Exact solution for the correlation times of dielectric relaxation of a single axis rotator with two equivalent sites

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It is shown how exact formulas for the longitudinal and transverse dielectric correlation times and complex polarizability tensor, of a single axis rotator with two equivalent sites may be found. This is accomplished by writing the Laplace transforms of the dipole autocorrelation functions as three term recurrence relations and solving them in terms of continued fractions. The solution of these recurrence relations, in the zero frequency limit, yields the correlation times in terms of modified Bessel functions of the first kind. The previous result of Lauritzen and Zwanzig for the longitudinal relaxation time, based on an asymptotic expansion of the Sturm–Liouville equation, is regained in the limit of high potential barriers.

I. INTRODUCTION

Debye[1] in 1929 introduced a model of dielectric relaxation of a crystalline solid which assumes that a dipole may take up only two oppositely directed orientations on either side of a potential barrier to rotation. He then demonstrated that such a model yields relaxation behavior similar in form to that predicted by his theory of rotational Brownian motion, however, the relaxation time now depends exponentially on the height of the potential barrier. This approach was subsequently generalized and extended by a number of authors[2–5] to explain the dielectric relaxation behavior of polar crystals.

The simplest site model[6] has two equivalent sites, leading to a single relaxation time proportional to $\exp(U/kT)$, where U is the potential barrier between the sites, k is the Boltzmann constant, and T is the absolute temperature. According to Lauritzen and Zwanzig,[6] the site model will provide a close approximation to the relaxation behavior if the energy barrier to rotation is large and if the orientational sites are closely defined by the crystalline field. The assumption of the site model that only two orientations are possible for the dipole will fail[6] when the ratio of the barrier energy to the temperature falls below a certain value. Thus in order to comprehensively analyze the relaxation behavior, Lauritzen and Zwanzig abandoned the discrete orientation model and assumed a continuous distribution of orientations the evolution of which is governed by the Smoluchowski equation. In order to simplify their calculations they constrained the dipole to rotate about a single axis under the influence of a potential $U\sin^2\phi$ determined by the crystalline field. ϕ is the angle describing the orientation of the dipole about its axis of rotation. This potential determines two potential minima on the sites at $\phi=0$ and $\phi=\pi$ as well as two energy barriers located at $\phi=\pi/2$ and $\phi=3\pi/2$.

A representative dipole of the assembly rotates in two dimensions. Thus having written down the Smoluchowski equation for the density of orientations in the configuration space ϕ, Lauritzen and Zwanzig were able to calculate numerically the relaxation behavior for (a) an electric field applied perpendicular to the axis of rotation and parallel to the axis defined by the two minima of the potential function; (b) a field applied perpendicular to the axis of rotation and parallel to the axis defined by the two maxima of the potential function.

Process (a) is the longitudinal relaxation and leads in practice to a single relaxation time proportional to $\exp(U/kT)$. In such a process the applied field leads to an increased occupation of one site with relaxation of the orientational polarization requiring that the dipoles abandon one site for another by crossing over the potential barrier. This process corresponds to that calculated using the two-equivalent site model.[1–5] There are an infinite number of relaxation modes in the longitudinal relaxation.[6] However, almost all the contribution to the polarization arises from the activation process corresponding to the slow leakage of the dipoles across the potential barrier so that the decay is relatively slow.

Process (b) is the transverse relaxation which unlike (a) does not arise from an activation process. Here the applied field leads to a bias in the occupation of the sites. The orientational polarization can now relax without the dipoles crossing the potential barrier. Thus the relaxation time is not governed by an activation process. It is thus relatively insensitive to the temperature and the corresponding decay takes place relatively quickly.

The analysis of Lauritzen and Zwanzig[6] proceeded

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from the Smoluchowski equation by using the method of separation of the variables in order to convert the solution of that equation to a Sturm–Liouville problem. They then integrated the Sturm–Liouville equation by the fourth-order Runge–Kutta method.[6] Hence they found the eigenvalues and eigenfunctions by trial and error. Thus they were able to plot the transverse and longitudinal relaxation times and corresponding complex polarizabilities as a function of the barrier height. Hence they were able to conclude that the longitudinal relaxation is dominated by the lowest eigenvalue which characterizes the barrier crossing process. Thus the relaxation effectively occurs by means of a single exponential decay. In the transverse process, on the other hand, they found that for very large values of the barrier height parameter two modes contribute to the relaxation. Nevertheless, the relaxation times of these modes are approximately equal and the relaxation is effectively a *single* exponential decay. For intermediate barrier heights they found that the relaxation process may be closely represented by the sum of two time decaying exponentials with different time constants, while for $U=0$ the relaxation occurs through a single exponential decay. In addition to this numerical treatment of the problem they used a method based on the smallness of the lowest eigenvalue of the Sturm–Liouville equation to obtain an asymptotic expansion for the greatest longitudinal relaxation time in the limit of high potential barriers. In particular they showed that the greatest longitudinal relaxation time is

$$\tau_{\|}(\sigma)=\tau\frac{\pi}{8\sigma}\exp(2\sigma), \tag{1}$$

where

$$2\sigma=\frac{U}{kT};\quad \tau=\zeta/kT. \tag{2}$$

2σ is the barrier height parameter, τ is the Debye relaxation time for a two dimensional rotator, ζ is the viscous drag coefficient of the rotator. In passing, one should note that this relaxation time is also of major interest in the theory of magnetic relaxation of single domain ferromagnetic particles.[7]

The analytic formula of Ref. 6 is only valid for large barrier heights which limits its range of applicability. In addition, the complex polarizabilities may only be obtained numerically. It is the purpose of this paper to show how exact analytic formulas (valid for all barrier heights) for the longitudinal and transverse correlation times may be obtained from the zero frequency limit of the Laplace transforms of the corresponding decay functions. In addition, we shall show how analytic formulas for the corresponding complex polarizabilities may be written down and how Eq. (1) may be recovered from the exact solution in the high σ approximation. It will also be shown how Eq. (1) may be obtained from the transition state theory of Kramers.[8]

The customary method of analysis proceeds by regarding the correlation time as the reciprocal of the smallest eigenvalue of the Smoluchowski equation when that equation is converted to a Sturm–Liouville problem.[7] We shall not use this method here. Rather we shall expand the solution of the Smoluchowski equation as a Fourier series in the angle ϕ. This automatically leads to a set of coupled differential-difference equations for the relaxation behavior of the system. These may also be written down by averaging the Langevin equation as described in Ref. 9. The differential-difference equations are then arranged in the matrix form

$$\dot{\mathbf{X}}=\mathbf{A}\mathbf{X}, \tag{3}$$

which is in a form suitable for numerical calculations. Alternatively, on noting that the Laplace transform of the hierarchy of equations is a three term recurrence relation, one may then solve that hierarchy for the Laplace transform of the decay function. This solution is in terms of products of infinite continued fractions in the frequency s and barrier height parameter σ as shown in the Appendix. On proceeding to the limit of zero frequency, one may write down expressions for the correlation times in terms of products of infinite continued fractions in the barrier height parameter σ only. This expression, on simplification, may be expressed in terms of a series of modified Bessel functions of integer and half-integer order which allows one to write down an exact expression for the longitudinal correlation time. A similar procedure can be used in the perpendicular case. The validity of these expressions may be checked using a numerical solution of Eq. (3) which in the zero frequency limit merely amounts to the calculation of $\mathbf{A}^{-1}$. The longitudinal and transverse complex polarizabilities $\alpha_{\|}(\omega)$ and $\alpha_{\perp}(\omega)$ may be written down from the Laplace transform of the appropriate decay functions by means of linear response theory.

