Here

$$f(x)=-\int_{x_1}^{x}[A(x')-\langle A\rangle_0]W_0(x')dx', \tag{41}$$

$W_0(x)=Ce^{-U(x)}$ is the equilibrium (stationary) distribution function (it is assumed that the probability current $S=0$ at equilibrium), the symbol $\langle\,\rangle_0$ designates the statistical averages over $W_0(x)$, and x is assumed to be defined in the range $x_1<x<x_2$. For the problem under consideration $x_1=0$, $x_2=2\pi$, and $D^{(2)}(x)=\tau_D^{-1}$.

The lowest eigenvalue λ_1 calculated from Eq. (30) agrees closely for all σ with the numerical solution $\lambda_1^{\rm num}$ gained as the smallest root of the characteristic Eq. (25) (see Table I and Fig. 1). In Fig. 1 and in Table I $\lambda_1^{\rm as}$ calculated from the asymptotic Eq. (35) is also presented. As one can see, all the quantities λ_1, $\lambda_1^{\rm as}$, $\lambda_1^{\rm num}$, and τ^{-1} are in excellent agreement in the high barrier limit. Moreover, λ_1, $\lambda_1^{\rm num}$, and τ^{-1} are very close to each other *for all barrier heights*. This is due to the fact that the condition (10), which for the problem in question reads

$$\left|\frac{\tau_D\lambda_1 S_3''(0)}{2S_3'(0)}\right|\ll 1, \tag{42}$$

still holds even for $\sigma=0$, where $\lambda_1\tau_D\equiv 1$, and $S_3''(0)/2S_3'(0)=-\frac{1}{9}$.

IV. THREE-DIMENSIONAL ROTATIONAL BROWNIAN MOTION IN A UNIAXIAL POTENTIAL

Let us now consider the problem of three-dimensional noninertial rotational Brownian motion of a rigid symmetric-

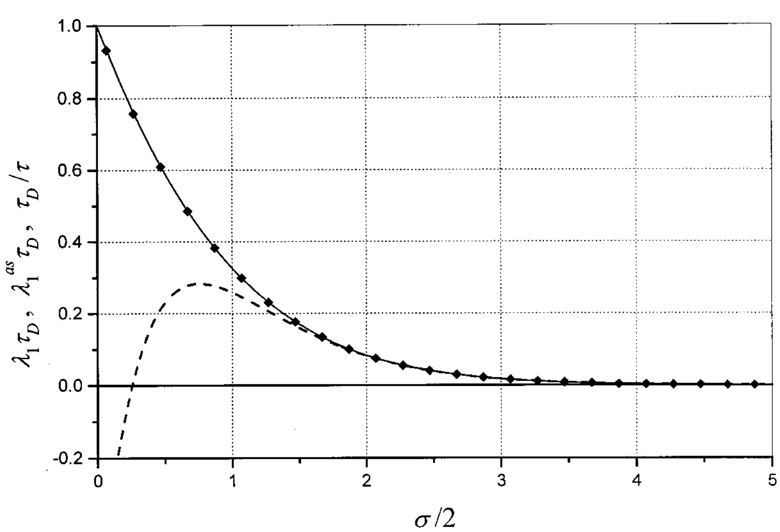

FIG. 1. λ_1 (solid line) for a single-axis rotator as a function of the barrier height σ compared with the asymptotic solution $\lambda_1^{\rm as}$ [Eq. (35)] (dashed line) and the solution rendered by the inverse of the correlation time τ^{-1} [Eq. (37)] (diamonds).

