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Analytical solutions for rotational diffusion in the mean field potential: application to the theory of dielectric relaxation in nematic liquid crystals

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A theory of dielectric relaxation in nematics is developed for a molecular dipole moment directed at an arbitrary angle to the molecular long axis. Both exact and simple approximate analytical formulae for the longitudinal and transverse components of the complex dielectric permittivity tensor are obtained for the non-inertial rotational Brownian motion of a molecule in the mean field potential of Maier and Saupe. It appears that both longitudinal and transverse relaxation processes are effectively described by two Debye type mechanisms with corresponding relaxation times and dielectric strengths expressed in terms of the order parameter. The generalization of the theory for an arbitrary axially symmetric mean field potential is given.

1. Introduction

Dielectric relaxation processes in liquid crystalline materials are determined by structural properties, intermolecular interactions and reorientations of the molecules. The complex dielectric permittivity of a nematic liquid crystal has very different dispersion regions and qualitative behaviour in the parallel ($\mathbf{E} \| \mathbf{n}$) and perpendicular ($\mathbf{E} \perp \mathbf{n}$) alignment ($\mathbf{E}$ is the measuring a.c. field and $\mathbf{n}$ is the director of the nematic). The origin of these dispersion regions is in general due to hindered reorientations of the molecules about the molecular long and short axes in strong orientational forces of the nematic phase [1, 2]. Dielectric relaxation in nematic liquid crystals is usually interpreted in the context of a model of non-inertial rotational Brownian motion of a particle in a mean field potential field U (see for example [1–11]), although the mean field approximation has a restricted area of applicability as it ignores local order effects. In spite of this drawback the model nevertheless is easily visualized and moreover allows us to carry out quantitative

evaluations of the dielectric parameters of nematics [1, 2]. The usual approach to the problem is to solve the Fokker–Planck equation for the distribution function W of the orientations of a unit vector $\mathbf{u}$, fixed in the molecule [1, 3]:

$$2\tau_D \frac{\partial}{\partial t} W = \nabla_\Omega^2 W + \frac{1}{kT} \operatorname{div}(W \operatorname{grad} U) \qquad (1)$$

where ∇_Ω^2 is the Laplace operator in angular variables, k is the Boltzmann constant, T is the temperature, $\tau_D = (2D_\perp)^{-1}$ is the orientational relaxation time in the isotropic phase, and $D_\perp$ is the rotational diffusion coefficient with respect to the axis which is perpendicular to the axis of symmetry of the molecule. Equation (1) can be formally solved by the method of the separation of variables (e.g. [7]), which reduces the solution to a Sturm–Liouville problem. An alternative method is to expand the distribution function W in spherical harmonics (for example [11]). The problem is then reduced to the solution of infinite-dimensional systems of linear differential-recurrence equations for the statistical moments (averaged spherical harmonics) which may be

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written down in the matrix form:

$$\frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{X}(t) = \boldsymbol{A}\boldsymbol{X}(t). \qquad (2)$$

Various methods of solution of equations (1) and (2) have been discussed, for example, in [4–8, 12, 13].

The basic model for the calculation of the components of the complex dielectric permittivity tensor and dielectric relaxation times of nematics is the rotational diffusion model of symmetric top molecules in the self-consistent mean field potential of Maier and Saupe [3, 4]:

$$\frac{U}{kT} = -\sigma \cos^2 \vartheta \qquad (3)$$

where ϑ is the angle between the axis of symmetry of the molecule and the Z axis of the laboratory coordinate system. The calculation of the complex dielectric susceptibility and associated relaxation times for a potential of the form of equation (3) has already been considered (for instance [3–7]) and also a clear physical understanding of dielectric relaxation in nematics has been achieved [4, 5]. Nevertheless, for the most part, numerical and approximate solutions only have been obtained. These solutions are in general either so complicated or are of such restricted range of applicability that their use in practice is difficult. In recent studies [11], on the other hand, we have obtained both exact and rather simple approximate solutions when the dipole moment of the molecule μ is *directed along the axis of symmetry of the molecule*. Here the general case, where the vector μ is *directed at an arbitrary angle β to the molecular axis of symmetry*, is considered that allows us substantially to extend the scope of the applicability of the results of ref. [11]. In order to accomplish this we use the basic concepts of a recently developed method [12] for the evaluation of the parameters governing the linear response of systems with dynamics described by the Fokker–Planck equation. This method is based on an exact solution of the recurrence relations for the spectra of the statistical moments using either ordinary or matrix continued fractions and does offer, to our mind, real advantages over direct matrix algebra methods (e.g. [5]), because the calculations can be carried out even using a pocket calculator. Moreover, the approximate solutions are derived by utilizing the concepts of the integral relaxation (correlation) time and the effective eigenvalue, so allowing us to generalize the theory to an *arbitrary* axially symmetric mean field potential. The simple approximate formulae so obtained relate the longitudinal and transverse components of the complex dielectric susceptibility and corresponding relaxation

times to the order parameter S and are valid for *any* strength of the nematic potential. They are presented in the form suitable for comparison with dielectric relaxation measurements and can easily be tested with experimentally available data. We remark, that from a mathematical point of view the calculation of the dielectric response of polar molecules in a mean field potential closely resembles the problem of magnetic relaxation of single domain ferromagnetic particles [14–16].

2. Exact solution for the Maier–Saupe model

The complex dielectric permittivity tensor $\varepsilon_{ij}(\omega) = \varepsilon'_{ij}(\omega) - \mathrm{i}\varepsilon''_{ij}(\omega)$ of a nematic is diagonal and has only two independent components, one perpendicular $[\varepsilon_\perp(\omega) = \varepsilon_{XX}(\omega) = \varepsilon_{YY}(\omega)]$ and the other parallel $[\varepsilon_\parallel(\omega) = \varepsilon_{ZZ}(\omega)]$ to the director vector **n** in the laboratory coordinate system XYZ, where the Z axis coincides with the director.

If we ignore intermolecular correlations, the components of the complex dielectric permittivity tensor are determined by the relations [9, 17]:

$$\varepsilon_\gamma(\omega) - \varepsilon_{\gamma\infty} = \frac{4\pi\mu^2 N_0 R_\gamma(\omega)}{kT}$$
$$\times \left[C_\gamma(0) - \mathrm{i}\omega \int_0^\infty C_\gamma(t)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t \right],$$
$$(\gamma = \parallel, \perp) \qquad (4)$$

where

$$C_\parallel(t) = \langle u_Z(0)u_Z(t)\rangle_0 \qquad (5)$$
$$C_\perp(t) = \langle u_X(0)u_X(t)\rangle_0 \qquad (6)$$

are the components of the dipole autocorrelation function, u_X, u_Z are the projections of the unit vector **u** along μ onto the axes X and Z, N_0 is the concentration of molecules, $\varepsilon_{\infty\gamma}$ are the high frequency limits of the components of the complex dielectric permittivity tensor, and $R_\gamma(\omega)$ is the frequency dependent factor of the internal field. For an ellipsoidal cavity in an anisotropic dielectric [17] for example

$$R_\gamma(\omega) = \frac{\varepsilon_\gamma(\omega)}{\varepsilon_\gamma(\omega) - \sigma_\gamma(\omega)[\varepsilon_\gamma(\omega) - \varepsilon_{\infty\gamma}]} \qquad (7)$$

where $\sigma_\gamma(\omega)$ are the components of the depolarization tensor (equations for $\sigma_\gamma(\omega)$ are given, for example, in [9, 17]).