We illustrate our method of obtaining exact solutions for the correlation times by referring to the motion of a two dimensional rotator in a $U\sin^2\phi$ potential. The methods we describe should also be applicable whenever the Laplace transform of the differential-difference equations arising from the Smoluchowski equation may be written as a three term recurrence relation. Such recurrence relations may always be solved in terms of products of infinite continued fractions. The zero frequency limit of these may usually be written in terms of confluent hypergeometric functions (Kummer's functions).[10] These have well defined asymptotic expansions which allow the high barrier limits of the correlation times to be obtained analytically. As an example we refer to the relaxation of single domain ferromagnetic particles which was originally considered by Brown[7] using the Kramers theory.[8] If the Laplace transform of the differential-difference equations is not expressible as a three term recurrence relation then the Laplace transform of the decay function may always be obtained by writing the set of differential-difference equations as

$$\dot{\mathbf{X}}=\mathbf{A}\mathbf{X}$$

then calculating the Laplace transform

$$\tilde{\mathbf{X}}(s)=(s\mathbf{I}-\mathbf{A})^{-1}\mathbf{X}(0),$$

and proceeding as in Sec. II below. This procedure has been described in detail for a variety of potentials by

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Risken.[11] In particular in this context we should mention the Lanczos algorithm. The Laplace transform of a correlation function may be readily expressed by this algorithm in terms of a continued fraction as has been demonstrated by Wassam and Torres-Vega[12] using the calculation of the spectral density of the incoherent scattering function of a Brownian particle in a spatially homogeneous isotropic environment as an example. The particular advantage of the Lanczos algorithm in the present context has been emphasized by Moro and Freed.[13] They point out that typical Fokker–Planck equations arising from stochastic modeling of molecular dynamics are representable by very sparse complex symmetric matrices. Thus the calculation of the associated correlation function may be very efficiently implemented by the Lanczos algorithm. This is particularly important in problems which involve diffusion in phase space.[14]

II. REPRESENTATION OF THE LONGITUDINAL RELAXATION PROBLEM AS A SET OF DIFFERENTIAL-DIFFERENCE EQUATIONS

The Smoluchowski equation for a particle free to rotate about an axis normal to itself under the influence of a potential

$$V(\phi)=U\sin^2\phi-\mu E\cos\phi \tag{4}$$

is[6]

$$\frac{\partial W}{\partial t}=\frac{\partial}{\partial\phi}\left(\frac{W}{\zeta}\frac{\partial V}{\partial\phi}\right)+\frac{1}{\tau}\frac{\partial^2 W}{\partial\phi^2}, \tag{5}$$

where $W(\phi,t)$ is the probability density of orientations of a dipole on the unit circle. μ is the dipole moment of the rotator. In order to study the longitudinal relaxation behavior we suppose that the constant field **E** is switched off at $t=0$ that is we seek the after-effect solution. Since the solution of Eq. (5) must be periodic in ϕ we may assume that it has the form of the Fourier series

$$W(\phi,t)=\sum_{p=-\infty}^{p=\infty}a_p(t)e^{ip\phi}. \tag{6}$$

On substituting Eq. (6) into Eq. (5) we have, using the orthogonality properties of the circular functions

$$\dot{a}_p(t)+\frac{p^2}{\tau}a_p(t)=\frac{\sigma p}{\tau}\left[a_{p-2}(t)-a_{p+2}(t)\right], \tag{7}$$

where we note that

$$\begin{aligned}\langle\cos p\phi\rangle&=\frac{\int_0^{2\pi}\Sigma_{p=-\infty}^{p=\infty}a_p(t)e^{ip\phi}\cos p\phi\,d\phi}{\int_0^{2\pi}\Sigma_{p=-\infty}^{p=\infty}a_p(t)e^{ip\phi}\,d\phi}\\&=\frac{a_{-p}+a_p}{2a_0}\\&=f_p(t),\ \text{say.}\end{aligned} \tag{8}$$

The differential-difference equation for $a_{-p}(t)$ is from Eq. (7)

$$\dot{a}_{-p}(t)+\frac{p^2}{\tau}a_{-p}(t)=\frac{\sigma p}{\tau}\left[a_{-(p-2)}(t)-a_{-(p+2)}(t)\right]. \tag{9}$$

Whence we have with Eq. (8)

$$\dot{f}_p(t)+\frac{p^2}{\tau}f_p(t)=\frac{\sigma p}{\tau}\left[f_{p-2}(t)-f_{p+2}(t)\right]. \tag{10}$$

By inspection of Eq. (8) it is obvious that

$$f_{-p}(t)=f_p(t) \tag{11}$$

so that the solution of Eq. (10) need only be determined for positive p. Eq. (10) may further be decomposed into a set of equations for the odd and even $f_i(t)$ which are totally decoupled from each other. Here only the odd $f_i(t)=f_{2p+1}(t)$ are of interest since we seek the relaxation behavior of $f_1(t)$. The odd $f_i(t)$ satisfy

$$\begin{aligned}&\dot{f}_{2p+1}(t)+\frac{(2p+1)^2}{\tau}f_{2p+1}(t)\\&=\frac{\sigma(2p+1)}{\tau}\left[f_{2p-1}(t)-f_{2p+3}(t)\right].\end{aligned} \tag{12}$$

The set of Eqs. (12) may be solved numerically by forming the vector

$$\mathbf{X}=\begin{pmatrix}f_1(t)\\f_3(t)\\\vdots\\f_{2p+1}(t)\\\vdots\end{pmatrix} \tag{13}$$

and writing them in the form

$$\dot{\mathbf{X}}=\mathbf{A}\mathbf{X}, \tag{14}$$

where

$$\mathbf{A}=-\frac{1}{\tau}\begin{pmatrix}(1-\sigma)&\sigma&0&0&0&\cdots\\-3\sigma&9&3\sigma&0&0&\cdots\\0&-5\sigma&25&5\sigma&0&\cdots\\\cdots&\cdots&\cdots&\cdots&\cdots&\cdots\end{pmatrix}. \tag{15}$$

In Eq. (13) p is taken large enough (equal to P, say) to ensure convergence of the set of Eqs. (14). For σ less than 10 a 25×25 matrix is sufficient.

The lowest eigenvalue which corresponds to the reciprocal of the longest relaxation time is then the smallest root of the characteristic equation

$$\det(\lambda\mathbf{I}-\mathbf{A})=0. \tag{16}$$

The relaxation modes of $f_1(t)$ may be found from Eq. (14) by assuming that **A** has a linearly independent set of P eigenvectors $(\mathbf{R}_1,\ldots,\mathbf{R}_P)$ so that[15]

$$\mathbf{R}^{-1}\mathbf{A}\mathbf{R}=\mathbf{B}, \tag{17}$$

where **R** is the matrix consisting of the P eigenvectors $\mathbf{R}_i$ of **A** and

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TABLE I. Amplitudes a_{2p+1} of the first three modes of the decay of the longitudinal polarization as a function of the barrier height parameter σ and corresponding eigenvalues λ_{2p+1}, $p=0$, 1, 2. in the form $\lambda_{2p+1}\tau$. A 25×25 matrix **A** is always sufficiently large to yield convergence for σ values up to 10.

σ	λ_1	λ_3	λ_5	a_1	a_3	a_5
0	1	9	25	0.5	0	0
1	0.323 7	9.61	25.52	0.719	0.004 54	0.000 021 9
2	0.081 98	11.62	27.09	0.842	0.006 65	0.000 175
3	0.017 16	15.19	29.71	0.9	0.004 48	0.000 376
4	0.003 177	20.31	33.36	0.929	0.002 39	0.000 477
5	0.000 546 3	26.83	37.97	0.945	0.001 25	0.000 471
6	0.000 089 66	34.52	43.45	0.955	0.000 702	0.000 41
7	0.000 014 26	43.05	49.68	0.962	0.000 439	0.000 336
8	0.000 002 217	52	56.51	0.967	0.000 304	0.000 27
9	$3.389E-07$	60.99	63.8	0.971	0.000 228	0.000 217
10	$5.112E-08$	69.8	71.41	0.974	0.000 179	0.000 176

$$\mathbf{B}=\begin{pmatrix}\lambda_1 & 0 & 0 & \cdots\\ 0 & \lambda_2 & 0 & \cdots\\ 0 & 0 & \lambda_3 & \cdots\\ \cdots & \cdots & \cdots & \cdots\end{pmatrix}. \tag{18}$$

Whence

$$\mathbf{X}(t)=\mathbf{R}\exp(\mathbf{B}t)\mathbf{R}^{-1}\mathbf{X}_0, \tag{19}$$

where

$$\exp(\mathbf{B}t)=\begin{pmatrix}e^{\lambda_1 t} & 0 & 0 & \cdots\\ 0 & e^{\lambda_2 t} & 0 & \cdots\\ 0 & 0 & e^{\lambda_3 t} & \cdots\\ \cdots & \cdots & \cdots & \cdots\end{pmatrix} \tag{20}$$

and $\mathbf{X}_0$ is the matrix of the initial values of the $f_{2p+1}(t)$. The solution of Eq. (14) may then be exhibited in the form[15]

$$\mathbf{X}(t)=b_1e^{\lambda_1 t}\mathbf{R}_1+b_2e^{\lambda_2 t}\mathbf{R}_2+\cdots+b_pe^{\lambda_p t}\mathbf{R}_p+\cdots, \tag{21}$$

where the constants b_p are to be determined from the initial conditions. The initial value vector $\mathbf{X}_0$ is determined as follows. At time $t=0$ the steady field $\mathbf{E}(t)$ is switched off. Thus

$$f_{2p+1}(0)=\langle\cos(2p+1)\phi\rangle=\frac{\int_0^{2\pi}\cos(2p+1)\phi e^{(\sigma\cos 2\phi+\xi\cos\phi)}\,d\phi}{\int_0^{2\pi}e^{(\sigma\cos 2\phi+\xi\cos\phi)}\,d\phi}, \tag{22}$$

where

$$\xi=\mu E/kT,$$

which in the linear approximation is

$$f_{2p+1}(0)=\frac{\int_0^{2\pi}\cos(2p+1)\phi e^{\sigma\cos 2\phi}[1+\xi\cos\phi]d\phi}{\int_0^{2\pi}e^{\sigma\cos 2\phi}[1+\xi\cos\phi]d\phi}. \tag{23}$$