top polar particle in the uniaxial potential

$$V(\vartheta)=K\sin^2\theta, \tag{43}$$

where K is an anisotropy constant. This is a complete three-dimensional analog of the two-dimensional problem considered in Sec. III. The particle contains a rigid electric dipole $\boldsymbol{\mu}$ directed along the long axis. Let us take a unit vector $\mathbf{u}(t)$ through the center of mass of the particle in the direction of $\boldsymbol{\mu}$. Then one can write down an equation of motion for the rate of change of $\mathbf{u}(t)$ of the particle [12]

$$\varsigma\frac{d\mathbf{u}(t)}{dt}=-\frac{\partial}{\partial\mathbf{u}}V+\mathbf{u}(t)\left(\mathbf{u}(t)\cdot\frac{\partial}{\partial\mathbf{u}}V\right)+\boldsymbol{\lambda}(t)\times\mathbf{u}(t), \tag{44}$$

where ς is the friction coefficient and $\boldsymbol{\lambda}(t)$ is the white noise driving torque due to Brownian movement. Equation (44) is the vectorial Langevin equation. The corresponding noninertial FPE for the probability density distribution W of orientations of molecular dipoles in configuration space is given by [12]

$$2\tau_D\frac{\partial}{\partial t}W=\Delta W+\frac{1}{kT}\mathrm{div}(W\,\mathrm{grad}\,V), \tag{45}$$

where

$$\tau_D=\varsigma/2kT \tag{46}$$

is the Debye relaxation time for the isotropic diffusion and Δ is the Laplacian on the surface of unit sphere. The rotational Brownian motion of a particle in the uniaxial potential (43) arises in a variety of problems. Examples can be found in dielectric and Kerr-effect relaxation of polar and polarizable symmetric-top molecules [3] and dielectric relaxation of nematic liquid crystals [22]. Moreover, the theory of dielectric relaxation of nematic liquid crystals with uniaxial physical properties developed by Martin, Meier, and Saupe [22] bears a close resemblance to the theory of magnetic relaxation of single-domain ferromagnetic particles as formulated by Brown [7].

For the problem under consideration, the differential-recurrence equations for the moments $f_n(t)=\langle P_n(\cos\theta(t))\rangle$ [the expectation values of the Legendre polynomials $P_n(z)$] are given by [12]

$$\begin{aligned}\frac{d}{dt}f_{2n+1}(t)=&\frac{(2n+1)(n+1)}{\tau_D}\\&\times\left(\frac{2\sigma}{(4n+1)(4n+5)}-1\right)f_{2n+1}(t)\\&+\frac{4\sigma(n+1)(2n+1)}{\tau_D(4n+3)}\\&\times\left(\frac{n}{(4n+1)}f_{2n-1}(t)-\frac{(2n+3)}{2(4n+5)}f_{2n+3}(t)\right),\end{aligned} \tag{47}$$

where

$$\sigma=\frac{K}{kT} \tag{48}$$

is the barrier height parameter.

The set of Eqs. (47) may be solved numerically by transforming it into the matrix Eq. (8), the lowest eigenvalue λ_1 of which is then the smallest root of the characteristic Eq. (25), where

$$\mathbf{A}=-\frac{1}{\tau_D}\begin{pmatrix}(1-\frac{2}{5}\sigma) & \frac{2}{5}\sigma & 0 & 0 & 0 & \cdots\\ -\frac{24}{35}\sigma & (6-\frac{4}{15}\sigma) & \frac{20}{21}\sigma & 0 & 0 & \cdots\\ 0 & -\frac{40}{33}\sigma & (15-\frac{10}{39}\sigma) & \frac{210}{143}\sigma & 0 & \cdots\\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots\end{pmatrix}. \tag{49}$$

In the context of the continued fraction approach the smallest eigenvalue λ_1 is given by Eq. (26), where

$$q_{2m-1}=-m(2m-1)\left(1-\frac{2\sigma}{(4m-3)(4m+1)}\right), \tag{50}$$

$$q^-_{2m-1}=\frac{4\sigma m(m-1)(2m-1)}{(4m-3)(4m-1)}, \tag{51}$$

$$q^+_{2m-1}=-\frac{2\sigma m(4m^2-1)}{16m^2-1}, \tag{52}$$

and the continued fraction $S_n(0)$ is defined as

$$S_n(0)=\frac{2\sigma(n-1)}{4n^2-1-[2\sigma/(2n+3)][2n+1-(n+2)(2n-1)S_{n+2}(0)]},$$

TABLE II. Numerical values for the uniaxial potential Eq. (43).

