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## Liquid Crystals

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## On the calculation of the dielectric relaxation times of a nematic liquid crystal from the non-inertial Langevin equation

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The theory of dielectric relaxation of uniaxial nematic liquid crystals is developed without recourse to the Fokker–Planck equation by direct averaging of the non-inertial Langevin equation for the rotational brownian motion of the linear molecule in a mean-field nematic potential. The non-inertial equation is regarded as a non-linear Stratonovich stochastic differential equation. The molecular equations for the average values of the dipole moment components so obtained involve both the nematic field and a suddenly applied weak DC measuring field. The equations are linearized in the DC field so that the AC response may be found by linear response theory. The Laplace transform of the equations is closed by a procedure which corresponds exactly to the effective eigenvalue method. It allows one to obtain formulae valid for all barrier heights for the longitudinal  $\tau_{\parallel}$  and transverse  $\tau_{\perp}$  relaxation times for an arbitrary uniaxial nematic potential in terms of the order parameter. The complex susceptibility induced by a weak AC field applied parallel and perpendicular to the axis of symmetry is also calculated.

### 1. Introduction

The theory of dielectric relaxation of nematic liquid crystals due to Martin *et al.* [1] proceeds from the Fokker–Planck equation without explicit reference to the underlying Langevin equation. Their aim is to extend the Debye theory of dielectric relaxation of assemblies of non-interacting polar molecules subjected to a weak alternating (AC) field to include the effects of a strong intermolecular potential giving rise to the nematic state. The AC response is usually obtained indirectly from linear response theory [2] by considering the response to a small DC step field.

The essence of the diffusion equation method [3] is to write down the particular form of the Fokker–Planck equation known as the Smoluchowski equation, for the transition probability of orientations of dipoles in configuration space. This is solved [1] by the method of separation of the variables. The separation procedure gives rise to an equation of Sturm–Liouville type [3] in the space variable which is related to Legendre's equation. The reciprocal of the lowest eigenvalue of the Sturm–Liouville equation yields the longest relaxation time of the probability density of orientations. Furthermore on expanding the dipole moment as a series of eigenfunctions of the Sturm–Liouville equation and averaging over the distribution function the orientational polarization may be expressed [3] as an infinite set of discrete Debye type relaxation mechanisms with relaxation times and amplitudes determined by the eigenvalues of the Sturm–Liouville equation. Approximate analytic solutions for the

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lowest eigenvalue of the distribution function may be found for high and low nematic potential barriers [1]. We shall call the Sturm–Liouville method Method I. This is commonly used [4] in the study of nematic liquid crystals.

An alternative approach to the problem [5] is to expand the transition probability as a series of spherical harmonics. This yields the time behaviour of the transition probability as an infinite hierarchy of differential–difference equations. The lowest order member of the hierarchy governs the time dependence of the polarization but is coupled to all the higher members by the differential–difference scheme, thus giving an infinite number of relaxation modes. In the frequency domain the hierarchy may often be written as an infinite continued fraction which facilitates its solution. The most general method of solution is effected by converting the hierarchy into the set of ordinary differential equations [5]

$$\dot{\mathbf{X}} = \mathbf{A}\mathbf{X} + \mathbf{B}U \quad (1)$$

and successively increasing the size of the system matrix  $\mathbf{A}$  [3, 5] by means of the recurrence relations of the hierarchy until convergence is attained. The reciprocal of the lowest eigenvalue of this set yields the longest relaxation time of the system of equations (1). We shall call this Method II.

Method I based on the Sturm–Liouville equation has also been used in the study of the Néel relaxation process in ferromagnetic domains in conjunction with various asymptotic methods [6] in order to obtain analytic solutions for the lowest eigenvalue of the distribution function for high and low anisotropy. Having assumed that the contribution of higher order eigenvalues to the polarization may be neglected so that it can be described by a *single* eigenvalue it is further assumed that the reciprocal of the lowest eigenvalue may be identified with the Néel relaxation time characterizing a flip of the magnetization [6]. Both Methods I and II have been used in [7] in conjunction with linear response theory [8] in the study of the dispersion of the magnetic susceptibility of fine ferromagnetic particles.