We also have[16]

$$e^{\sigma\cos 2\phi}=\sum_{m=-\infty}^{m=\infty}I_m(\sigma)e^{i2m\phi}, \tag{24}$$

where $I_m(\sigma)$ is the modified Bessel function of the first kind of order m. Whence using the orthogonality property of the circular functions

$$\frac{1}{2\pi}\int_0^{2\pi}e^{i(p-q)\phi}\,d\phi=\delta_{pq} \tag{25}$$

and noting that[16]

$$I_{-m}(\sigma)=I_m(\sigma), \tag{26}$$

we have

$$\langle\cos(2p+1)\phi\rangle=f_{2p+1}(0)=\frac{\xi}{2}\frac{[I_{p+1}(\sigma)+I_p(\sigma)]}{I_0(\sigma)}, \tag{27}$$

so yielding the initial value vector $\mathbf{X}_0$. The set of Eqs. (14) may now be solved to any desired degree of accuracy to yield the decay of the longitudinal component of the dipole moment in the form

$$\mu f_1(t)=\mu\langle\cos\phi\rangle=\frac{\mu^2E}{kT}\sum_{k=0}^{\infty}a_{2k+1}e^{-\lambda_{2k+1}t}. \tag{28}$$

The first three eigenvalues and amplitudes a_{2k+1} are given in Table I as a function of σ, whence the lowest mode contributes almost all the decay. The quantity of most interest to us is the area under the curve of the longitudinal autocorrelation function. The longitudinal autocorrelation function of the dipole in the linear approximation in ξ is

$$\frac{f_1(t)}{f_1(0)}=C_1(t) \tag{29}$$

so that the longitudinal correlation time is from Eq. (28)

$$T_{\parallel}=\int_0^{\infty}C_1(t)dt=\frac{\Sigma_k a_{2k+1}\lambda_{2k+1}^{-1}}{\Sigma_k a_{2k+1}}, \tag{30}$$

so that by inspection of the Table I, $T_{\parallel}$ is effectively the reciprocal of the lowest eigenvalue. Another quantity which we shall require is the effective eigenvalue or weighted decay rate defined as[17,18]

$$\lambda_{\mathrm{ef}}^{\parallel}=-\dot{C}_1(0)=\frac{\Sigma_k a_{2k+1}\lambda_{2k+1}}{\Sigma_k a_{2k+1}}, \tag{31}$$

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which may also be evaluated from Table I. λ_{ef} is the reciprocal time constant associated with the initial slope of the correlation function. It contains contributions from all the eigenvalues as does the correlation time T. The behavior of T and λ_{ef}^{-1} is sometimes similar. In fact,[18] if a single eigenvalue dominates the decay of the correlation function, $T=\lambda_{ef}^{-1}$. However, if different time scales are involved T and λ_{ef}^{-1} can be quite different and in this case λ_{ef} gives precise information on the initial decay of the correlation function.

III. MATRIX FORMULA FOR THE CORRELATION TIME

The definition of the correlation time given above [Eq. (30)] suggests a simpler way of finding $T_\parallel$ than solving the characteristic equation

$$\det(s\mathbf{I}-\mathbf{A})=0. \tag{32}$$

First we note that[19]

$$T_\parallel=\lim_{s\to 0}\int_0^\infty C_1(t)e^{-st}\,dt=\lim_{s\to 0}\tilde{C}_1(s)=\tilde{C}_1(0), \tag{33}$$

where $\tilde{C}_1(s)$ is the Laplace transform of $C_1(t)$ and $\tilde{C}_1(0)$ is the value of that quantity at zero frequency. The Laplace transform of Eq. (3) is

$$s\tilde{\mathbf{X}}(s)-\mathbf{X}(0)=\mathbf{A}\tilde{\mathbf{X}}(s), \tag{34}$$

which, noting the final value theorem for Laplace transforms, namely,[19]

$$\lim_{s\to 0} s\tilde{f}(s)=\lim_{t\to\infty} f(t), \tag{35}$$

becomes

$$\mathbf{X}(\infty)-\mathbf{X}(0)=\mathbf{A}\tilde{\mathbf{X}}(0). \tag{36}$$

Furthermore,

$$\mathbf{X}(\infty)=0 \tag{37}$$

because the field ξ is switched off at $t=0$ so that all the $f_{2p+1}(\infty)$ vanish. Thus Eq. (36) becomes

$$-\mathbf{X}(0)=\mathbf{A}\tilde{\mathbf{X}}(0) \tag{38}$$

with solution

$$\tilde{\mathbf{X}}(0)=-\mathbf{A}^{-1}\mathbf{X}(0). \tag{39}$$

Equation (38) may be expanded in the form

$$\begin{pmatrix} f_1(0) \\ f_3(0) \\ \vdots \\ f_{2p+1}(0) \\ \vdots \end{pmatrix}=-\frac{1}{\tau}\begin{pmatrix} (1-\sigma) & \sigma & 0 & 0 & 0 & \cdots \\ -3\sigma & 9 & 3\sigma & 0 & 0 & \cdots \\ 0 & -5\sigma & 25 & 5\sigma & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}\times\begin{pmatrix} \tilde{f}_1(0) \\ \tilde{f}_3(0) \\ \vdots \\ \tilde{f}_{2p+1}(0) \\ \vdots \end{pmatrix}. \tag{40}$$

The function

$$\frac{\tilde{f}_1(0)}{f_1(0)}=T_\parallel \tag{41}$$

may now be extracted from the set above by simply calculating $\mathbf{A}^{-1}$ which is a function of σ only. This is much simpler than finding the lowest eigenvalue from Eq. (32), which always requires to solve a high order polynomial equation, and has the great advantage of yielding $T_\parallel$ directly as a function of σ. It should be noted that the method is not confined to the set of differential-difference equations for the f_{2p+1}, but may be applied to the after-effect solution whenever the set of equations for the expansion coefficients in the corresponding Fokker–Planck equation may be written in the matrix form [Eq. (3)]. It also allows us to calculate all the functions $\tilde{f}_{2p+1}(0)$ and thus the correlation times of the other $f_{2p+1}(t)$. We will now demonstrate how an exact analytical formula for $T_\parallel$ may be obtained.

IV. ANALYTIC FORMULAS FOR THE LONGITUDINAL POLARIZABILITY AND CORRELATION TIME

Consider the Laplace transform of the recurrence relation for $\tilde{f}_1(s)$ which using

$$\tau\dot{f}_1(t)+f_1(t)=\sigma[f_1(t)-f_3(t)] \tag{42}$$

is

$$\tilde{f}_1(s)=\frac{f_1(0)\tau-\sigma\tilde{f}_3(s)}{s\tau+(1-\sigma)}. \tag{43}$$

This only holds for $p=1$. In general we will have for $p>1$

$$s\tilde{f}_p(s)-f_p(0)+\frac{p^2}{\tau}\tilde{f}_p(s)=\frac{\sigma p}{\tau}[\tilde{f}_{p-2}(s)-\tilde{f}_{p+2}(s)], \tag{44}$$

which on writing

$$\tilde{R}_p(s)=\frac{\tilde{f}_p(s)}{\tilde{f}_{p-2}(s)} \tag{45}$$

may be rearranged as the inhomogeneous recurrence relation

$$\tilde{R}_p(s)\left[s+\frac{p^2}{\tau}+\frac{\sigma p}{\tau}\tilde{R}_{p+2}(s)\right]=\frac{f_p(0)}{\tilde{f}_{p-2}(s)}+\frac{\sigma p}{\tau}. \tag{46}$$