σ	$\tau_D\lambda_1^{\mathrm{num}}$ [Eq. (25)]	$\tau_D\lambda_1$ [Eq. (54)]	$\tau_D\lambda_1^{\mathrm{as}}$ [Eq. (57)]	τ_D/τ [Eq. (59)]
0	1.0	1.0	$-\infty$	1.0
1	0.653 14	0.652 47	0.0	0.654 46
2	0.403 84	0.402 86	0.215 96	0.406 45
3	0.235 70	0.235 03	0.194 61	0.238 20
4	0.129 84	0.129 53	0.124 00	0.131 47
5	0.067 70	0.067 60	0.068 00	0.068 55
6	0.033 61	0.033 58	0.034 26	0.033 98
7	0.016 00	0.016 00	0.016 33	0.016 15
8	0.007 36	0.007 36	0.007 50	0.007 41
9	0.003 29	0.003 29	0.003 34	0.003 31
10	0.001 44	0.001 44	0.001 46	0.001 45

which may in turn be expressed [23] in terms of the confluent hypergeometric (Kummer) functions $M(a,b,z)$ ([19], Sec. 13), viz.,

$$S_{2k+1}(0)=\frac{4k\sigma}{(4k+1)(4k+3)}\frac{M(k+1,2k+\frac{5}{2},\sigma)}{M(k,2k+\frac{1}{2},\sigma)}. \quad (53)$$

Thus we obtain from Eqs. (26) and (50)–(53)

$$\lambda_1\tau_D=\left[\frac{3\pi}{8M(1,\frac{5}{2},\sigma)}\sum_{n=0}^{\infty}\left(-\frac{\sigma^2}{4}\right)^n \times\frac{\Gamma(2n+1)M^2(n+1,2n+\frac{5}{2},\sigma)}{(n+1)\Gamma(2n+\frac{3}{2})\Gamma(2n+\frac{5}{2})}\right]^{-1}, \quad (54)$$

which is the solution in terms of known functions. Here we have also used the fact that [23]

$$1-2\sigma[1-S_3(0)]/5=1/M(1,\tfrac{5}{2},\sigma).$$

For $\sigma\ll 1$, one can evaluate from Eq. (54) the Taylor series expansion of λ_1, viz.,

$$\lambda_1\tau_D=1-\frac{2\sigma}{5}+\frac{4}{75}\sigma^2+O(\sigma^3). \quad (55)$$

On the other hand, on using the asymptotic expansion of Kummer's functions [19], viz.,

$$M(a,b,z)=\frac{\Gamma(b)e^z z^{a-b}}{\Gamma(a)\Gamma(b-a)\Gamma(1-a)}\times\left[\sum_{n=0}^{S-1}\frac{\Gamma(b-a+n)\Gamma(1-a+n)}{\Gamma(n+1)z^n}+O(z^{-S})\right],$$

one obtains for $\sigma\gg 1$

$$\lambda_1^{\mathrm{as}}\tau_D\sim\frac{2\sigma^{3/2}e^{-\sigma}}{\sqrt{\pi}}. \quad (56)$$

Equation (56) is in full agreement with the leading term of the previous asymptotic solution [21],

$$\lambda_1^{\mathrm{as}}\tau_D\sim\frac{2\sigma^{3/2}e^{-\sigma}}{\sqrt{\pi}}\left(1-\frac{1}{\sigma}\right). \quad (57)$$