The disadvantage of the diffusion equation method is that in all the applications one first has to derive that equation from the Chapman–Kolmogorov equation in curvilinear coordinates and the underlying Langevin equation. Next one has either to use elaborate mathematical formulae involving spherical harmonics in order to deduce the set of differential–difference equations or else one must study the properties of Sturm–Liouville equations the solution of which cannot generally be given in terms of known functions. In both methods it is impossible to identify the longest relaxation time with that of the polarization unless the effect of the nematic potential may be ignored, neither is it possible to easily generalize the results to an arbitrary nematic potential.

It is the purpose of this paper to show how the differential–difference equations (alluded to above Method II) for a nematic liquid crystal for the Meier–Saupe potential arise naturally from the non-inertial Langevin equation written in vector form and defined as a Stratonovich equation thus bypassing the diffusion equation entirely. Having derived the differential–difference equations by averaging the Langevin equation it is then shown how closed form expressions of the Debye type valid for all barrier heights may be obtained for the complex susceptibility. The results are given for an AC field applied parallel and perpendicular to the axis of symmetry. The corresponding relaxation times for each field direction are given in terms of the order parameter for an arbitrary uniaxial nematic potential. The availability of all these expressions rests on the assumption that the contribution to the dynamical behaviour

of all processes which occur on a timescale  $< \tau_D/3$  where  $\tau_D$  is the Debye relaxation time may be adequately approximated by their equilibrium values. The above assumption may be stated more precisely as that in the Laplace transform of the equation describing the behaviour of the mean dipole moment the ratio of the Laplace transforms of the averages may be replaced by their zero frequency values. It corresponds to the effective eigenvalue method described by San Miguel *et al.* [9], i.e.  $\lambda_{\text{eff}}$  which gives precise details of the initial decay of the polarization. The growth and decay of the mean dipole moment is thus characterized by a *single* exponential with a relaxation time (the reciprocal of the effective eigenvalue  $\lambda_{\text{eff}}$ ) which is a function of the nematic potential so allowing a precise definition of the term 'relaxation time of the polarization' when an external potential is present. The effective eigenvalue may also be defined in terms of the eigenvalues of the Sturm–Liouville equation. It is however, very difficult to evaluate  $\lambda_{\text{eff}}$  from that equation as a knowledge of the law of formation of the eigenvalues and their corresponding amplitudes is required. Such information is rarely available. The method to be described here avoids this difficulty by expressing the effective eigenvalue in terms of the equilibrium order parameter.

## 2. The non-inertial Langevin equation for a nematic liquid crystal

We study the rotational brownian movement of a linear molecule subject to the mean nematic field  $\mathbf{E}_0$  and external electric field  $\mathbf{E}_1(t)$ . The molecule contains a rigid electric dipole  $\boldsymbol{\mu}$  along the axis of symmetry. The angular velocity  $\boldsymbol{\omega}(t)$  of the molecule satisfies the kinematic relation [8, 10]

$$\frac{d\boldsymbol{\mu}(t)}{dt} = \boldsymbol{\omega}(t) \times \boldsymbol{\mu}(t). \quad (2)$$

We specialize equation (2) to the rotational brownian motion of a molecule by supposing that  $\boldsymbol{\omega}$  obeys the Euler–Langevin equation

$$I \frac{d\boldsymbol{\omega}(t)}{dt} + \zeta \boldsymbol{\omega}(t) = \boldsymbol{\lambda}(t) + \boldsymbol{\mu}(t) \times \mathbf{E}(t). \quad (3)$$