We shall consider an ensemble of rigid dipolar molecules, where the vector μ is oriented at an angle β to the direction of the long axis of the molecule. The orientation of a moving coordinate system xyz, fixed in

the molecule, with respect to the laboratory system XYZ is defined by the Euler angles $\Omega = \{\varphi, \vartheta, \psi\}$, where φ, ϑ and ψ are the azimuthal and polar angles, and the angle describing rotation of a molecule around its axis of symmetry, respectively. The components of the tensor dipole autocorrelation function from equations (5) and (6) may be represented as [5]:

$$C_\parallel(t) = \cos^2 \beta f^1_{00}(t) + \sin^2 \beta f^1_{01}(t) \qquad (8)$$

$$C_\perp(t) = \cos^2 \beta f^1_{10}(t) + \sin^2 \beta f^1_{11}(t) \qquad (9)$$

where

$$f^1_{nm}(t) = \langle D^1_{nm}(0) D^{1*}_{nm}(t) \rangle_0$$

$$= \int D^1_{nm}(\Omega_0) W_0(\Omega_0)\,d\Omega_0 \int D^{1*}_{nm}(\Omega) W(\Omega, t|\Omega_0)\,d\Omega \qquad (10)$$

are the equilibrium autocorrelation functions, $W_0(\Omega_0) = C \exp(-U/kT)$ and $W(\Omega, t|\Omega_0)$ are, respectively, the equilibrium distribution function and conditional probability density to have a molecule with orientation Ω at an instant t provided that at $t = 0$ that molecule had orientation Ω_0; the asterisk denotes the complex conjugate, $d\Omega \equiv \sin \vartheta\,d\vartheta\,d\varphi\,d\psi$, and $D^J_{MM'}(\Omega) = \exp(iM\varphi)d^J_{MM'}(\vartheta)\exp(iM'\psi)$ are Wigner's D-functions. The $d^J_{MM'}(\vartheta)$ are given, for example, in ref. [18] and can be expressed in terms of the Legendre polynomials $P_n(\cos \vartheta)$, e.g.

$$d^j_{00}(\vartheta) = P_j(\cos \vartheta),$$

$$d^j_{\pm 11}(\vartheta) = \frac{1 \pm \cos \vartheta}{j(j+1)} \left\{ \frac{dP_j(\cos \vartheta)}{d\cos \vartheta} \right.$$

$$\left. \mp [1 \mp \cos \vartheta] \frac{d^2 P_j(\cos \vartheta)}{d\cos \vartheta^2} \right\},$$

$$d^j_{\pm 10}(\vartheta) = \mp \frac{\sin \vartheta}{[j(j+1)]^{1/2}} \frac{dP_j(\cos \vartheta)}{d\cos \vartheta},$$

$$d^j_{0\pm 1}(\vartheta) = \pm \frac{\sin \vartheta}{[j(j+1)]^{1/2}} \frac{dP_j(\cos \vartheta)}{d\cos \vartheta}.$$

We seek a solution of equation (1) in the form

$$W(\Omega, t|\Omega_0) = \sum_{j=0}^{\infty} \sum_{n=-j}^{j} \sum_{m=-j}^{j} (2j+1) c^j_{nm}(t) D^j_{nm}(\Omega) \qquad (11)$$

with the initial condition

$$W(\Omega, 0|\Omega_0) = \delta(\Omega - \Omega_0). \qquad (12)$$

Thus, the conditional probability density $W(\Omega, t|\Omega_0)$ is the Green's function of the Fokker–Planck equation (1). Noting the representation of the Dirac δ-function [18]

$$\delta(\Omega - \Omega_0) = \sum_{j=0}^{\infty} \sum_{n=-j}^{j} \sum_{m=-j}^{j} (2j+1) D^j_{nm}(\Omega_0) D^j_{nm}(\Omega) \qquad (13)$$

we have the initial values for $c^j_{nm}(0) = D^j_{nm}(\Omega_0)$. Substituting equations (3) and (11) into (1) we have

$$\frac{1}{D_\perp} \sum_{jnm} (2j+1) D^j_{nm}(\Omega) \frac{\partial}{\partial t} c^j_{n,m}(t)$$

$$= \sum_{jnm} (2j+1) c^j_{n,m}(t) \left\{ \nabla^2_\Omega D^j_{nm}(\Omega) + 2\sigma \right.$$

$$\left. \times \left[\cos \vartheta \sin \vartheta \frac{\partial}{\partial \vartheta} D^j_{nm}(\Omega) + (3\cos^2 \vartheta - 1) D^j_{nm}(\Omega) \right] \right\}. \qquad (14)$$

On using ([18], pp. 79, 82)

$$\cos \vartheta D^j_{nm}(\Omega)$$

$$= \frac{[(j^2 - n^2)(j^2 - m^2)]^{1/2}}{j(2j+1)} D^{j-1}_{nm}(\Omega) + \frac{nm}{j(j+1)} D^j_{nm}(\Omega)$$

$$+ \frac{\{[(j+1)^2 - n^2][(j+1)^2 - m^2]\}^{1/2}}{(j+1)(2j+1)} D^{j+1}_{nm}(\Omega) \qquad (15)$$

$$\sin \vartheta \frac{\partial}{\partial \vartheta} D^j_{nm}(\Omega)$$

$$= - \frac{(j+1)[(j^2 - n^2)(j^2 - m^2)]^{1/2}}{j(2j+1)} D^{j-1}_{nm}(\Omega)$$

$$- \frac{nm}{j(j+1)} D^j_{nm}(\Omega)$$

$$+ \frac{j\{[(j+1)^2 - n^2][(j+1)^2 - m^2]\}^{1/2}}{(j+1)(2j+1)} D^{j+1}_{nm}(\Omega) \qquad (16)$$

and [5, 19]

$$\nabla^2_\Omega D^j_{nm}(\Omega) = -\{j(j+1) + m^2[(D_\parallel/D_\perp) - 1]\} D^j_{nm}(\Omega)$$

($D_\parallel$ is the rotational diffusion coefficient about the axis of symmetry of the molecule), we have the set of

equations for $c_{nm}^j(t)$:

$$\tau_D \frac{d}{dt} c_{nm}^j(t) + \left\{ \frac{j(j+1)}{2} + m^2 \Delta \right.$$
$$\left. - \sigma \frac{[j(j+1)-3m^2][j(j+1)-3n^2]}{j(j+1)(2j-1)(2j+3)} \right\} c_{nm}^j(t)$$

$$= \frac{\sigma}{(2j+1)} \left\{ \frac{(j+1)\{[j^2-n^2][(j-1)^2-n^2]}{\times [j^2-m^2][(j-1)^2-m^2]\}^{1/2}}{j(j-1)(2j-1)} c_{nm}^{j-2}(t) \right.$$

$$+ \frac{mn(j+3)\{[j^2-n^2][j^2-m^2]\}^{1/2}}{j(j-1)(j+1)} c_{nm}^{j-1}(t)$$

$$- \frac{mn(j-2)\{[(j+1)^2-n^2][(j+1)^2-m^2]\}^{1/2}}{j(j+1)(j+2)} c_{nm}^{j+1}(t)$$