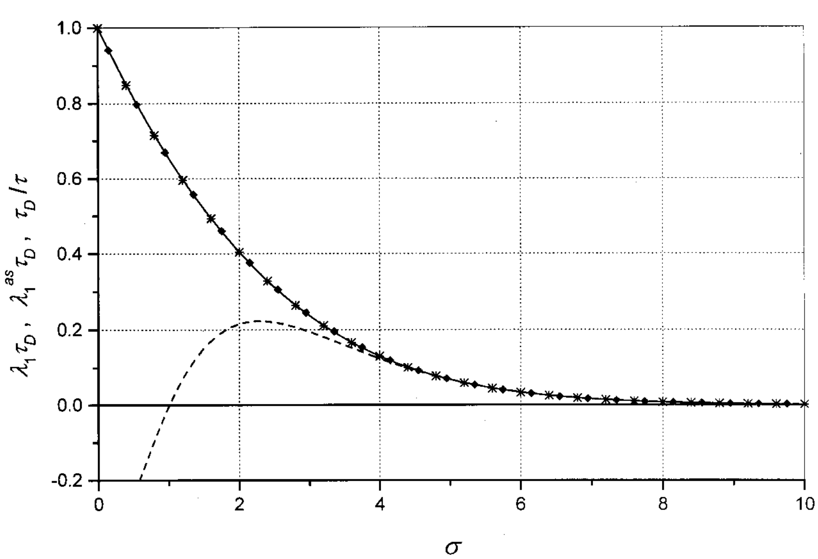

FIG. 2. λ_1 [Eq. (54), solid line, and Eq. (25), stars] for the $\cos^2\theta$ potential as a function of the barrier height σ compared with the asymptotic solution λ_1^{as} [Eq. (57)] (dashed line) and the solution rendered by the inverse of the correlation time τ^{-1} [Eq. (59)] (diamonds).

The lowest eigenvalue λ_1 from Eq. (54) is in very good agreement with the numerical solutions λ_1^{num} of the characteristic equation [Eq. (25)] for all σ (see Table II and Fig. 2.) In Fig. 2 and in Table II λ_1^{as} calculated from the asymptotic Eq. (57) is also presented. Just as for planar rotators, the behavior of λ_1 is similar to that of the relaxation time τ of the dipole correlation function, which may be presented as a series [23],

$$\frac{\tau}{\tau_D}=\frac{3}{2}\sum_{n=0}^{\infty}\frac{(-\sigma^2)^n(n+\frac{3}{4})\Gamma(n+\frac{3}{2})\Gamma(n+\frac{1}{2})}{(n+1)\Gamma^2(2n+\frac{5}{2})M(\frac{3}{2},\frac{5}{2},\sigma)}\times M(n+\tfrac{3}{2},2n+\tfrac{5}{2},\sigma)M(n+1,2n+\tfrac{5}{2},\sigma) \quad (58)$$

or in a quadrature [Eq. (40)] [14,24], viz.,

$$\frac{\tau}{\tau_D}=\frac{3}{\sigma M(\frac{3}{2},\frac{5}{2},\sigma)}\int_0^1\frac{\cosh[\sigma(1-z^2)]-1}{1-z^2}dz. \quad (59)$$

λ_1, λ_1^{as}, and τ^{-1} are in excellent agreement in the high barrier limit and, moreover, λ_1, λ_1^{num}, and τ^{-1} are very close to each other for all barrier heights. Thus, Eq. (54) may be used to calculate λ_1 for all values of σ. The reason for this is that the condition of applicability [Eq. (42)] of Eq. (54) may be considered as fulfilled with sufficient accuracy even for $\sigma=0$, where $\lambda_1\tau_D\equiv 1$, and $S_3''(0)/2S_3'(0)=-\frac{1}{6}$.