In equation (3)  $I$  is the moment of inertia of the molecule about any line through the origin perpendicular to the line of symmetry,  $\zeta \boldsymbol{\omega}$  is the damping torque due to brownian movement and  $\boldsymbol{\lambda}(t)$  is the white noise driving torque, also due to brownian movement so that  $\boldsymbol{\lambda}(t)$  satisfies the relations

$$\overline{\boldsymbol{\lambda}(t)} = 0, \quad (4)$$

and

$$\overline{\lambda_i(t)\lambda_j(t')} = 2kT\zeta\delta_{ij}\delta(t-t'), \quad (5)$$

where  $\delta_{ij}$  is Kronecker's delta,  $i, j = 1, 2, 3$ , which correspond to cartesian axes;  $(x, y, z)$ , fixed in the molecule. This is the assumption that the random torques about different axes are statistically independent.  $\delta(t)$  is the Dirac delta function. The term  $\boldsymbol{\mu} \times \mathbf{E}(t)$ , in equation (3), is the torque due to the nematic mean field  $\mathbf{E}_0$  and externally applied field, i.e.  $\mathbf{E}(t) = \mathbf{E}_0 + \mathbf{E}_1(t)$ . The overbar means 'statistical average of'.

Equation (3) includes the inertia of the molecule. The non-inertial response is the response when  $I$  tends to zero or when  $\zeta$ , the friction coefficient, becomes very large. In this limit the angular velocity vector is

$$\boldsymbol{\omega}(t) = \frac{\boldsymbol{\lambda}(t)}{\zeta} + \frac{\boldsymbol{\mu} \times \mathbf{E}(t)}{\zeta}. \quad (6)$$

We combine this with the kinematic relation (see equation (2)) yielding

$$\frac{d\boldsymbol{\mu}(t)}{dt} = \frac{\lambda(t)}{\zeta} \times \boldsymbol{\mu}(t) + \frac{\{\boldsymbol{\mu}(t) \times \mathbf{E}(t)\} \times \boldsymbol{\mu}(t)}{\zeta}, \quad (7)$$

or

$$\frac{d\boldsymbol{\mu}}{dt} = \frac{\lambda(t)}{\zeta} \times \boldsymbol{\mu} + \frac{\mu^2 \mathbf{E}(t)}{\zeta} - \frac{\boldsymbol{\mu} \{ \boldsymbol{\mu} \cdot \mathbf{E}(t) \}}{\zeta}. \quad (8)$$

which is the Langevin equation for the rotational motion of the dipole moment  $\boldsymbol{\mu}$  of the molecule in the non-inertial limit.

### 3. Averaged equations of motion

Let us suppose that the molecule is under the influence of a mean nematic field  $\mathbf{E}_0 = -\text{grad } V$ , where  $V(\vartheta)$  is the nematic potential. We confine ourselves to a uniaxial potential, where  $\mathbf{E}_0$  has only a  $\mathbf{k}$  component. Hence

$$\mathbf{E}_0 = \mathbf{k} \left( -\frac{\partial V}{\mu \partial \cos \vartheta} \right).$$

Let us suppose that at  $t=0$  a small field  $\mathbf{E}_1 U(t)$ , where  $U(t)$  is the unit step function is applied along the  $z$  axis, so that

$$\mathbf{E}(t) = \mathbf{E}_0 + E_1 U(t) \mathbf{k} \quad (9)$$

equation (8) then becomes, with the aid of equation (9)

$$\dot{\mu}_x = \frac{1}{\zeta} (\lambda_y \mu_z - \lambda_z \mu_y) - \frac{\mu_x \mu_z}{\zeta} [E_0 + E_1 U(t)], \quad (10)$$

$$\dot{\mu}_y = \frac{1}{\zeta} (\lambda_z \mu_x - \lambda_x \mu_z) - \frac{\mu_y \mu_z}{\zeta} [E_0 + E_1 U(t)], \quad (11)$$

$$\dot{\mu}_z = \frac{1}{\zeta} (\lambda_x \mu_y - \lambda_y \mu_x) + \frac{(\mu^2 - \mu_z^2)}{\zeta} [E_0 + E_1 U(t)]. \quad (12)$$