$$- \frac{j\{[(j+2)^2-n^2][(j+1)^2-n^2]}{\times [(j+2)^2-m^2][(j+1)^2-m^2]\}^{1/2}}{(j+2)(j+1)(2j+3)} c_{nm}^{j+2}(t) \left. \right\}$$

$$(17)$$

where

$$\Delta = \frac{1}{2} \left[\frac{D_\parallel}{D_\perp} - 1 \right].$$

It is now possible to derive from equations (10), (11) and (17) systems of differential-recurrence relations for the equilibrium correlation functions

$$f_{00}^j(t) = \langle D_{00}^1(0) D_{00}^1(t) \rangle_0,$$
$$f_{01}^j(t) = [j(j+1)/2]^{1/2} \langle D_{01}^1(0) D_{01}^{1*}(t) \rangle_0$$
$$f_{11}^j(t) = \langle D_{11}^1(0) D_{11}^{1*}(t) \rangle_0,$$
$$f_{10}^j(t) = [j(j+1)/2]^{1/2} \langle D_{10}^1(0) D_{10}^{1*}(t) \rangle_0.$$
$$(18)$$

These equations are the three 3-term recurrence relations:

$$\frac{2\tau_D}{j(j+1)} \frac{d}{dt} f_{00}^j(t) + \left[1 - \frac{2\sigma}{(2j-1)(2j+3)} \right] f_{00}^j(t)$$
$$= \frac{2\sigma}{2j+1} \left[\frac{j-1}{2j-1} f_{00}^{j-2}(t) - \frac{j+2}{2j+3} f_{00}^{j+2}(t) \right] \quad (19)$$

$$\frac{2\tau_D}{j(j+1)} \frac{d}{dt} f_{10}^j(t) + \left[1 - \frac{2\sigma[1-3/j(j+1)]}{(2j-1)(2j+3)} \right] f_{10}^j(t)$$
$$= \frac{2\sigma}{2j+1} \left[\frac{j+1}{2j-1} f_{10}^{j-2}(t) - \frac{j}{2j+3} f_{10}^{j+2}(t) \right] \quad (20)$$

$$\tau_D \frac{d}{dt} f_{01}^j(t) + \left[\frac{j(j+1)}{2} + \Delta - \frac{\sigma[j(j+1)-3]}{(2j-1)(2j+3)} \right] f_{01}^j(t)$$
$$= \frac{\sigma j(j+1)}{2j+1} \left[\frac{j+1}{2j-1} f_{01}^{j-2}(t) - \frac{j}{2j+3} f_{01}^{j+2}(t) \right] \quad (21)$$

and the five-term recurrence relation

$$\tau_D \frac{d}{dt} f_{11}^j(t) + \left[\frac{j(j+1)}{2} + \Delta - \frac{\sigma[j(j+1)-3]^2}{j(j+1)(2j-1)(2j+3)} \right] f_{11}^j(t)$$

$$= \frac{\sigma}{2j+1} \left[\frac{(j-2)(j+1)^2}{2j-1} f_{11}^{j-2}(t) + \frac{j+3}{j} f_{11}^{j-1}(t) \right.$$
$$\left. - \frac{j-2}{j+1} f_{11}^{j+1}(t) - \frac{j^2(j+3)}{2j+3} f_{11}^{j+2}(t) \right] \quad (22)$$

with $j = 1, 2, \ldots$ and $f_{nm}^{-1}(t)$, $f_{nm}^0(t) = 0$.

The Laplace transform of these systems may be reduced to infinite systems of inhomogeneous linear algebraic equations, the exact solution of which is determined using a method developed in [12]. This method constitutes a further development of Risken's continued fraction method [13]. It allows us to solve the inhomogeneous recurrent relations, which are necessary for the calculation of dielectric permittivity spectra and relaxation times.

We remark that equations (19) and (20) are mathematically identical to those describing dielectric relaxation when $\beta = 0$ [11]. Such equations have been comprehensively described in ref. [11] so we merely quote the main results here. Using the method of ref. [12], we have a solution of equation (19) for the Laplace transform $\tilde{f}_{00}^1(s) = \int_0^\infty \exp(-st) f_{00}^1(t) \, dt$ in terms of scalar continued fractions, namely (for details see ref. [11]):

$$\tilde{f}_{00}^1(s) = \frac{\tau_D}{s\tau_D + 1 - 2\sigma[1 - S_{00}^3(s)]/5}$$

$$\times \left[f_{00}^1(0) + \sum_{n=1}^\infty (-1)^n \frac{(4n+3)\Gamma\left(n+\frac{1}{2}\right) f_{00}^{2n+1}(0)}{2\pi^{1/2}\Gamma(n+2)} \right.$$

$$\left. \times \prod_{k=1}^n S_{00}^{2k+1}(s) \right] \quad (23)$$

where $S_{00}^n(s)$ is the continued fraction defined as

$$S_{00}^n(s) = \frac{2\sigma(n-1)}{4n^2-1} \left[\frac{2\tau_D s}{n(n+1)} + 1 - \frac{2\sigma}{(2n-1)(2n+3)} \right.$$
$$\left. + \frac{2\sigma(n+2)}{(2n+1)(2n+3)} S_{00}^{n+2}(s) \right]^{-1}. \quad (24)$$

The initial conditions $f_{00}^{2n+1}(0)$ are given by

$$f_{00}^{2n+1}(0)$$

$$= \frac{1}{4n+3} S_{00}^{2n}(0) S_{00}^{2n-2}(0) \dots S_{00}^{2}(0)$$

$$\times [2(n+1) S_{00}^{2n+2}(0) + 2n+1]$$

$$= \frac{2(n+1)\langle P_{2n+2}(\cos\vartheta)\rangle_0 + (2n+1)\langle P_{2n}(\cos\vartheta)\rangle_0}{4n+3}$$

$$= \frac{\sigma^n \Gamma\left(n+\frac{3}{2}\right) M\left(n+\frac{3}{2}, 2n+\frac{5}{2}, \sigma\right)}{2\Gamma\left(2n+\frac{5}{2}\right) M\left(\frac{1}{2}, \frac{3}{2}, \sigma\right)} \quad (25)$$

where $\langle\rangle_0$ designates the equilibrium ensemble average, the $P_n(x)$ are the Legendre polynomials [20], $\Gamma(z)$ is the gamma function [20], and $M(a, b, z)$ is the confluent hypergeometric function defined as [20]

$$M(a, b, z) = \frac{\Gamma(b)}{\Gamma(a)} \sum_{n=0}^{\infty} \frac{\Gamma(a+n)}{\Gamma(b+n)} \frac{z^n}{n!}.$$

In the derivation of equation (25) we note that [11]

$$\langle P_{2n}(\cos\vartheta)\rangle_0 = S_{00}^{2n}(0) S_{00}^{2n-2}(0) \dots S_{00}^{2}(0)$$

$$= \frac{\sigma^n \Gamma\left(n+\frac{1}{2}\right) M\left(n+\frac{1}{2}, 2n+\frac{3}{2}, \sigma\right)}{2\Gamma\left(2n+\frac{3}{2}\right) M\left(\frac{1}{2}, \frac{3}{2}, \sigma\right)} \quad (26)$$

and

$$S_{00}^{2n}(0) = \frac{2(2n-1)\sigma M\left(n+\frac{1}{2}, 2n+\frac{3}{2}, \sigma\right)}{(16n^2-1) M\left(n-\frac{1}{2}, 2n-\frac{1}{2}, \sigma\right)}.$$