V. BROWNIAN PARTICLE IN A 2-4 DOUBLE WELL POTENTIAL

As another example let us consider the model of noninertial translational Brownian motion of a particle in a quartic potential:

$$V(x)=\frac{ax^2}{2}+\frac{bx^4}{4}, \quad (60)$$

where a and b $(b>0)$ are constants, $-\infty<x<\infty$. This model is very often used to describe noise-driven motion in a variety of bistable physical and chemical systems [25–27]. The relaxational dynamics of the model in the high friction limit, where the inertia of the particle may be neglected, has been extensively studied by solving the noninertial Fokker-Planck (Smoluchowski) equation underlying the problem (see, e.g., [28–32] and references cited therein). The model of Brownian particle in the potential (60) poses the problem of solving *divergent* differential-recurrence relations for statistical moments [13,32]. Here Risken's continued fraction method [11] and, in particular, Eq. (7), is no longer applicable as all the continued fractions involved diverge. However, as we shall demonstrate below, our approach succeeds in this case. We shall also show how the asymptotic solution of Larson and Kostin [28] may be recovered from the continued fraction solution [Eq. (15)] in the high barrier limit. In addition, these will be compared with the solutions of Perico *et al.* [29] and Kalmykov, Coffey, and Waldron [13] for the relaxation time of the positional correlation function.

The noninertial Langevin equation for the one-dimensional noninertial translational Brownian motion of a particle in the potential Eq. (60) is given by [13]

$$\zeta\dot{x}(t)+ax(t)+bx^3(t)=f(t). \quad (61)$$

In Eq. (57), $x(t)$ specifies the position of the particle at time t, $\zeta\dot{x}$ is the viscous drag experienced by it, and $f(t)$ is the white noise driving force. The underlying noninertial FPE for the probability distribution function W of the position x is

$$\zeta\frac{\partial}{\partial t}W=\frac{\partial}{\partial x}\left(W\frac{\partial}{\partial x}V\right)+kT\frac{\partial^2}{\partial x^2}W \quad (62)$$

[cf. Eq. (18)].

Equation (61) or (62) may be recast [13,29] as a hierarchy of equations for the normalized correlation functions $C_n(t)$ defined as

$$C_n(t)=\frac{\langle x(0)x^n(t)\rangle_0}{\langle x^2(0)\rangle_0^{(n+1)/2}}, \quad (63)$$

where $\langle\,\rangle_0$ designates equilibrium ensemble averages. Thus, the $C_n(t)$ satisfy

$$\tau_\varepsilon\frac{d}{dt}C_n(t)=n(n-1)C_{n-2}(t)-2nAC_n(t)-4nBC_{n+2}(t), \quad (64)$$

where

$$A=\frac{a\langle x^2\rangle_0}{2kT},\quad B=\frac{b\langle x^2\rangle_0^2}{4kT},\quad \tau_\varepsilon=\frac{\zeta\langle x^2\rangle_0}{kT}. \quad (65)$$

We recall that when $a<0$ the potential (60) has a barrier at $x=0$ where the potential has a maximum and the height relative to the minimum is equal to [29]

$$\sigma=\frac{A^2}{4B}. \quad (66)$$

In the context of the approach developed here, the smallest eigenvalue λ_1 is given by Eq. (26), where

$$q_{2m-1}=-2A(2m-1),\quad q_{2m-1}^{+}=-4B(2m-1),$$
$$q_{2m-1}^{-}=2m(2m-1), \quad (67)$$

and the continued fraction $S_n(0)$ is given by

$$S_n(0)=\frac{(n-1)}{2A+4BS_{n+2}(0)}. \quad (68)$$

However, now Eq. (26) is meaningful in the computational sense only for $a>0$, when the continued fractions $S_n(0)$ from Eq. (68) *converge*. For $a<0$, which is the case of our interest, the continued fractions $S_n(0)$ *diverge* and Eqs. (26) and (68) are purely formal solutions. This is a consequence of the divergence of the recurrence equation (64). Another consequence is that the direct matrix method [Eq. (25)] does not apply to the solution of Eq. (64) as well. Nevertheless, we shall demonstrate below that the approach suggested in Ref. [13] for the solution of divergent recurrence relations might still be used to render the solution for λ_1.