Equations (10)–(12) contain multiplicative noise terms;  $\lambda_i \mu_j$ . Risken [11] has shown, taking the Langevin equation for  $N$  stochastic variables  $\{\xi\} = \{\xi_1, \xi_2, \xi_3, \dots, \xi_N\}$  as

$$\dot{\xi}_i = h_i(\{\xi\}, t) + g_{ij}(\{\xi\}, t) \Gamma_j(t), \quad (13)$$

with

$$\left. \begin{aligned} \overline{\Gamma_j(t)} &= 0, \\ \overline{\Gamma_i(t) \Gamma_j(t')} &= 2\delta_{ij} \delta(t-t') \end{aligned} \right\} \quad (14)$$

and interpreting it as a Stratonovich [11] equation, that the drift coefficient is

$$\begin{aligned} D_i(\{x\}, t) &= \dot{x}_i = \lim_{\tau \rightarrow 0} \left( \frac{1}{\tau} \overline{\xi_i(t+\tau) - x_i} \right) \Bigg|_{\xi_k(t) = x_k} \\ &= h_i(\{x\}, t) + g_{kj}(\{x\}, t) \frac{\partial}{\partial x_k} g_{ij}(\{x\}, t), \quad k = 1, 2, \dots, N. \end{aligned} \quad (15)$$

The last term in equation (15) is called the noise-induced or spurious drift [11]. In equation (15)  $\xi_i(t+\tau)$  ( $\tau > 0$ ) is a solution of equation (13) which has the sharp value

$\xi_k(t) = x_k$  for  $k = 1, 2, \dots, N$ . It should be noted that the quantities  $x_k$  in equation (15) are themselves random variables with the probability density function  $W(\{x\}, t)$  defined such that  $Wdx_k$  is the probability of finding  $x_k$  in the range  $x_k$  to  $x_k + dx_k$ .

We now use this theorem to evaluate the average of the multiplicative noise terms in equation (12). We have

$$g_{ij} \frac{\partial}{\partial \mu_i} g_{zj} = \frac{-2kT}{\zeta} \mu_z \tag{16}$$

which is the noise-induced drift. We must now further average equation (16) over the density distribution function  $W(\{\mu\}, t)$  of dipole orientations in configuration space at time  $t$ . On performing this average equation (16) then becomes  $-(2kT/\zeta)\langle\mu_z\rangle$  where the symbol  $\langle f \rangle$  denotes averaging a function  $f$  over the density function  $W(\{\mu\}, t)$  namely  $\langle f(\mu) \rangle = \int f(\{\mu\})W(\{\mu\}, t) d\mu$ . Thus the averaged equation of motion of the dipole is

$$\frac{d}{dt} \langle \mu_z \rangle + \frac{2kT}{\zeta} \langle \mu_z \rangle = \frac{[E_1 U(t)]}{\zeta} \langle \mu^2 - \mu_z^2 \rangle + \frac{1}{\zeta} \langle E_0(\mu^2 - \mu_z^2) \rangle. \tag{17}$$

In the transverse case the step change in the field is applied parallel to the  $x$  axis so that we need to determine the behaviour of  $\langle \mu_x \rangle$ . We find as before that the  $x$  component of the dipole moment satisfies

$$\frac{d}{dt} \langle \mu_x \rangle + \frac{2kT}{\zeta} \langle \mu_x \rangle = \frac{\mu^2}{\zeta} E_1 U(t) - \frac{\langle \mu_x^2 \rangle}{\zeta} E_1 U(t) - \frac{\langle \mu_x \mu_x E_0 \rangle}{\zeta}. \tag{18}$$

#### 4. The relaxation times for an arbitrary uniaxial nematic potential

The calculation of the relaxation times can be carried out by means of a procedure which has been used by Morita [13] in conjunction with the Fokker-Planck equation. A similar approach may be used in the context of the averaged Langevin equation as has been demonstrated in [8] in connection with the simpler problem of the linear response in the presence of an DC bias field. This is the [9] effective eigenvalue method. The goal of this method is to describe the system by a single effective eigenvalue which [9] contains the weighted contribution of all the other eigenvalues.