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The solution of Eqs. (43) and (46) will allow us to determine $\tilde{f}_1(s)$. We note that the homogeneous equation (46) [i.e., with $f_p(0)=0$] may be readily solved in terms of the continued fraction

$$\tilde{S}_p(s)=\frac{(\sigma p/\tau)}{s+(p^2/\tau)+(\sigma p/\tau)\tilde{S}_{p+2}(s)}, \quad p=3,5,\cdots \tag{47}$$

so that

$$\tilde{S}_3(s)=\cfrac{3\sigma}{s\tau+9+3\sigma\cfrac{5\sigma}{s\tau+25+5\sigma\cfrac{7\sigma}{s\tau+49+7\sigma\tilde{S}_9(s)}}}. \tag{48}$$

As shown in the Appendix we can then solve the inhomogeneous equation (46) in terms of the $\tilde{S}_p(s)$ by successively eliminating the other variables to get

$$\tilde{f}_1(s)=\frac{\tau}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}\left[f_1(0)-f_3(0)\frac{\tilde{S}_3(s)}{3}+f_5(0)\frac{\tilde{S}_3(s)\tilde{S}_5(s)}{5}-f_7(0)\frac{\tilde{S}_3(s)\tilde{S}_5(s)\tilde{S}_7(s)}{7}+\cdots\right] \tag{49}$$

or

$$\tilde{f}_1(s)=\frac{\tau}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}\left[f_1(0)+\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}f_{2p+1}(0)\prod_{k=1}^{p}\tilde{S}_{2k+1}(s)\right], \tag{50}$$

which on inserting the initial conditions explicitly becomes

$$\tilde{f}_1(s)=\frac{\tau(\xi/2)}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}\left[\frac{I_1(\sigma)+I_0(\sigma)}{I_0(\sigma)}+\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}\left\{\frac{I_{p+1}(\sigma)+I_p(\sigma)}{I_0(\sigma)}\right\}\prod_{k=1}^{p}\tilde{S}_{2k+1}(s)\right]. \tag{51}$$

This exact formula allows one to calculate the frequency dependence of the longitudinal component of the polarizability since[20]

$$\frac{\alpha_\parallel(\omega)}{\alpha_\parallel'(0)}=1-i\omega\int_0^\infty e^{-i\omega t}C_1(t)\,dt=1-i\omega\frac{\tilde{f}_1(\omega)}{f_1(0)}.$$

Thus on recalling that [cf. Eq. (27)]

$$\alpha_\parallel'(0)=\frac{\mu^2}{kT}\frac{I_1(\sigma)+I_0(\sigma)}{2I_0(\sigma)}$$

we have

$$\frac{\alpha_\parallel(\omega)}{\alpha_\parallel'(0)}=\frac{1}{i\omega\tau+(1-\sigma)+\sigma\tilde{S}_3(i\omega)}\left[(1-\sigma)+\sigma\tilde{S}_3(i\omega)-i\omega\tau\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}\left\{\frac{I_{p+1}(\sigma)+I_p(\sigma)}{I_1(\sigma)+I_0(\sigma)}\right\}\times\prod_{k=1}^{p}\tilde{S}_{2k+1}(i\omega)\right]. \tag{52}$$

The most significant feature of Eq. (51) is however that it is capable of yielding an exact expression for the correlation time. We have, on setting $s=0$

$$T_\parallel=\frac{\tilde{f}_1(0)}{f_1(0)}=\frac{\tau}{(1-\sigma)+\sigma\tilde{S}_3(0)}\left[1+\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}\left\{\frac{I_{p+1}(\sigma)+I_p(\sigma)}{I_1(\sigma)+I_0(0)}\right\}\prod_{k=1}^{p}\tilde{S}_{2k+1}(0)\right]. \tag{53}$$

Let us now consider the modified Bessel functions of the first kind of half-integer order. The modified Bessel function of the first kind of order ν satisfies

$$I_{\nu-1}(z)-I_{\nu+1}(z)=\frac{2\nu}{z}I_\nu(z), \tag{54}$$

which may be written as

$$\frac{I_\nu(z)}{I_{\nu-1}(z)}=\frac{z/2\nu}{1+\dfrac{z}{2\nu}\dfrac{I_{\nu+1}(z)}{I_\nu(z)}}, \tag{55}$$

which is a continued fraction.

If we now write $\nu=k+\frac{1}{2}$ where k is an integer this expression becomes

$$\frac{I_{k+1/2}}{I_{k-1/2}}=\cfrac{z}{2k+1+\cfrac{z}{2k+1}\cfrac{I_{k+3/2}(z)}{I_{k+1/2}(z)}}. \tag{56}$$

Now the definition of $\tilde{S}_{2k+1}(0)$ given by Eq. (47), namely,

$$\tilde{S}_{2k+1}(0)=\cfrac{\sigma}{2k+1+\cfrac{\sigma}{2k+1}\tilde{S}_{2k+3}(0)} \tag{57}$$

is identical to Eq. (56) on expansion. Hence the $\tilde{S}_{2k+1}(0)$ may be expressed in closed form as

$$\tilde{S}_{2k+1}(0)=\frac{I_{k+1/2}(\sigma)}{I_{k-1/2}(\sigma)}. \tag{58}$$

The modified Bessel functions of the first kind are chosen rather than the Macdonald[16] functions $K_\nu(\sigma)$, which also satisfy Eq. (57), as $T_\parallel$ must be finite at $\sigma=0$. The advantage of this representation in modified Bessel functions of

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half-integer order is that these functions have simple representations[21] in terms of elementary functions. Eq. (53) now becomes

$$T_{\parallel}=\frac{\tau}{(1-\sigma)+\sigma\dfrac{I_{3/2}(\sigma)}{I_{1/2}(\sigma)}}\left[1+\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}\times\left[\frac{I_{p+1}(\sigma)+I_p(\sigma)}{I_1(\sigma)+I_0(\sigma)}\right]\prod_{k=1}^{p}\frac{I_{k+1/2}(\sigma)}{I_{k-1/2}(\sigma)}\right]. \tag{59}$$

On simplifying the product in Eq. (59) this equation reduces to

$$T_{\parallel}=\frac{\tau}{(1-\sigma)+\sigma\dfrac{I_{3/2}(\sigma)}{I_{1/2}(\sigma)}}\left[1-\frac{1}{3}\frac{f_3(0)}{f_1(0)}\frac{I_{3/2}(\sigma)}{I_{1/2}(\sigma)}+\frac{1}{5}\frac{f_5(0)}{f_1(0)}\frac{I_{5/2}(\sigma)}{I_{1/2}(\sigma)}-\frac{1}{7}\frac{f_7(0)}{f_1(0)}\frac{I_{7/2}(\sigma)}{I_{1/2}(\sigma)}+\frac{1}{9}\frac{f_9(0)}{f_1(0)}\frac{I_{9/2}(\sigma)}{I_{1/2}(\sigma)}-\cdots\right] \tag{60}$$

$$=\frac{\tau}{(1-\sigma)+\sigma\dfrac{I_{3/2}(\sigma)}{I_{1/2}(\sigma)}}\left[1+\frac{1}{f_1(0)I_{1/2}(\sigma)}\times\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}f_{2p+1}(0)I_{p+1/2}(\sigma)\right], \tag{61}$$

where for convenience we have written

$$\frac{f_{2p+1}(0)}{f_1(0)}=\frac{I_{p+1}(\sigma)+I_p(\sigma)}{I_1(\sigma)+I_0(\sigma)}. \tag{62}$$

Equation (61) may be written as

$$T_{\parallel}=\frac{\tau}{(1-\sigma)+\sigma\dfrac{I_{3/2}(\sigma)}{I_{1/2}(\sigma)}}[1+Q(\sigma)], \tag{63}$$

where

$$Q(\sigma)=\frac{1}{f_1(0)I_{1/2}(\sigma)}\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}f_{2p+1}(0)I_{p+1/2}(\sigma). \tag{64}$$

Now from Refs. 16 and 21 we have

$$\frac{I_{3/2}(\sigma)}{I_{1/2}(\sigma)}=\frac{\cosh\sigma-(1/\sigma)\sinh\sigma}{\sinh\sigma}=L(\sigma), \tag{65}$$

where the Langevin function[20]

$$L(\sigma)=\coth\sigma-\frac{1}{\sigma}. \tag{66}$$

Thus

$$T_{\parallel}=\frac{\tau}{2\sigma}(e^{2\sigma}-1)(1+Q(\sigma)). \tag{67}$$

In order to simplify $Q(\sigma)$ we define the generalized Langevin functions $L_p(\sigma)$ as

$$L_p(\sigma)=\frac{I_{p+1/2}(\sigma)}{I_{1/2}(\sigma)}, \tag{68}$$

where the $L_p(\sigma)$ satisfy the recurrence relation

$$L_{p-1}(\sigma)-L_{p+1}(\sigma)=\frac{2p+1}{\sigma}L_p(\sigma). \tag{69}$$

Thus

$$T_{\parallel}=\frac{\tau}{2\sigma}(e^{2\sigma}-1)\left[1+\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}\frac{f_{2p+1}(0)}{f_1(0)}L_p(\sigma)\right]. \tag{70}$$