In order to proceed we recall [13] that for $a<0$ the continued fraction $S_n(0)$ from Eq. (68) can be expressed in terms of Whittaker's parabolic cylinder functions $D_\nu(x)$ [19], viz.,

$$S_n(0)=\frac{(n-1)}{2\sqrt{2B}}\frac{D_{-(n+1)/2}(-\sqrt{2\sigma})}{D_{-(n-1)/2}(-\sqrt{2\sigma})}. \tag{69}$$

Thus, on using Eq. (69), the relations [19]

$$xD_{-\nu}(x)-D_{-\nu+1}(x)=-\nu D_{-\nu-1}(x), \tag{70}$$

and [13]

$$2A+4BS_3(0)=\frac{2\sqrt{2B}e^{-\sigma/2}}{D_{-1}(-\sqrt{2\sigma})},$$

Eq. (26) yields

$$\lambda_1\tau_0=\left(\frac{e^{\sigma/2}}{D_{-1}(-\sqrt{2\sigma})}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\times\Gamma(n+1)D^2_{-n-1}(-\sqrt{2\sigma})\right)^{-1}, \tag{71}$$

where the characteristic relaxation time τ_0 is given by

$$\tau_0=\frac{2\sqrt{2B}}{\tau_\varepsilon}=\frac{\zeta}{\sqrt{2bkT}}. \tag{72}$$

On using the integral representation of the parabolic cylinder functions [19]

$$D_\nu(x)=\frac{e^{-x^2/4}}{\Gamma(-\nu)}\int_0^\infty e^{-u^2/2-xu}u^{-\nu-1}du \quad (\nu<0), \tag{73}$$

the series in Eq. (71) can be summed exactly to yield

$$\lambda_1\tau_0=\left(\frac{e^{\sigma}}{1+\mathrm{erf}(\sqrt{\sigma})}\times\int_0^\infty\int_0^\infty e^{-(s-\sqrt{\sigma})^2-(t-\sqrt{\sigma})^2}\frac{\mathrm{erf}(\sqrt{2st})}{\sqrt{st}}ds\,dt\right)^{-1}. \tag{74}$$

Here we have taken into account the relation [19]

$$D_{-1}(z)=e^{z^2/4}\sqrt{\pi/2}[1-\mathrm{erf}(z/\sqrt{2})]$$

and the following Taylor expansion of the error function erf(x) [19]:

$$\mathrm{erf}(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt=\frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n x^{2n+1}}{n!(2n+1)}.$$

On noting that erf(x)$\sim$1 at $x\to\infty$, one can obtain from Eq. (74) a simple asymptotic expression in the high barrier limit $(\sigma\to\infty)$, viz.,

$$\lambda_1\tau_0\sim\frac{2e^{-\sigma}\sqrt{\sigma}}{\pi}, \tag{75}$$

which is in agreement with the asymptotic solution obtained by Larson and Kostin [28] (in our notation):

TABLE III. Numerical values for the 2-4 potential Eq. (60).

σ	$\lambda_1\tau_0$ [Eq. (74)]	$\lambda_1^{\mathrm{as}}\tau_0$ [Eq. (76)]	τ_0/τ [Eq. (77)]
0	0.937 206	∞	0.980 499
1	0.256 730	0.146 375	0.274 517
2	0.111 443	0.098 999	0.118 609
3	0.048 852	0.048 036	0.051 471
4	0.020 951	0.021 134	0.021 850
5	0.087 591	0.008 872	0.009 059
6	0.003 583	0.003 624	0.003 682
7	0.001 441	0.001 454	0.001 474
8	0.000 571	0.000 576	0.000 582
9	0.000 225	0.000 226	0.000 228
10	0.000 088	0.000 088	0.000 089

$$\lambda_1^{\mathrm{as}}\tau_0\sim\frac{2e^{-\sigma}\sqrt{\sigma}}{\pi}\left(1-\frac{3}{8\sigma}\right) \quad (\sigma\to\infty). \tag{76}$$