We first consider the equation of motion of  $\langle \mu_z \rangle$ . We suppose that a small field  $E_1(t) = E_1(t)\mathbf{k}$  is applied along the  $z$  axis at time  $t = 0$ . We require as before the linear response to  $E_1(t)$ . We therefore assume that  $\langle \mu_z \rangle$  and  $\langle E_0(\mu^2 - \mu_z^2) \rangle$  can be represented as

$$\langle \mu_z \rangle = \langle \mu_z \rangle_0 + \langle \mu_z \rangle_1, \tag{19}$$

$$\langle E_0(\mu^2 - \mu_z^2) \rangle = \langle E_0(\mu^2 - \mu_z^2) \rangle_0 + \langle E_0(\mu^2 - \mu_z^2) \rangle_1, \tag{20}$$

where the subscript 0 denotes the equilibrium ensemble average in the absence of the field  $E_1(t)$  viz.

$$\langle (\dots) \rangle_0 = \int_0^{2\pi} \int_0^\pi (\dots) W_0(\vartheta) \sin \vartheta d\vartheta d\phi,$$

$$W_0(\vartheta) = C \exp\left(-\frac{V(\vartheta)}{kT}\right)$$

is the equilibrium distribution function,  $\vartheta$  and  $\phi$  are the polar and azimuthal angles respectively and  $C$  is the normalizing constant, and the subscript 1 denotes the portion

of the ensemble average which is linear in  $E_1(t)$ . Thus we have, from equations (17), (19) and (20),

$$\frac{d}{dt} \langle \mu_z \rangle_1 + \frac{1}{\tau_D} \langle \mu_z \rangle_1 = \zeta^{-1} \langle E_0(\mu^2 - \mu_z^2) \rangle_1 + \zeta^{-1} \langle \mu^2 - \mu_z^2 \rangle_0 E_1(t). \quad (21)$$

The characteristic equation of the system then becomes (see for detail [8])

$$s + \tau_D^{-1} - \zeta^{-1} \frac{\mathcal{L} \langle E_0(\mu^2 - \mu_z^2) \rangle_1}{\mathcal{L} \langle \mu_z \rangle_1} = 0, \quad (22)$$

where the symbol  $\mathcal{L}$  means the Laplace transform

$$\mathcal{L}f = \int_0^\infty \exp(-st) f(t) dt.$$

If we suppose, again following Morita [13], that

$$\frac{\mathcal{L} \langle E_0(\mu^2 - \mu_z^2) \rangle_1}{\mathcal{L} \langle \mu_z \rangle_1} = \frac{\mathcal{L} \langle E_0(\mu^2 - \mu_z^2) \rangle - \mathcal{L} \langle E_0(\mu^2 - \mu_z^2) \rangle_0}{\mathcal{L} \langle \mu_z \rangle - \mathcal{L} \langle \mu_z \rangle_0}$$

may be replaced by its final (equilibrium) value (i.e. its value as  $t$  tends to infinity) namely

$$\lim_{t \rightarrow \infty} \frac{\langle E_0(\mu^2 - \mu_z^2) \rangle_1}{\langle \mu_z \rangle_1} = \lim_{s \rightarrow 0} \frac{s \mathcal{L} \langle E_0(\mu^2 - \mu_z^2) \rangle_1}{s \mathcal{L} \langle \mu_z \rangle_1},$$

equation (22) may then be evaluated as follows. At equilibrium ( $t \rightarrow \infty$ )

$$\langle \mu_z \rangle = \langle \mu_z \rangle_0 + \frac{E_1}{kT} (\langle \mu_z^2 \rangle_0 - \langle \mu_z \rangle_0^2), \quad (23)$$

by equation (19) *et seq.* [14], likewise

$$\langle E_0(\mu^2 - \mu_z^2) \rangle = \langle E_0(\mu^2 - \mu_z^2) \rangle_0 + \frac{\mu^3 E_1}{kT} \langle E_0(\cos \vartheta - \langle \cos \vartheta \rangle_0)(1 - \cos^2 \vartheta) \rangle_0. \quad (24)$$