This is an exact formula for $T_{\parallel}$ which is valid for all σ. It is instructive to write out the first few terms of the series. We have using Eq. (54)

$$T=\frac{\tau}{2\sigma}(e^{2\sigma}-1)\left\{1-\frac{1}{3}\frac{1+\dfrac{I_1(\sigma)}{I_0(\sigma)}\left(1-\dfrac{2}{\sigma}\right)}{\dfrac{I_1(\sigma)}{I_0(\sigma)}+1}L(\sigma)+\frac{1}{5}\frac{\dfrac{I_1(\sigma)}{I_0(\sigma)}\left(1-\dfrac{2}{\sigma}+\dfrac{8}{\sigma^2}\right)+\left(1-\dfrac{4}{\sigma}\right)}{\dfrac{I_1(\sigma)}{I_0(\sigma)}+1}\left[1-\frac{3L(\sigma)}{\sigma}\right]-\frac{1}{7}\frac{\dfrac{I_1(\sigma)}{I_0(\sigma)}\left(1-\dfrac{8}{\sigma}+\dfrac{8}{\sigma^2}-\dfrac{48}{\sigma^3}\right)+\left(1-\dfrac{4}{\sigma}+\dfrac{24}{\sigma^2}\right)}{\dfrac{I_1(\sigma)}{I_0(\sigma)}+1}\times\left[L(\sigma)-\frac{5}{\sigma}\left\{1-\frac{3L(\sigma)}{\sigma}\right\}\right]+\cdots\right\}. \tag{71}$$

In writing down Eq. (71) from Eq. (70) we have simplified $f_{2p+1}(0)/f_1(0)$ by utilizing Eq. (54). The $I_p(\sigma)$ for large values of σ are of the form[10,16]

$$I_p(\sigma)\cong\frac{e^{\sigma}}{\sqrt{2\pi\sigma}}\left[1+O\left(\frac{1}{\sigma}\right)\right]. \tag{72}$$

This equation when combined with the fact that[20]

$$\lim_{\sigma\to\infty}L(\sigma)=1 \tag{73}$$

means that for large σ

$$T_{\parallel}\cong\left(\frac{\tau}{2\sigma}e^{2\sigma}\right)\sum_{p=0}^{\infty}\frac{(-1)^p}{(2p+1)}=\frac{\tau}{2\sigma}e^{2\sigma}\beta(1)=\left(\frac{\tau}{2\sigma}e^{2\sigma}\right)\frac{\pi}{4}, \tag{74}$$

by the properties of the Riemann–Zeta function. [See Eq. (23.2.30) of Ref. 10]. This is Eq. (49) of Lauritzen and

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TABLE II. Longitudinal correlation time in the form $T_\parallel/\tau$ as yielded by the exact solution [Eq. (70)] compared with the correlation time regarded as the numerical solution of the characteristic equation [Eq. (16)] for the inverse of the lowest eigenvalue. In calculating Eq. (70) $p=8$ is sufficient to attain convergence for σ values up to 10.

σ	$1/(\lambda_1\tau)$	T/τ
1	3.089 07	3.070 25
2	12.198	12.100 6
3	58.2856	57.9727
4	314.76	313.787
5	1 830.49	1827.12
6	11 153.5	11 140.2
7	70 132.9	70 074.9
8	45 1068	450 793
9	2.95*E*+06	2.95*E*+06
10	1.96*E*+07	1.96*E*+07

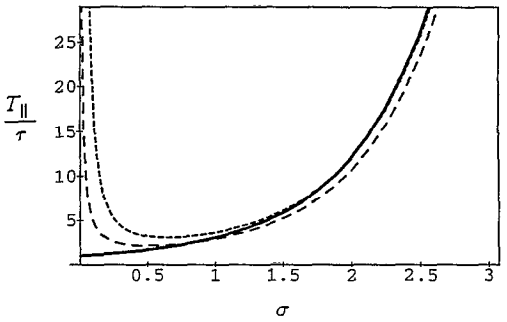


FIG. 2. Exact solution [Eq. (70)] for the longitudinal correlation time in the form $T_\parallel/\tau$ (solid line) compared with the asymptotic solution [Eq. (74)] (large dashed line) of Lauritzen and Zwanzig. The small dashed line is the solution rendered by the asymptotic formula of Crothers [Eq. (75)].

Zwanzig[6] which they derived using an asymptotic expansion of the Sturm–Liouville equation based on the smallness of the lowest eigenvalue.

The correlation time computed from Eq. (70) (see Table II) agrees satisfactorily with the numerical solutions for all σ gained from the matrix approach by regarding $T_\parallel$ as the reciprocal of the smallest root of the characteristic equation [Eq. (16)]. In Fig. 1 we show the correlation time calculated from Eq. (70) and the asymptotic expression [Eq. (74) of Lauritzen and Zwanzig[6]]. We also show in Fig. 1 the effective relaxation time $\tau_{\rm ef}^\parallel=(\lambda_{\rm ef}^\parallel)^{-1}$. The limiting procedure leading to Eq. (74) has been carried out using the high σ limit of the modified Bessel functions I_p. In doing this we implicitly assume that σ exceeds p the order of the Bessel function. A more mathematically rigorous way of proceeding to the high σ limit which also has the advantage of allowing asymptotic correction terms of order σ^{-2} and higher to be easily computed has been accomplished by Crothers.[22] His method is to write the products $I_{p+1/2}(\sigma)I_p(\sigma)$ and $I_{p+1/2}(\sigma)I_{p+1}(\sigma)$ occurring in the summation in Eq. (61) as integrals using formulae given by Watson[16] [p. 441 Sec. 13.72, Eq. (2)]. This procedure in effect allows one to replace the entire summation over p by an integral so eliminating the p dependence.

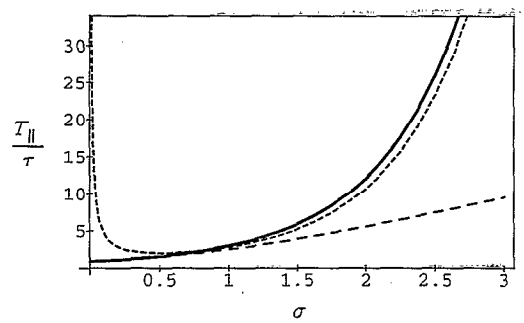


FIG. 1. Exact solution [Eq. (70)] for the longitudinal correlation time in the form $T_\parallel/\tau$ (solid line) compared with the asymptotic solution [Eq. (74)] (small dashed line) of Lauritzen and Zwanzig. The large dashed line is the solution rendered by the effective relaxation time $\tau_{\rm ef}^\parallel$ [Eq. (79)].

Application of the method of steepest descents as in Ref. 23 then leads to

$$\frac{T_\parallel}{\tau}=\frac{\pi}{8\sigma}e^{2\sigma}\left(1+\frac{1}{4\sigma}\right), \tag{75}$$

which is Eq. (74) with a small correction term. The form of the correction term agrees with the result of Visscher[24] [his Eq. (14)], who studied the escape of a particle from a single potential well using a refined version of the Kramers transition state method. A striking feature of the asymptotic formula (74) is that it deviates by a small amount from the exact solution for high σ. This behavior persists as $\sigma\to\infty$. If instead of Eq. (74) we use Eq. (75) which has the small correction term $(4\sigma)^{-1}$ then the exact solution is reproduced by the asymptotic solution to a high degree of accuracy as shown in Fig. 2.