Just as for the problems considered in Secs. III and IV, the lowest eigenvalue λ_1 for the potential (60) completely determines the behavior of the correlation time τ of the positional correlation function $C_1(t)$, which may be presented as [13]

$$\tau=\frac{\tau_0 2^{3/4}e^{3\sigma/2}}{D_{-3/2}(-\sqrt{2\sigma})}\times\int_0^\infty\int_0^\infty e^{-(s-\sqrt{\sigma})^2-(t-\sqrt{\sigma})^2}\frac{\mathrm{erf}(\sqrt{2st})}{\sqrt{s}}ds\,dt. \tag{77}$$

As one can see in Table III and in Fig. 3, the lowest eigenvalue λ_1 calculated from Eq. (74) agrees closely with τ^{-1} from Eq. (77) for all σ. In Fig. 3 and Table III λ_1^{as} calculated from the asymptotic Eq. (76) is also presented. The calculation demonstrates that λ_1, λ_1^{as}, and τ^{-1} are in agreement in the high barrier limit. Moreover, λ_1 and τ^{-1} are very close to each other for all barrier heights.

VI. CONCLUSIONS

We have derived a simple approximate analytic formula Eq. (15) for the smallest eigenvalue λ_1 of the Fokker-Planck equation for the Brownian motion of a particle in a potential in the context of the continued fraction approach. This equation is applicable to the calculation of λ_1 if the solution of the FPE can be reduced to the solution of a scalar three-term recurrence equation for the moments (the expectation values of the dynamic quantities of interest), and it is also very useful for analytical purposes. As was shown on considering particular problems, λ_1 from Eq. (15) may further be represented in terms of known mathematical functions. An advantage of the present analysis is that it can be applied to models where the relaxation behavior is governed by divergent three-term recurrence relations. As was also demonstrated, Eq. (15) has a wide area of applicability, namely, it allows one to evaluate λ_1 with good accuracy in high, intermediate, and small barriers. The reason for this is that both the exact Eq. (7) and the approximate Eq. (15) predict the correct behavior of λ_1 both in the high and in the low barrier limits.

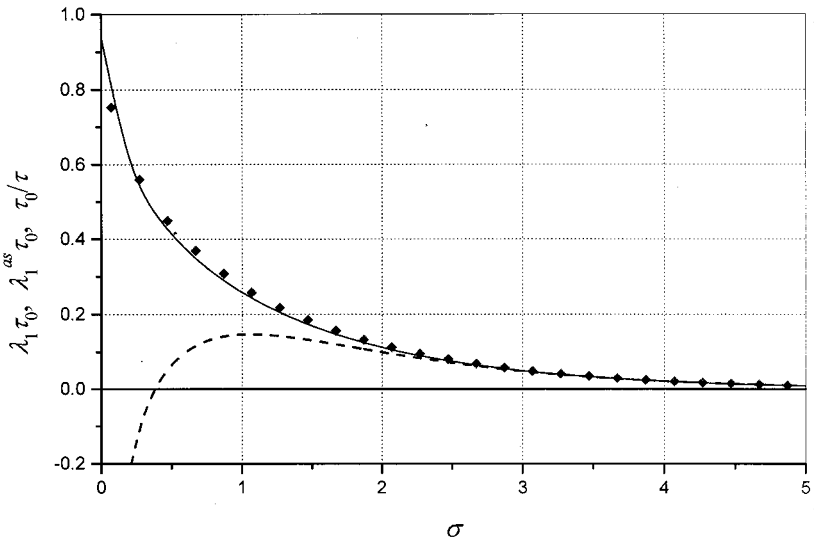

FIG. 3. λ_1 (solid line) for the 2-4 potential Eq. (60) as a function of the barrier height parameter σ compared with the asymptotic solution λ_1^{as} of Larson and Kostin [Eq. (76)] (dashed line) and the solution rendered by the inverse of the correlation time τ^{-1} [Eq. (77)] (diamonds).

This has the merit that one now has an analytic formula for the smallest eigenvalue λ_1 for all ranges of barrier heights. Moreover, as we shall demonstrate in the forthcoming paper [33], a similar (matrix continued fraction) approach can also be used for the calculation of λ_1 for systems whose dynamics is governed by multiterm recurrence equations, providing good estimates for λ_1 for all barrier heights and covering a wide range of the friction parameter of the FPE (from overdamped up to low damping).