On applying the method of ref. [12] to the solution of systems of equations (20) and (21), we have $\tilde{f}_{10}^{1}(s)$ and $\tilde{f}_{01}^{1}(s)$ in terms of scalar continued fractions:

$$\tilde{f}_{\substack{10 \\ \{01\}}}^{1}(s) = \frac{\tau_D}{4\sigma\pi^{1/2}} \sum_{n=0}^{\infty} \frac{(-1)^n (4n+3) \Gamma\left(n+\frac{1}{2}\right)}{(2n+1)(n+1)\Gamma(n+2)}$$

$$\times f_{\substack{10 \\ \{01\}}}^{2n+1}(0) \prod_{k=0}^{n} S_{\substack{10 \\ \{01\}}}^{2k+1}(s) \quad (27)$$

where

$$S_{10}^{n}(s) = \frac{\sigma n(n+1)^2}{4n^2-1} \Bigg[\tau_D s + \frac{n(n+1)}{2} - \frac{\sigma[n(n+1)-3]}{(2n-1)(2n+3)}$$

$$+ \frac{\sigma n^2(n+1)}{(2n+1)(2n+3)} S_{10}^{n+2}(s) \Bigg]^{-1} \quad (28)$$

$$S_{01}^{n}(s) = S_{10}^{n}\left(s + \frac{\Delta}{\tau_D}\right) \quad (29)$$

$$f_{10}^{2n+1}(0) = f_{01}^{2n+1}(0)$$

$$= \frac{(n+1)(2n+1)}{4n+3} S_{00}^{2n}(0) S_{00}^{2n-2}(0) \dots S_{00}^{2}(0)$$

$$\times [1 - S_{00}^{2n+2}(0)]$$

$$= \frac{(n+1)(2n+1)}{4n+3}$$

$$\times [\langle P_{2n}(\cos\vartheta)\rangle_0 - \langle P_{2n+2}(\cos\vartheta)\rangle_0]$$

$$= \frac{\sigma^n (n+1) \Gamma\left(n+\frac{3}{2}\right) M\left(n+\frac{1}{2}, 2n+\frac{5}{2}, \sigma\right)}{2\Gamma\left(2n+\frac{5}{2}\right) M\left(\frac{1}{2}, \frac{3}{2}, \sigma\right)}. \quad (30)$$

We remark that all the confluent hypergeometric functions appearing in equations (25), (26) and (30) may be expressed in terms of the more familiar error function of imaginary argument, viz. $\mathrm{erfi}(x) = 2/\pi^{1/2} \int_0^x \exp(t^2)\,\mathrm{d}t$. In particular ([21], pp. 580, 581)

$$M\left(\frac{1}{2}, \frac{3}{2}, z\right) = \frac{1}{2}\left(\frac{\pi}{2}\right)^{1/2} \mathrm{erfi}(z^{1/2})$$

$$M\left(\frac{3}{2}, \frac{7}{2}, z\right) = \frac{15}{8z^2}\left[3\exp(z) - \frac{3+2z}{2}\left(\frac{\pi}{z}\right)^{1/2} \mathrm{erfi}(z^{1/2}) \right].$$

Equations for the other M functions occurring in equation (30) may be obtained from table 7.11.2 of ref. [22] and the recurrence relations for the confluent hypergeometric function.

In order to obtain $\tilde{f}_{11}^{1}(s)$ from equation (22) we can also apply the general matrix method of solving five-term differential-recurrence relations (22) developed in refs [12, 23]. Equation (22) may be transformed to the matrix equation

$$\tau_D \frac{\mathrm{d}}{\mathrm{d}t} \mathbf{C}_n(t) = \mathbf{Q}_n^{-}\mathbf{C}_{n-1}(t) + \mathbf{Q}_n\mathbf{C}_n(t) + \mathbf{Q}_n^{+}\mathbf{C}_{n+1}(t) \quad (31)$$

with $\mathbf{C}_0(t) = 0$ if we represent that equation as follows

$$
\tau_D \frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} f_{11}^{2j-1}(t) \\ f_{11}^{2j}(t) \end{pmatrix}
$$

$$
= \begin{pmatrix} \dfrac{4\sigma j^2(2j-3)}{(4j-1)(4j-3)} & \dfrac{2\sigma(j+1)}{(2j-1)(4j-1)} \\[2ex] 0 & \dfrac{2\sigma(j-1)(2j+1)^2}{(4j-1)(4j+1)} \end{pmatrix} \begin{pmatrix} f_{11}^{2j-3}(t) \\ f_{11}^{2j-2}(t) \end{pmatrix}
$$

$$
+ \begin{pmatrix} \dfrac{\sigma[2j(2j-1)-3]^2}{2j(2j-1)(4j+1)(4j-3)} & -\dfrac{\sigma(2j-3)}{2j(4j-1)} \\ -j(2j-1)-\varDelta & \\[2ex] \dfrac{\sigma(2j+3)}{2j(4j+1)} & \dfrac{\sigma[2j(2j+1)-3]^2}{2j(2j+1)(4j-1)(4j+3)} \\ & -j(2j+1)-\varDelta \end{pmatrix}
$$

$$
\times \begin{pmatrix} f_{11}^{2j-1}(t) \\ f_{11}^{2j}(t) \end{pmatrix}
$$

$$
+ \begin{pmatrix} -\dfrac{2\sigma(j+1)(2j-1)^2}{(4j-1)(4j+1)} & 0 \\[2ex] -\dfrac{2\sigma(j-1)}{(2j+1)(4j+1)} & -\dfrac{4\sigma j^2(2j+3)}{(4j+1)(4j+3)} \end{pmatrix} \begin{pmatrix} f_{11}^{2j+1}(t) \\ f_{11}^{2j+2}(t) \end{pmatrix}.
$$

$$(32)$$

The *exact solution* of equation (32) in terms of matrix continued fractions is [12]

$$
\begin{pmatrix} \tilde{f}_{11}^1(s) \\ \tilde{f}_{11}^2(s) \end{pmatrix}
$$

$$
= \tau_D [\tau_D s \mathbf{I} - \mathbf{Q}_1 - \mathbf{Q}_1^+ \mathbf{S}_{11}^2(s)]^{-1}
$$

$$
\times \left\{ \mathbf{C}_1(0) + \sum_{n=2}^{\infty} \prod_{k=2}^{n} \mathbf{Q}_{k-1}^+ \mathbf{S}_{11}^k(s)(\mathbf{Q}_k^-)^{-1} \mathbf{C}_n(0) \right\}
$$

$$(33)$$

where $\mathbf{I}$ is the unit matrix, $\mathbf{Q}_n$, $\mathbf{Q}_n^{\pm}$ are the matrices defined by equations (31) and (32), and the matrix continued fraction $\mathbf{S}_{11}^n(s)$ is given by

$$
\mathbf{S}_{11}^n(s) = [\tau_D s \mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{S}_{11}^{n+1}(s)]^{-1} \mathbf{Q}_n^-.
$$