In order to define the effective relaxation time we refer to Eq. (42). The effective eigenvalue, on using Eqs. (31) and (42) at $t=0$ is,[17,18]

$$\lambda_{\rm ef}^\parallel=-\frac{\dot f_1(0)}{f_1(0)}=\frac{1}{\tau}\left[1-\sigma+\sigma\frac{f_3(0)}{f_1(0)}\right], \tag{76}$$

where according to Eq. (27)

$$\frac{f_3(0)}{f_1(0)}=\frac{\langle\cos 3\phi(0)\rangle}{\langle\cos\phi(0)\rangle}=\frac{I_2(\sigma)+I_1(\sigma)}{I_1(\sigma)+I_0(\sigma)}. \tag{77}$$

Thus

$$\lambda_{\rm ef}^\parallel=\frac{1}{\tau}\left[(1-\sigma)+\sigma\frac{I_2(\sigma)+I_1(\sigma)}{I_1(\sigma)+I_0(\sigma)}\right]=\frac{1}{\tau}\frac{I_0(\sigma)-I_1(\sigma)}{I_0(\sigma)+I_1(\sigma)}. \tag{78}$$

The effective relaxation time is then using Eq. (54)

$$\tau_{\rm ef}^\parallel=\tau\frac{I_0(\sigma)+I_1(\sigma)}{I_0(\sigma)-I_1(\sigma)}, \tag{79}$$

which for large values of σ becomes

$$\tau_{\rm ef}^\parallel=4\sigma\tau,$$

and for small σ

$$\tau_{\rm ef}^\parallel=\tau(1+\sigma).$$

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It is evident from Fig. 1 that the effective relaxation time is a poor approximation to the longitudinal correlation time for $\sigma > 1$ as is also apparent from Eq. (75). This is not so for the transverse relaxation time where the effective relaxation time provides a close approximation to the exact solution. This behavior has been noted in the theory of magnetic relaxation.[25] The reason for the failure of $\tau_{\rm eff}^{\parallel}$ in this instance is because the lowest eigenvalue decreases exponentially with σ while all the others increase. It is evident from Fig. 2 that Eq. (75) reproduces to a high degree of accuracy, the asymptotic behavior.

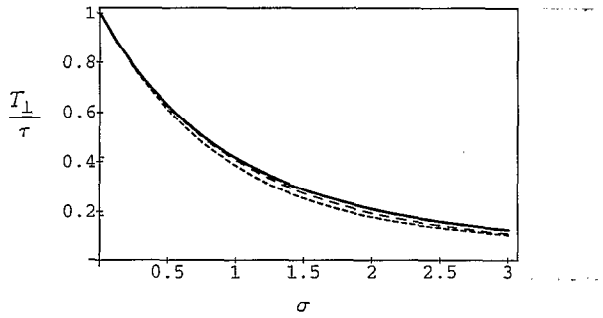


FIG. 3. Exact solution (large dashing) for the transverse correlation time in the form $T_\perp/\tau$ [Eq. (86)], compared with the inverse of the lowest eigenvalue as yielded by the numerical solution of Eq. (81) (solid line). The small dashed line represents the solution rendered by the effective relaxation time $\tau_{\rm ef}^{\perp}$ [Eq. (89)].

V. THE TRANSVERSE RELAXATION TIME AND POLARIZABILITY

The correlation time and polarizability for the transverse relaxation may be also calculated by the methods described in Sec. III.

The transverse behavior is determined by the $\langle \sin p\phi \rangle$ averages. Thus defining

$$g_p = \frac{a_{-p} - a_p}{2ia_0} \tag{80}$$

we have for the odd $g_i(t)$

$$\dot{g}_1(t) + \frac{1}{\tau} g_1(t) = -\frac{\sigma}{\tau}\,[g_1(t) + g_3(t)] \tag{81}$$

and

$$\dot{g}_{2p+1}(t) + \frac{(2p+1)^2}{\tau} g_{2p+1}(t) = \frac{\sigma(2p+1)}{\tau}\,[g_{2p-1}(t) - g_{2p+3}(t)], \quad p = 0,1,2,\ldots \tag{82}$$

with

$$g_{-p} = -g_p. \tag{83}$$

The initial conditions are

$$g_{2p+1}(0) = \frac{\int_0^{2\pi} \sin(2p+1)\phi e^{\sigma \cos 2\phi}(1+\xi \sin\phi)\,d\phi}{\int_0^{2\pi} e^{\sigma \cos 2\phi}(1+\xi \sin\phi)\,d\phi} = \frac{\xi}{2}\frac{I_p(\sigma) - I_{p+1}(\sigma)}{I_0(\sigma)}. \tag{84}$$

Similar calculations to those of the longitudinal case now lead us to the following expression for the normalized transverse polarizability:

$$\frac{\alpha_\perp(\omega)}{\alpha_\perp'(0)} = \frac{1}{i\omega\tau + (1+\sigma) + \sigma\tilde{S}_3(i\omega)} \left[(1+\sigma) + \sigma\tilde{S}_3(i\omega) - i\omega\tau \sum_{p=1}^{\infty} \frac{(-1)^p}{(2p+1)} \frac{I_p(\sigma) - I_{p+1}(\sigma)}{I_0(\sigma) - I_1(\sigma)} \times \prod_{k=1}^{p} \tilde{S}_{2k+1}(i\omega) \right]. \tag{85}$$

Similarly, we find that the transverse correlation time is

$$T_\perp = \frac{\tau}{2\sigma}(1 - e^{-2\sigma})[1 + R(\sigma)], \tag{86}$$

where

$$R(\sigma) = \frac{1}{g_1(0) I_{1/2}(\sigma)} \sum_{p=1}^{\infty} \frac{(-1)^p}{(2p+1)} g_{2p+1}(0) I_{p+1/2}(\sigma). \tag{87}$$

The difference between Eq. (86) and Eq. (70) is striking as the first member of the leading term in Eq. (70) *increases* exponentially with barrier height while the second member of the leading term in Eq. (86) *decreases* exponentially with σ. This behavior is entirely due to the different symmetries of the equations for the g_i and f_i. Another interesting property of Eq. (86) is that it is not possible to write down directly an equation for $T_\perp$ in the limit of large σ using the asymptotic values of the I_p [Eq. (72)] as we did in writing down Eq. (74). This procedure simply leads to an alternating series for $T_\perp$ in the limit of large σ. In order to circumvent this difficulty we must again utilize the more refined approach of Crothers[22] based on the integral representation of a product of Bessel functions which in turn allows the replacement of the p dependent sum in Eq. (85) by an integral. Application of the method of steepest descents then leads to the following formula for $T_\perp$ in the limit of large σ

$$T_\perp = \frac{\tau}{4\sigma}\left(1 + \frac{1}{2\sigma}\right) \tag{88}$$

showing explicitly that the transverse relaxation is not governed by an activation process.

It is interesting to compare these results with the effective relaxation time. The inverse of the lowest eigenvalue computed from this set is shown in Fig. 3. The transverse effective relaxation time is from Eq. (81) using the fact that $\lambda_{\rm ef}^{\perp} = -\dot{g}_1(0)/g_1(0)$

$$\tau_{\rm ef}^{\perp} = \tau \frac{I_0(\sigma) - I_1(\sigma)}{I_0(\sigma) + I_1(\sigma)}, \tag{89}$$

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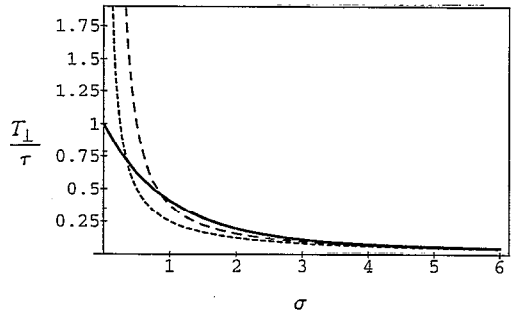


FIG. 4. Exact solution (bold line) for the transverse correlation time in the form $T_\perp/\tau$ [Eq. (86)] compared with the asymptotic formula of Crothers [Eq. (88)] (large dashing) and the asymptotic formula [Eq. (90)] (small dashing) which ignores terms $O(1/\sigma^2)$.

which provides quite a good approximation for all σ as is evident from Fig. 3. We note that for large σ, by the properties of the $I_p(\sigma)$,

$$\tau_{\rm ef}^{\perp}=\frac{\tau}{4\sigma} \tag{90}$$

which coincides with the leading term of Eq. (88), and that for small σ,

$$\tau_{\rm ef}^{\perp}=\tau(1-\sigma). \tag{91}$$

It is apparent that the same arguments regarding the asymptotic behavior apply to Eqs. (88) and (90) as apply to Eqs. (74) and (75). The $1/2\sigma$ term in Eq. (88) ensures that the asymptotic solution for $T_\perp$ agrees to a high degree of accuracy with the exact solution for large σ. The asymptotic solution $T_\perp$ rendered by Eq. (88) is shown in Fig. 4.