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[1] G. Barone and A. Paterno, *Physics and Applications of the Josephson Effect* (Wiley, New York, 1982).
[2] H. Watanabe and A. Morita, Adv. Chem. Phys. **56**, 255 (1993).
[3] J. L. Déjardin, *Dynamic Kerr Effect* (World Scientific, Singapore, 1995).
[4] W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach, New York, 1980).
[5] P. L. Nordio, G. Rigatti, and U. Segre, Mol. Phys. **25**, 129 (1973).
[6] W. Dieterich, P. Fulde, and I. Peschel, Adv. Phys. **29**, 527 (1980).
[7] W. F. Brown, Jr., IEEE Trans. Magn. **15**, 1196 (1979).
[8] L. J. Geoghegan, W. T. Coffey, and B. Mulligan, Adv. Chem. Phys. **100**, 475 (1997).
[9] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[10] R. L. Stratonovich, *Topics in the Theory of Random Noise* (Gordon and Breach, New York, 1963), Vol. I; (1967), Vol. II.
[11] H. Risken, *The Fokker-Planck Equation*, 2nd ed. (Springer, Berlin, 1989).
[12] W. T. Coffey, Yu. P. Kalmykov, and J. T. Waldron, *The Langevin Equation* (World Scientific, Singapore, 1996).
[13] Yu. P. Kalmykov, W. T. Coffey, and J. T. Waldron, J. Chem. Phys. **105**, 2112 (1996).
[14] W. T. Coffey and D. S. F. Crothers, Phys. Rev. E **54**, 4768 (1996).
[15] W. T. Coffey, J. Chem. Phys. **111**, 8350 (1999).
[16] W. T. Coffey, Yu. P. Kalmykov, and E. S. Massawe, Adv. Chem. Phys. **85**, 667 (1993).
[17] J. I. Lauritzen and R. Zwanzig, Jr., Adv. Mol. Relax. Interact. Processes **5**, 339 (1973).
[18] W. T. Coffey, Yu. P. Kalmykov, E. S. Massawe, and J. T. Waldron, J. Chem. Phys. **99**, 4011 (1993).
[19] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun (Dover, New York, 1964).
[20] A. P. Prudnikov, Yu. A. Brychkov, and O. I. Marichev, *Integrals and Series. Special Functions* (Gordon and Breach, New York, 1990), Vol. 2.
[21] W. T. Coffey, D. S. F. Crothers, and J. T. Waldron, Physica A **203**, 600 (1994).
[22] A. J. Martin, G. Meier, and A. Saupe, Faraday Symp. Chem. Soc. **5**, 119 (1971).
[23] W. T. Coffey, D. S. F. Crothers, Yu. P. Kalmykov, E. S. Massawe, and J. T. Waldron, Phys. Rev. E **49**, 1869 (1994).
[24] D. A. Garanin, Phys. Rev. E **54**, 3250 (1996).
[25] R. S. Larson and M. D. Kostin, J. Chem. Phys. **72**, 1392 (1980).
[26] W. T. Coffey, M. W. Evans, and P. Grigolini, *Molecular Diffusion and Spectra* (Wiley, New York, 1984).
[27] C. Blomberg, Physica A **86**, 67 (1977).
[28] R. S. Larson and M. D. Kostin, J. Chem. Phys. **69**, 4821 (1978).
[29] A. Perico, R. Pratolongo, K. F. Freed, R. W. Pastor, and A. Szabo, J. Chem. Phys. **98**, 564 (1993).
[30] A. Schenzel and H. Brand, Phys. Rev. A **20**, 1628 (1979).
[31] R. Graham and A. Schenzel, Phys. Rev. A **25**, 1731 (1982).
[32] I. I. Fedchenia, J. Phys. A **25**, 6733 (1992).
[33] Yu. P. Kalmykov, Phys. Rev. E (to be published).