The second term on the right hand side of equation (24) can be evaluated to yield

$$\begin{aligned} & \langle E_0(\cos \vartheta - \langle \cos \vartheta \rangle_0)(1 - \cos^2 \vartheta) \rangle_0 \\ &= -\frac{kT}{\mu} [1 - 3\langle \cos^2 \vartheta \rangle_0 + 2\langle \cos \vartheta \rangle_0^2]. \end{aligned} \quad (25)$$

In the nematic phase  $\langle \cos \vartheta \rangle_0$  is equal to zero. Substituting equation (25) into (24) we obtain

$$\langle E_0(\mu^2 - \mu_z^2) \rangle = \langle E_0(\mu^2 - \mu_z^2) \rangle_0 - E_1(\mu^2 - 3\langle \mu_z^2 \rangle_0). \quad (26)$$

The effective eigenvalue  $\lambda_{\parallel}$  with this procedure is then

$$\begin{aligned} \lambda_{\parallel} &= \tau_D^{-1} - \zeta^{-1} \frac{\langle E_0(\mu^2 - \mu_z^2) \rangle - \langle E_0(\mu^2 - \mu_z^2) \rangle_0}{\langle \mu_z \rangle - \langle \mu_z \rangle_0} \\ &= (2\tau_D)^{-1} \frac{1 - \langle \cos^2 \vartheta \rangle_0}{\langle \cos^2 \vartheta \rangle_0}. \end{aligned} \quad (27)$$

We have used equations (23) and (26) here. Thus the longitudinal relaxation time  $\tau_{\parallel} = \lambda_{\parallel}^{-1}$  may be expressed in terms of the equilibrium averages as

$$\tau_{\parallel} = 2\tau_D \frac{\langle \cos^2 \vartheta \rangle_0}{1 - \langle \cos^2 \vartheta \rangle_0} = \tau_D \frac{2S + 1}{1 - S}, \tag{28}$$

where  $P_2$  is the Legendre polynomial of order 2 [12],  $S = \langle P_2 \rangle_0$  is the order parameter.

We now calculate the transverse relaxation time  $\tau_{\perp}$ . We consider the same problem as above but this time the step change in the field  $E_1(t) = iU(t)E_1(t)$  is applied parallel to the  $x$  axis so that we need to determine the behaviour of  $\langle \mu_x \rangle$  from equation (18). We find just as before that the eigenvalue equation is

$$s + \tau_D^{-1} - \zeta^{-1} \frac{\langle E_0 \mu_x \mu_z \rangle_1}{\langle \mu_x \rangle_1} = 0, \quad (t \rightarrow \infty). \tag{29}$$

Now

$$\langle \mu_x \rangle \cong \frac{\mu^2 E_1}{kT} \langle \sin^2 \vartheta \cos^2 \phi \rangle_0 = \frac{\mu^2 E_1}{2kT} (1 - \langle \cos^2 \vartheta \rangle_0), \tag{30}$$

$$\langle E_0 \mu_x \mu_z \rangle \cong -\mu^2 E_1 (1 - 3\langle \cos^2 \vartheta \rangle_0) / 2, \tag{31}$$

$$\langle E_0 \mu_y \rangle = 0. \tag{32}$$

Thus the effective eigenvalue  $\lambda_{\perp}$  is given by

$$\lambda_{\perp} = \tau_D^{-1} - \zeta^{-1} \frac{\langle E_0 \mu_x \mu_z \rangle}{\langle \mu_x \rangle} = (2\tau_D)^{-1} \frac{1 + \langle \cos^2 \vartheta \rangle_0}{1 - \langle \cos^2 \vartheta \rangle_0}. \tag{33}$$