All the matrices in equation (33) are of size 2×2. The initial value vectors $\mathbf{C}_n(0)$ are given by

$$
\mathbf{C}_n(0)
$$

$$
= \begin{pmatrix} f_{11}^{2n-1}(0) \\ f_{11}^{2n}(0) \end{pmatrix}
$$

$$
= \frac{1}{2} \begin{pmatrix} \dfrac{1}{4n-1}[2n\langle P_{2n-2}(\cos\vartheta)\rangle_0 + (2n-1)\langle P_{2n}(\cos\vartheta)\rangle_0] \\[2ex] \langle P_{2n}(\cos\vartheta)\rangle_0 \end{pmatrix}.
$$

Here we have used the equality [18]

$$
D_{11}^1(\Omega) D_{-1-1}^j(\Omega) = \frac{1}{2}\left[\frac{j+1}{2j+1}P_{j-1}(\cos\vartheta) \right.
$$

$$
\left. + \frac{j}{2j+1}P_{j+1}(\cos\vartheta) + P_j(\cos\vartheta) \right].
$$

On using equations (23), (27) and (33), we may calculate from (8) and (9) the spectra of the dipolar correlation functions:

$$
\tilde{C}_{\parallel}(\mathrm{i}\omega) = \cos^2\beta\,\tilde{f}_{00}^1(\mathrm{i}\omega) + \sin^2\beta\,\tilde{f}_{01}^1(\mathrm{i}\omega) \tag{34}
$$

$$
\tilde{C}_{\perp}(\mathrm{i}\omega) = \cos^2\beta\,\tilde{f}_{10}^1(\mathrm{i}\omega) + \sin^2\beta\,\tilde{f}_{11}^1(\mathrm{i}\omega) \tag{35}
$$

and so the components of the complex dielectric permittivity tensor from equation (4).

Although the exact solutions (23), (27) and (33) in terms of scalar and matrix continued fractions may appear unusual to a general reader of *Liquid Crystals*, they are very convenient for computations (various algorithms for calculating ordinary and matrix continued fractions are discussed in ref. [13], Chap. 9). Here all the continued fractions and series involved converge very rapidly, and thus 10 downward iterations in calculating these continued fractions and 8–10 terms in the series (23), (27) and (33) are enough to arrive at not less than six significant digits in the majority of cases. Equations (23), (27) and (33) are applicable for any values of the parameters σ, β and $D_{\parallel}/D_{\perp}$ (at $\beta = 0$ the results obtained agree with those of [11]). Furthermore, they allow us to determine the accuracy of the various approximate solutions (for example [6, 7]). In ref. [11] we also obtained simple approximate expressions for the correlation functions at $\beta = 0$ using the concepts of the correlation time and effective eigenvalue. It is also possible to deduce similar approximate formulae for $\beta \neq 0$ and to test their accuracy by comparing them with the exact solutions given above.

We recall that one can calculate the integral relaxation times τ_{nm}, defined as the areas under the curves of the normalized correlation functions, from the equation [12]:

$$
\tau_{nm} = \frac{1}{f_{nm}^1(0)} \int_0^{\infty} f_{nm}^1(t)\,\mathrm{d}t = \frac{\tilde{f}_{nm}^1(0)}{f_{nm}^1(0)}. \tag{36}
$$

The relaxation times τ_{nm} may equivalently be defined in the context of the Sturm–Liouville equation as

$$
\tau_{nm} = \frac{\sum\limits_k C_k^{nm}/\lambda_k^{nm}}{\sum\limits_k C_k^{nm}} \tag{37}
$$

where λ_k^{nm} and C_k^{nm} are the eigenvalues and their corresponding weight coefficients (amplitudes), as the

correlation functions $f_{nm}^1(t)$ are given by

$$f_{nm}^1(t) = \sum_k C_k^{nm} \exp(-\lambda_k^{nm} t).$$

Yet another time constant characterizing the relaxation process is the inverse of the effective eigenvalue $(\lambda_{nm}^{\text{ef}})^{-1} = \tau_{nm}^{\text{ef}}$ defined as

$$\tau_{nm}^{\text{ef}} = -\frac{f_{nm}^1(0)}{\dot{f}_{nm}^1(0)} = \frac{\sum_k C_k^{nm}}{\sum_k \lambda_k^{nm} C_k^{nm}} \tag{38}$$

(a review of the effective eigenvalue method is given in [24]). The effective time also includes contributions from all the eigenvalues. Moreover it gives precise information on the initial relaxation of the polarization in the time domain. The behaviour of τ_{nm} and τ_{nm}^{ef} is sometimes similar. Indeed, if a single eigenvalue dominates the relaxation $\tau_{nm} \cong \tau_{nm}^{\text{ef}}$. However if different time scales are involved, as happens in activation processes, the behaviour of τ_{nm} and τ_{nm}^{ef} may be very different [11].

It is usually impossible to evaluate analytically both τ_{nm} and τ_{nm}^{ef} from the above formulae using the Sturm–Liouville equation as a knowledge of the law of formation of the eigenvalues and their corresponding weights (amplitudes) is required. The approach we shall use below, just as in [11, 24], does not attempt to calculate τ_{nm} and τ_{nm}^{ef} by explicitly calculating the eigenvalue spectrum as required by equations (37) and (38); rather it gives τ_{nm} and τ_{nm}^{ef} in terms of the exact integral representation for τ_{nm} and in terms of the order parameter S for τ_{nm}^{ef}.

3. Comparison of exact and approximate solutions

The behaviour of the correlation function $f_{00}^1(t) = \langle D_{00}^1(0) D_{00}^1(t) \rangle_0$ can be approximated by a single exponential as has been shown in ref. [11]:

$$f_{00}^1(t) \approx f_{00}^1(0) \exp(-t/\tau_{00}) = \frac{1+2S}{3} \exp(-t/\tau_{00}) \tag{39}$$

where

$$S = \frac{3}{2} \langle \cos^2 \vartheta \rangle_0 - \frac{1}{2} = \frac{3 \exp(\sigma)}{4\sigma M\left(\frac{1}{2}, \frac{3}{2}, \sigma\right)} - \frac{3}{4\sigma} - \frac{1}{2} \tag{40}$$

is the order parameter, and τ_{00} is the relaxation time given by equation (36) at $n, m = 0$. Both exact and approximate formulae for the integral relaxation time

τ_{00} valid for all values of σ were deduced accordingly in refs [11, 16, 25] and [26, 27] as:

$$\frac{\tau_{00}}{\tau_D} = \frac{3}{2} \sum_{n=0}^{\infty} \frac{(-\sigma^2)^n \left(n+\frac{3}{4}\right) \Gamma^2\left(n+\frac{3}{2}\right)}{(n+1)\left(n+\frac{1}{2}\right) \Gamma^2\left(2n+\frac{5}{2}\right) M\left(\frac{3}{2}, \frac{5}{2}, \sigma\right)}$$
$$\times M\left(n+\frac{3}{2}, 2n+\frac{5}{2}, \sigma\right) M\left(n+1, 2n+\frac{5}{2}, \sigma\right)$$
$$= \frac{3 \exp(\sigma)}{\sigma^2 M\left(\frac{3}{2}, \frac{5}{2}, \sigma\right)} \int_0^1 \frac{\cosh[\sigma(z^2-1)]-1}{1-z^2} dz \tag{41}$$

$$\frac{\tau_{00}^{\text{ap}}}{\tau_D} \approx \frac{\exp(\sigma)-1}{\sigma} \left[\frac{2\sigma(\sigma/\pi)^{1/2}}{1+\sigma} + 2^{-\sigma} \right]^{-1}. \tag{42}$$