The values of the first three eigenvalues and their corresponding amplitudes calculated by numerical solutions of the set of differential-difference equations (82) are shown in Table III. These bear out the conclusions of Lauritzen and Zwanzig.[6] The most striking feature noted by them is the domination of the relaxation process for large σ by the modes characterized by λ_1 and λ_3 which coincide. In Table IV we show the transverse correlation time compared with the reciprocal of the effective eigenvalue $(\lambda_{\rm ef}^{\perp})^{-1}$ and the reciprocal of the lowest eigenvalue $(\lambda_1^{\perp})^{-1}$. It is apparent that $(\lambda_1^{\perp})^{-1}$ slightly overestimates $T_\perp$ for intermediate σ while $(\lambda_{\rm ef}^{\perp})^{-1}$ slightly underestimates it. The results of the numerical solution of the set of Eqs. (82) for $T_\perp$ using the matrix method [Eq. (39)] agree completely with the analytical formula (86).

TABLE IV. Transverse correlation time in the form $T_\perp/\tau$ as yielded by the exact solution [Eq. (86)] compared with the correlation time regarded as the numerical solution of the characteristic equation of the set of equations (82) for the inverse of the lowest eigenvalue. The inverse of the effective eigenvalue namely $(\lambda_{\rm ef}^{\perp})^{-1}$ is also shown. Again $p=8$ is sufficient for convergence in Eq. (86).

σ	$1/(\lambda_1\tau)$	T/τ	$1/(\lambda_{\rm ef}\tau)$
1	0.414 07	0.405 533	0.382 753
2	0.210 214	0.194 062	0.178 013
3	0.124 672	0.110 981	0.104 981
4	0.083 232 3	0.075 193	0.073 236 2
5	0.060 920 9	0.057 018 3	0.056 310 2
6	0.047 848 6	0.046 140 8	0.045 828 6
7	0.039 551 8	0.038 838 9	0.038 673 9
8	0.033 862 3	0.033 565	0.033 466
9	0.029 694	0.029 565 1	0.029 500 4
10	0.026 483 3	0.026 422 8	0.026 378

VI. COMPARISON OF THE RELAXATION TIME $T_\parallel$ WITH THE RESULTS OF THE KRAMER'S THEORY

It is interesting to compare the asymptotic result of Eq. (74) for $T_\parallel$ with that yielded by the Kramers transition state method.[8,26] Kramers showed that the probability of escape per unit time (escape rate) of a rotator from a *single* potential well [characterized by a potential $V(\phi)$] is in the high friction limit $\beta\gg1$

$$\kappa=\frac{\omega_A\omega_C}{2\pi\beta}e^{-U/kT}=\nu e^{-U/kT}. \tag{92}$$

The notation used is principally that of Chandrasekhar.[27] The high friction limit is consistent with the use of the Smoluchowski equation. The theory supposes that the rotator which is originally caught in a potential hole at A will escape to B crossing the potential barrier of height U at C. Here

$$\omega_A^2=I^{-1}V''(\phi_A) \tag{93}$$

TABLE III. Amplitudes a_{2p+1} for the first three modes of decay of the transverse polarization as a function of the barrier height parameter σ and the corresponding eigenvalues λ_{2p+1}, $p=0,1,2$ in the form $\lambda_{2p+1}\tau$.

σ	λ_1	λ_3	λ_5	a_1	a_3	a_5
0	1	9	25	0.5	0	0
1	2.415	9.518	25.52	0.269	0.007 62	0.000 025 8
2	4.757	10.92	27.11	0.131	0.020 2	0.000 235
3	8.021	13.04	29.86	0.0684	0.026 1	0.000 533
4	12.01	15.74	33.94	0.0415	0.02 6	0.000 636
5	16.41	18.89	39.6	0.0291	0.023 6	0.000 504
6	20.9	22.38	47.06	0.0227	0.020 8	0.000 303
7	25.28	26.09	56.34	0.0189	0.018 2	0.000 158
8	29.53	29.94	67.26	0.0163	0.01 6	0.000 080 2
9	33.68	33.88	79.5	0.0143	0.014 2	0.000 042 9
10	37.76	37.85	92.65	0.0128	0.012 8	0.000 025 1

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is the squared angular frequency inside the metastable minimum and

$$\omega_C^2=I^{-1}|V''(\phi_C)| \tag{94}$$

is the squared angular frequency at the transition state. I is the moment of inertia of the rotator about an axis through its center

$$\beta=\zeta I^{-1}. \tag{95}$$

Here $\phi_A=0$, $\phi_C=0$ so that from Eq. (4) with $\mathbf{E}=0$

$$\omega_A^2=\omega_C^2=\frac{2U}{I}. \tag{96}$$

Thus with Eqs. (92) and (95) the prefactor is

$$\nu=\frac{U}{\pi kT\tau}=\frac{2\sigma}{\pi\tau} \tag{97}$$

so that

$$\kappa=\frac{2\sigma}{\pi\tau}e^{-2\sigma}. \tag{98}$$

This result supposes that there is a *single* escape route from the well and that barrier crossing by this route is irreversible. If there are two escape routes from a well, as in the present problem, the escape rate κ from a single well must be doubled.[28–32] In addition (as shown by Praestgaard and Van Kampen,[28] in the application of the Kramers theory to a two dimensional periodic potential with period $2\pi/M$ having M minima) the dipole autocorrelation function must, in the high damping and high barrier limit, have the approximate form [cf. their Eq. (38) and the accompanying discussion of the assumptions which lead to that equation][28]

$$C_1(t)=\exp\{-\kappa_M[1-\cos(2\pi/M)t]\}. \tag{99}$$

Here $M=2$ so that[32]

$$\kappa_2=2\kappa \tag{100}$$

[cf. Eq. (3) of Ref. 32 in the high damping limit] and Eq. (99) becomes

$$C_1(t)=e^{-4\kappa t}. \tag{101}$$

Thus the longitudinal relaxation time is

$$T_{\|}=\frac{1}{4\kappa}=\frac{\pi}{4}\tau\frac{e^{2\sigma}}{2\sigma} \tag{102}$$

showing that the result of the Kramers theory[8] is in agreement with the asymptotic solution, Eq. (74). If Visscher's[24] improved calculation of the Kramers escape rate is used in conjunction with the modification for a periodic potential of the present section we obtain Eq. (75).

VII. CONCLUSIONS

We have shown in this paper how exact solutions [Eqs. (70) and (86)] may be obtained for the longitudinal and transverse dielectric relaxation correlation times for the two dimensional rotator in a $\sin^2\phi$ potential. The formula for $T_{\|}$ contains the previous result of Lauritzen and Zwanzig[6] as the limiting case of high potential barriers and for low potential barriers it will reduce to that of perturbation theory in σ. The result for large σ is in agreement with the Kramers transition state theory. The crucial steps which allow us to represent the solution in closed form are first the representation of the correlation times as the zero frequency limit of the Laplace transforms of the respective autocorrelation functions and secondly the fact that the $\tilde{f}_p(s)$ and $\tilde{g}_p(s)$ satisfy three term recurrence relations. This allows us to express the $\tilde{f}_p(0)$ and $\tilde{g}_p(0)$ in terms of the modified Bessel functions of half-integer order. We remark that the method may be extended to the correlation times of the higher order averages $\langle\cos(2p+1)\phi\rangle$ and $\langle\sin(2p+1)\phi\rangle$ of the after-effect solution when these are of interest. We also remark that the matrix representation of the problem [Eq. (40)] (although not so convenient for the recognition of the existence of a solution in closed form) is very useful. Since it is not subject to the restriction (as the continued fraction method is) that the differential-difference equations constitute a three term recurrence relation. Thus the matrix procedure embodied in Eq. (39) is far more general than the continued fraction one. For example it may be used to calculate the correlation times in three dimensional problems involving cubic anisotropy[33–35] and so on. We note (in connection with the matrix formulation of the problem) that the calculation of T from Eqs. (40) and (41) unlike the representation of the correlation time as $(\lambda_1\tau)^{-1}$ which always requires one to solve numerically a high order polynomial equation in s, simply requires the calculation of $\mathbf{A}^{-1}$. This is, in general, much easier than solving the polynomial equation. An interesting facet of the problem is that the effective eigenvalue[18] yields a close approximation to the transverse relaxation time for all σ values while providing a poor approximation for the longitudinal one. The limitations of that method in relation to activation processes are thus exposed as has been discussed in.[17,36]