The main contribution to the relaxation of $f_{00}^1(t)$ is due to the overbarrier relaxation mode, which has the smallest non-vanishing eigenvalue. However, equation (39) ignores high frequency relaxation inside the wells [11, 28], which is detected as a very weak peak in the dielectric loss spectrum $\varepsilon''(\omega)$ when $\beta = 0$ and $\sigma \gg 1$ [11]. Here a better approximation for $f_{00}^1(t)$ is [29]

$$f_{00}^1(t) \approx \exp(-t/\tau_{00}) \{ \langle \cos \vartheta \rangle_{\text{well}}^2$$
$$+ [\langle \cos^2 \vartheta \rangle_0 - \langle \cos \vartheta \rangle_{\text{well}}^2] \exp(-t/\tau_W) \} \tag{43}$$

where $\tau_W \approx \tau_D/2\sigma$ is the time characterizing relaxation inside the wells [28],

$$\langle \cos \vartheta \rangle_{\text{well}} = \frac{\exp(\sigma)-1}{2\sigma M\left(\frac{1}{2}, \frac{3}{2}, \sigma\right)}$$

and $\langle \cdot \rangle_{\text{well}}$ means an average in a single potential well (for example in the domain $0 \leq \vartheta \leq \pi/2$).

Now as shown in ref. [11] the behaviour of the (transverse) correlation function $f_{10}^1(t) = \langle D_{10}^1(0) D_{10}^{1*}(t) \rangle_0$ may be accurately described by a single exponential by means of the effective eigenvalue method:

$$f_{10}^1(t) \approx f_{10}^1(0) \exp(-t/\tau_{10}) = \frac{(1-S)}{3} \exp(-t/\tau_{10}) \tag{44}$$

where

$$\tau_{10} \approx \tau_{10}^{\text{ef}} = -\frac{f_{10}^1(0)}{\dot{f}_{10}^1(0)} = \tau_D \left[1 + \frac{\sigma}{5} + \frac{2\sigma f_{01}^3(0)}{15 f_{01}^1(0)} \right]^{-1}$$
$$= 2\tau_D \frac{1-S}{2+S} \tag{45}$$

where τ_{10}^{ef} is the effective relaxation time, which is defined from equation (20) at $t = 0$.

In like manner, relaxation of both correlation functions $f_{01}^1(t)$ and $f_{11}^1(t)$, which mainly characterize the rotation of the molecule about the molecular long axis, can be described by the single exponentials

$$f_{01}^1(t) \approx \frac{(1-S)}{3} \exp(-t/\tau_{01}) \qquad (46)$$

$$f_{11}^1(t) \approx \frac{(2+S)}{6} \exp(-t/\tau_{11}) \qquad (47)$$

where

$$\tau_{01} \approx \overset{\text{ef}}{\tau_{01}} = -\frac{f_{01}^1(0)}{\dot{f}_{01}^1(0)} = \tau_D \left[1 + \frac{\sigma}{5} + \Delta + \frac{2\sigma f_{01}^3(0)}{15 f_{01}^1(0)} \right]^{-1}$$

$$= \tau_D \frac{1-S}{1+(1-S)\Delta+S/2} \qquad (48)$$

$$\tau_{11} \approx \overset{\text{ef}}{\tau_{11}} = -\frac{f_{11}^1(0)}{\dot{f}_{11}^1(0)} = \tau_D \left[1 - \frac{\sigma}{10} + \frac{1}{2}\left(\frac{D_\parallel}{D_\perp} - 1\right) \right.$$

$$\left. + \frac{4\sigma f_{11}^3(0)}{15 f_{11}^1(0)} - \frac{\sigma f_{11}^2(0)}{6 f_{11}^1(0)} \right]^{-1} \qquad (49)$$

$$= \tau_D \frac{2+S}{2+(2+S)\Delta-S/2}$$

where $\overset{\text{ef}}{\tau_{01}}$ and $\overset{\text{ef}}{\tau_{11}}$ are the effective relaxation times yielded by equations (21) and (22), respectively at $t=0$.

The results of the calculation of the relaxation times τ_{nm} and $\overset{\text{ef}}{\tau_{nm}}$ are shown in figure 1, where the exact and approximate relaxation times τ_{nm} and $\overset{\text{ef}}{\tau_{nm}}$ as functions of σ clearly are in complete agreement. The effective eigenvalue method is successful here in the evaluation of the decay of $f_{10}^1(t)$, $f_{01}^1(t)$ and $f_{11}^1(t)$, because the overbarrier relaxation (activation) mode is not involved in these relaxation processes, so that the behaviour of the correlation times τ_{01}, τ_{01} and τ_{11} and $\overset{\text{ef}}{\tau_{01}}$, $\overset{\text{ef}}{\tau_{01}}$ and

$\overset{\text{ef}}{\tau_{11}}$ is similar. This is not so for $f_{00}^1(t)$ where the effective relaxation time $\overset{\text{ef}}{\tau_{00}} = -f_{00}^1(0)/\dot{f}_{00}^1(0)$ diverges exponentially from the correlation time τ_{00} [11] on account of the activation process.

On using equations (4), (8), (9), (39), (44), (46) and (47), we can now derive simple approximate expressions for the normalized complex susceptibility spectra

$$\chi_\gamma(\omega) = \frac{kT[\varepsilon_\gamma(\omega) - \varepsilon_{\gamma\infty}]}{4\pi\mu^2 N_0 R_\gamma(\omega)}$$

$$= C_\gamma(0) - i\omega \tilde{C}_\gamma(i\omega), \qquad (\gamma = \parallel, \perp) \qquad (50)$$

which may be written as

$$\chi_\parallel(\omega) \approx \frac{1}{3}\left[\frac{(1+2S)\cos^2\beta}{1+i\omega\overset{\text{ap}}{\tau_{00}}} + \frac{(1-S)\sin^2\beta}{1+i\omega\overset{\text{ef}}{\tau_{01}}} \right] \qquad (51)$$

$$\chi_\perp(\omega) \approx \frac{1}{3}\left[\frac{(1-S)\cos^2\beta}{1+i\omega\overset{\text{ef}}{\tau_{10}}} + \frac{(1+S/2)\sin^2\beta}{1+i\omega\overset{\text{ef}}{\tau_{11}}} \right] \qquad (52)$$

with $\overset{\text{ap}}{\tau_{00}}$, $\overset{\text{ef}}{\tau_{01}}$, $\overset{\text{ef}}{\tau_{10}}$ and $\overset{\text{ef}}{\tau_{11}}$ given by equations (42), (45), (48) and (49), respectively. The results of the calculation of the dielectric loss spectra $\chi_\gamma''(\omega)$ from the exact and approximate formulae are shown in figures 2–5. For $\sigma \gg 1$ the longitudinal dielectric loss spectrum $\chi_\parallel''(\omega)$ has two loss peaks. The low frequency peak of $\chi_\parallel''(\omega)$ is due to the overbarrier relaxation mode of the parallel (to the molecular long axis) component of the dipole moment. On the other hand both high frequency longitudinal relaxation modes inside the wells and also the rotation of the perpendicular component of the dipole moment around the molecular long axis manifest themselves in the high frequency band. In contrast, in the transverse dielectric loss spectrum $\chi_\perp''(\omega)$ the two dispersion regions are not widely separated as they are
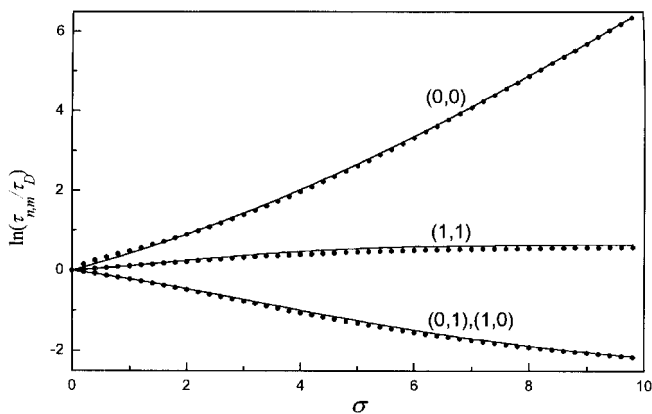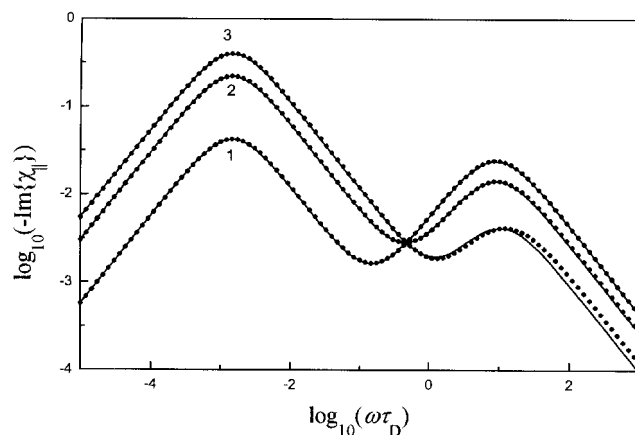

Figure 1. $\log(\tau_{nm}/\tau_D)$ as a function of σ, calculated from the exact formulae (23), (27), (33) and (36) for $D_\parallel/D_\perp = 1$ (solid lines). (••••)—the calculation from the approximate equations (42), (45), (48) and (49).

Figure 2. Spectrum $\chi_\parallel''(\omega)$ calculated from the exact equations (23), (27), (34) and (50) at $\sigma = 10$ and $D_\parallel/D_\perp = 1$ (solid lines). Curves 1, 2 and 3 correspond to $\beta = \pi/10$, $\pi/4$ and $2\pi/5$, respectively. (••••)—the calculation from equation (54) [at $\beta = \pi/10$ equation (43) was used].
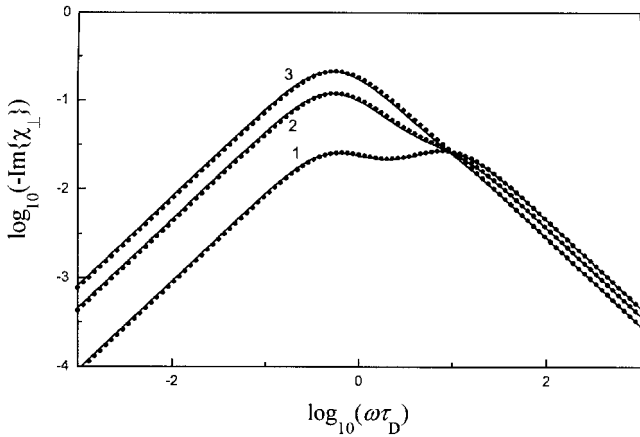
Figure 3. Spectrum $\chi''_{\perp}(\omega)$, calculated from the exact equations (27), (33), (35) and (50) at $\sigma = 10$ and $D_{\parallel}/D_{\perp} = 1$ (solid lines). Curves 1, 2 and 3 correspond to $\beta = \pi/10$, $\pi/4$ and $2\pi/5$, respectively. (••••)—the calculation from equation (52).

Figure 5. Spectrum $\chi''_{\perp}(\omega)$, calculated from the exact equations (27), (33), (35) and (50) at $\beta = \pi/4$ and $D_{\parallel}/D_{\perp} = 1$ (solid lines). Curves 1, 2 and 3 correspond to $\sigma = 1$, 5 and 10, respectively. (••••)—the calculation from equation (52).
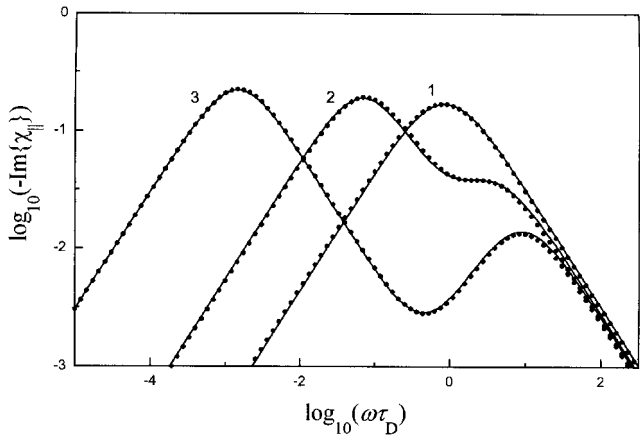

Figure 4. Spectrum $\chi''_{\parallel}(\omega)$, calculated from the exact equations (23), (27), (34) and (50) at $\beta = \pi/4$ and $D_{\parallel}/D_{\perp} = 1$ (solid lines). Curves 1, 2 and 3 correspond to $\sigma = 1$, 5 and 10, respectively. (••••)—the calculation from equation (51).

both located in the high frequency region. Nevertheless, if they can be distinguished (e.g. curve 1 in figure 3) one frequency dispersion band is associated with the rotation of the perpendicular component of the dipole moment about the molecular long axis, while the transverse relaxation modes contribute to another high frequency peak (or shoulder) of the spectrum $\chi''_{\perp}(\omega)$. Despite the large number of high frequency modes involved in both high frequency mechanisms, essentially two *near degenerate* modes only (so that they have approximately the same characteristic frequencies) determine both $\chi''_{\parallel}(\omega)$ and $\chi''_{\perp}(\omega)$ in the high frequency relaxation process [7, 11]. Thus both low and high frequency processes are still effectively governed by a single relaxation mode. As is apparent from figures 2–5, the results predicted by the approximate equations (51) and (52) agree to good
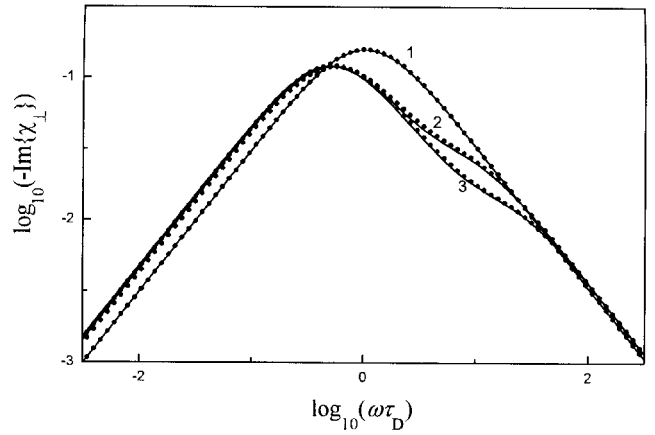
accuracy with the spectra calculated from the exact formulae (23), (27), (33), (34), (35) and (50). This means that for $\beta \neq 0$ both longitudinal and transverse dielectric relaxations can be approximately described by two exponential decays for all values of σ and β.