We remark that the solution for $\alpha_{\|}(\omega)$ and $\alpha_{\perp}(\omega)$ given here may be applied with some small changes to yield analytical formulae for the polarizability of assemblies of molecules containing rotating polar groups. The theory of dielectric relaxation of these was originally formulated by Budó.[37] The present method is far simpler than the usual approach[37,38] to the problem based on an eigenfunction expansion of the Sturm–Liouville equation as such an expansion always leads to periodic differential equations of the Hill type.[37,38]

The methods used to solve the present problem are also of importance in the context of Néel relaxation[39] of single domain ferromagnetic particles. This is analogous to the longitudinal dielectric relaxation problem. In particular, Brown[7] using the Kramers escape rate theory, and Scully *et al.*,[23] by using the method of steepest descents, have obtained the asymptotic formula for the longitudinal magnetization relaxation time $\tau_{\|}$, namely,

$$\tau_{\|}=\tau_N\frac{\sqrt{\pi}}{2}\sigma^{-3/2}e^{\sigma},\quad \sigma=\frac{vK}{kT},\quad \sigma>2 \tag{103}$$

in the three dimensional magnetic analog of the present

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problem. Here the potential in spherical polar coordinates has the simple uniaxial form $Kv\sin^2\vartheta$. K is the magnetic anisotropy, ϑ is the polar angle, τ_N is the Néel relaxation time[39] for vanishingly small σ, v is the volume of a single domain ferromagnetic particle. This problem which on expansion of the distribution function of the orientation of the magnetic moments on the unit sphere in Legendre polynomials also leads to a three term recurrence relation [Ref. 39, Eq. (383)] may also be solved exactly.[40] This is accomplished in the manner described here with the relaxation time being obtained in terms of Kummer's functions[10] which reduce to incomplete gamma functions.[10] Similar considerations apply to the analogous Martin–Maier–Saupe theory of dielectric relaxation of nematic liquid crystals.[17,41]

The methods we have given are also of interest in view of the recent work of Bessais *et al.*[42,43] and Aharoni.[44] They sought an empirical formula for the magnetization relaxation time for the simple uniaxial potential above which is valid for all barrier heights σ by curve fitting to the numerical solution for $(\lambda_1\tau_N)^{-1}$. The existence of an exact solution in closed form removes the need for such procedures.

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APPENDIX

We may give the solution of the inhomogeneous Eq. (46) which governs the exact solution for $\tilde{f}_1(s)$, Eq. (51) as follows.

We have for $p>1$

$$\tilde{R}_p(s)[s\tau+p^2+\sigma p\tilde{R}_{p+2}(s)]=\tau\frac{f_p(0)}{\tilde{f}_{p-2}(s)}+\sigma p. \tag{A1}$$

We seek a complete solution of the inhomogeneous Eq. (A1). We can regard Eq. (A1) as having a particular solution and a complementary solution. The particular solution satisfies Eq. (47), i.e.,

$$\tilde{S}_p(s)=\frac{\sigma p}{s\tau+p^2+\sigma p\tilde{S}_{p+2}(s)}. \tag{A2}$$

Following Cresser *et al.*[45] and Coffey[46] we write

$$\tilde{R}_p(s)=\tilde{S}_p(s)+\tilde{Q}_p(s). \tag{A3}$$

Equation (A1) then becomes

$$[\tilde{S}_p(s)+\tilde{Q}_p(s)]\{s\tau+p^2+\sigma p[\tilde{S}_{p+2}(s)+\tilde{Q}_{p+2}(s)]\}$$
$$=\sigma p+\tau\frac{f_p(0)}{\tilde{f}_{p-2}(s)}. \tag{A4}$$

Using Eq. (A2), Eq. (A4) simplifies to

$$(s\tau+p^2)\tilde{Q}_p(s)+\sigma p[\tilde{Q}_{p+2}(s)\tilde{S}_p(s)$$
$$+\tilde{Q}_p(s)\tilde{S}_{p+2}(s)+\tilde{Q}_p(s)\tilde{Q}_{p+2}(s)]=\tau\frac{f_p(0)}{\tilde{f}_{p-2}(s)} \tag{A5}$$

which may be arranged as

$$(s\tau+p^2)\tilde{f}_{p-2}\tilde{Q}_p+\sigma p[\tilde{Q}_{p+2}\tilde{f}_{p-2}(\tilde{S}_p+\tilde{Q}_p)$$
$$+\tilde{Q}_p\tilde{S}_{p+2}\tilde{f}_{p-2}]=f_p(0)\tau. \tag{A6}$$

We now introduce

$$q_p=\tilde{Q}_p\tilde{f}_{p-2}.$$

Whence

$$(s\tau+p^2)q_p$$
$$+\sigma p[\tilde{Q}_{p+2}\tilde{f}_{p-2}(\tilde{S}_p+\tilde{Q}_p)+q_p\tilde{S}_{p+2}]=f_p(0)\tau. \tag{A7}$$

Now

$$\tilde{R}_p=\tilde{S}_p+\tilde{Q}_p=\frac{\tilde{f}_p}{\tilde{f}_{p-2}} \tag{A8}$$

so that

$$\tilde{R}_p\tilde{f}_{p-2}=(\tilde{S}_p+\tilde{Q}_p)\tilde{f}_{p-2}=\tilde{f}_p. \tag{A9}$$

Whence Eq. (A7) is

$$(s\tau+p^2)q_p+\sigma p[\tilde{Q}_{p+2}\tilde{f}_p+q_p\tilde{S}_{p+2}]=f_p(0)\tau \tag{A10}$$

or

$$(s\tau+p^2)q_p+\sigma p[q_{p+2}+q_p\tilde{S}_{p+2}]=f_p(0)\tau. \tag{A11}$$

Equation (A11) may be solved for q_p to yield

$$q_p=\frac{f_p(0)\tau-\sigma pq_{p+2}}{s\tau+p^2+\sigma p\tilde{S}_{p+2}}. \tag{A12}$$

However, from Eq. (A9)

$$\tilde{f}_p=\tilde{S}_p\tilde{f}_{p-2}+q_p. \tag{A13}$$

Thus $\tilde{f}_p(s)$ is determined.

We shall now show how Eq. (A13) may be used to obtain Eq. (51) for $\tilde{f}_1(s)$. We find that $\tilde{f}_1(s)$ does not satisfy a three term recurrence relation but is simply related to $\tilde{f}_3(s)$ by

$$\tilde{f}_1(s)[s\tau+(1-\sigma)]=f_1(0)\tau-\sigma\tilde{f}_3(s) \tag{A14}$$

since

$$f_{-1}(t)=f_1(t). \tag{A15}$$

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On substituting Eq. (A13) for $p=3$ into (A14) we readily find that

$$\tilde{f}_1(s)=\frac{f_1(0)\tau-\sigma q_3(s)}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}, \tag{A16}$$

which on substituting for q_3 from Eq. (A12) becomes

$$\tilde{f}_1(s)=\frac{f_1(0)\tau}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}-\frac{\sigma[f_3(0)\tau-3\sigma q_5]}{[s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)][s\tau+9+3\sigma\tilde{S}_5(s)]} \tag{A17}$$

or continuing the process

$$\tilde{f}_1(s)=\frac{\tau}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}\left[f_1(0)-\frac{\sigma f_3(0)}{s\tau+9+3\sigma\tilde{S}_5(s)}+\frac{3\sigma^2 f_5(0)}{[s\tau+9+3\sigma\tilde{S}_5(s)][s\tau+25+5\sigma\tilde{S}_7(s)]}\right.$$
$$\left.-\frac{15\sigma^3 f_7(0)}{[s\tau+9+3\sigma\tilde{S}_5(s)][s\tau+25+5\sigma\tilde{S}_7(s)][s\tau+49+7\sigma\tilde{S}_9(s)]}+\cdots\right] \tag{A18}$$

so that

$$\tilde{f}_1(s)=\frac{\tau}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}\left[f_1(0)-\frac{1}{3}f_3(0)\tilde{S}_3(s)+\frac{1}{5}f_5(0)\tilde{S}_3(s)\tilde{S}_5(s)-\frac{1}{7}f_7(0)\tilde{S}_3(s)\tilde{S}_5(s)\tilde{S}_7(s)+\cdots\right],$$

which is evidently

$$\tilde{f}_1(s)=\frac{\tau}{s\tau+(1-\sigma)+\sigma\tilde{S}_3(s)}\left[f_1(0)+\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p+1)}f_{2p+1}(0)\prod_{k=1}^{p}\tilde{S}_{2k+1}(s)\right]. \tag{A19}$$

Thus Eq. (51) is obtained.

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