Just as for $\beta = 0$ we may formally introduce retardation factors for each effective mode (the retardation factor g_{nm} is defined as the ratio of relaxation times of the corresponding mode in the nematic and isotropic liquid phases). According to equations (42) and (48) the longitudinal relaxation retardation factors for the low and high frequency modes are given by

$$g_{00} = \frac{\exp(\sigma) - 1}{\sigma} \left[\frac{2\sigma(\sigma/\pi)^{1/2}}{1 + \sigma} + 2^{-\sigma} \right]^{-1} \quad (53)$$

and

$$g_{01} = \frac{(1 - S)(1 + \Delta)}{1 + (1 - S)\Delta + S/2} \quad (54)$$

respectively. The retardation factors for the low and high frequency modes for the transverse relaxation follow from equations (45) and (49) and are

$$g_{11} = \frac{(2 + S)(1 + \Delta)}{2 + (2 + S)\Delta - S/2} \quad (55)$$

and

$$g_{10} = \frac{1 - S}{1 + S/2}. \quad (56)$$

In equation (53) the retardation factor g_{00} is given as a function of the barrier height parameter σ. One can also express g_{00} as a function of the order parameter S by using the inverse function of equation (40) or by

using the extrapolating equation [30]

$$\sigma \approx \frac{3S(5 - \pi S)}{2(1 - S^2)} \qquad (57)$$

which provides a close approximation to $\sigma(S)$. The results of the calculation of σ as a function of the order parameter S from equations (40) and (57) are shown in figure 6.

The exact and approximate solutions for the retardation factors g_{00} and g_{10} for the Maier–Saupe potential given by equations (53) and (56) have been recently compared with the experiment by Urban et al. [31, 32]. They verified that the predictions of the theory are in qualitative agreement with the experiment. However, there are deviations from the experimental data [31, 32] in the temperature dependence of g_{00} and g_{10} predicted by equations (53) and (56). One would expect deviations of this kind as the mean field approximation provides only a qualitative description of relaxation processes in liquid crystals [4].

4. Generalization for an arbitrary axially symmetric mean field potential

The approach we have given for the evaluation of the dielectric parameters of nematics can be generalized to a mean field potential of the form

$$\frac{U}{kT} = -\sum_k \Lambda_k P_{2k}(\cos \vartheta). \qquad (58)$$

Here instead of equation (17) we have [22]

$$\frac{1}{D_\perp}\frac{d}{dt} c^j_{nm}(t) + \left[j(j+1) + m^2\left(\frac{D_\parallel}{D_\perp} - 1\right) \right] c^j_{nm}(t)$$
$$= \sum_r (R_{nm})_{jr} c^r_{nm}(t) \qquad (59)$$
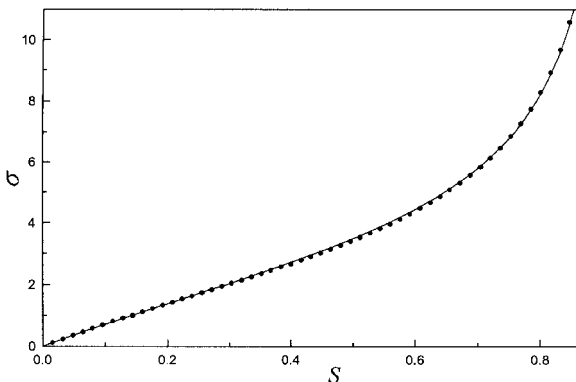

Figure 6. σ as a function of S calculated from the exact formula (40) (solid lines) and approximate equation (57) (••••).

where

$$(R_{nm})_{jr} = \frac{1}{2(2j+1)}\sum_k \Lambda_k [j(j+1) - r(r+1) + 2k(2k+1)]$$
$$\times C(2k, r, j; 0, n)C(2k, r, j; 0, m)$$

$C(j_1, j_2, j_3; m_1, m_2)$ are the Clebsch–Gordan coefficients [33]. In like manner it is possible to derive sets of equations for the equilibrium correlation functions $f^j_{00}(t)$, $f^j_{01}(t)$, $f^j_{10}(t)$, $f^j_{11}(t)$ from equations (10) and (59) which can be solved exactly with the help of matrix continued fractions.

Furthermore, the approximate relations (51) and (52) for the components of the normalized susceptibilities can also be applied with some modifications to a potential of the form of equation (58). Indeed, for the calculation of the relaxation time τ_{00} it is possible to use the exact integral representation [25, 34]:

$$\tau_{00} = \frac{6\tau_D}{(2S+1)Z}\int_{-1}^{1}\frac{\exp(U(x)/kT)}{1 - x^2}$$
$$\times \left[\int_{-1}^{x} x\exp(-U(x)/kT)\right]^2 dx \qquad (60)$$

where $x = \cos \vartheta$,

$$S = \frac{1}{Z}\int_{-1}^{1} P_2(x)\exp(-U(x)/kT)\,dx,$$
$$Z = \int_{-1}^{1}\exp(-U(x)/kT)\,dx. \qquad (61)$$

Equations (45), (47), (48) for the effective relaxation times τ^{ef}_{01}, τ^{ef}_{10}, τ^{ef}_{11} as functions of the order parameter S also remain valid for a potential of the form of equation (58) if we write them as follows

$$\tau_{10} \approx \tau^{ef}_{10} = 2\tau_D\frac{1 - S}{2 + S} \qquad (62)$$

$$\tau_{01} \approx \tau^{ef}_{01} = \tau_D\frac{1 - S}{1 + (1 - S)\Delta + S/2} \qquad (63)$$

$$\tau_{11} \approx \tau^{ef}_{11} = \tau_D\frac{2 + S}{2 + (2 + S)\Delta - S/2} \qquad (64)$$

where the order parameter S is given by equation (61). Equation (62) is valid for any axially symmetric potential as has been proved in ref. [10] and can be similarly extended to τ^{ef}_{01}, τ^{ef}_{11} given by equations (63) and (64) (see ref. [10] for details). Thus on using equations (51), (52), (60)–(64) we may calculate $\chi_\parallel(\omega)$ and $\chi_\perp(\omega)$ for any potential of the form of (58) with S as a parameter. In particular, equations (60), (62)–(64) provide simple

analytical solutions for the potential [35]

$$\frac{U}{kT} = -\Lambda_1 P_2(\cos \vartheta) - \Lambda_2 P_4(\cos \vartheta) \qquad (65)$$

and agree in all respects with the numerical solution of Nordio *et al.* [5] for this potential.

Thus we have shown in this paper how one may obtain exact solutions for the longitudinal and transverse components of the complex susceptibility tensor of a nematic liquid crystal possessing simple uniaxial anisotropy and with the dipole moment vector μ *directed at an arbitrary angle β to the molecular axis of symmetry.* Furthermore we have demonstrated that $\chi_\parallel(\omega)$ and $\chi_\perp(\omega)$ are each effectively governed by two relaxation mechanisms with their respective relaxation times and can be described by the simple equations (51) and (52).

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