Whence the transverse relaxation time  $\tau_{\perp} = \lambda_{\perp}^{-1}$  may be expressed in terms of the equilibrium averages as

$$\tau_{\perp} = 2\tau_D \frac{1 - \langle \cos^2 \vartheta \rangle_0}{1 + \langle \cos^2 \vartheta \rangle_0} = 2\tau_D \frac{1 - S}{2 + S}. \tag{34}$$

It should be noted that equations (28) and (34) for the relaxation times  $\tau_{\parallel}$  and  $\tau_{\perp}$  are valid for any axially symmetric potential of the crystalline anisotropy.

The retardation factors  $g_{\parallel}$  and  $g_{\perp}$  defined by

$$\tau_{\parallel} = g_{\parallel} \tau_D, \quad \tau_{\perp} = g_{\perp} \tau_D \tag{35}$$

may now be expressed entirely in terms of the order parameter  $S$  as

$$g_{\parallel} = \frac{2S + 1}{1 - S}, \quad g_{\perp} = \frac{2 - 2S}{2 + S}. \tag{36}$$

It should be noted that one can deduce from equation (36) two quite general relationships between the retardation factors:

$$g_{\parallel} = \frac{2 - g_{\perp}}{g_{\perp}}, \quad g_{\perp} = \frac{2}{g_{\parallel} + 1}. \tag{37}$$

### 5. Calculation of the frequency dependence of the susceptibility

Having determined the effective relaxation times for transverse and longitudinal fields, we may calculate the complex susceptibility as follows.

According to equation (21) the decay transient of the polarization

$$P_{\parallel}(t) = N \langle \mu_z \rangle_1, \tag{38}$$



(where  $N$  is the number of molecules per unit volume) following the removal of  $E_1(t)$  at  $t=0$  is

$$P_{\parallel}(t) = E_1 U(t) \chi_{\parallel}^s \exp(-t/\tau_{\parallel}), \quad (39)$$

where

$$\chi_{\parallel}^s(0) = \frac{\mu^2 N}{3kT} (2S + 1), \quad (40)$$

is the static susceptibility.

The after effect function  $f_{\parallel}(t)$  [2] is thus

$$f_{\parallel}(t) = \chi_{\parallel}^s \exp(-t/\tau_{\parallel}). \quad (41)$$

The frequency-dependent longitudinal component of the complex susceptibility  $\chi_{\parallel}(\omega) = \chi'_{\parallel}(\omega) - i\chi''_{\parallel}(\omega)$  arising from the imposition of an AC field  $E_1(t) \sim \exp(i\omega t)$  may then be written down (since we have limited the solution to terms linear in  $E_1$ ) from linear response theory [2] as

$$\begin{aligned} \chi_{\parallel}(\omega) &= f_{\parallel}(0) - i\omega \int_0^{\infty} f_{\parallel}(t) \exp(-i\omega t) dt \\ &= \frac{\chi_{\parallel}^s(0)}{1 + i\omega\tau_{\parallel}}. \end{aligned} \quad (42)$$

We then find just as for the parallel case that the complex susceptibility  $\chi_{\perp}(\omega)$  for a small transverse field  $E_1(t) \sim \exp(i\omega t)$  is

$$\chi_{\perp}(\omega) = \frac{\chi_{\perp}^s}{1 + i\omega\tau_{\perp}}, \quad (43)$$

where the static susceptibility  $\chi_{\perp}^s$  is given by

$$\chi_{\perp}^s(0) = \frac{\mu^2 N}{3kT} (1 - S). \quad (44)$$

## 6. Discussion and conclusions

We have shown how general formulae for  $\tau_{\parallel}$  and  $\tau_{\perp}$  (valid for an arbitrary uniaxial potential of the crystalline anisotropy) may be calculated directly in terms of the equilibrium order parameter  $S$  from the Langevin equation. That equation being regarded as a stochastic nonlinear equation of the Stratonovich type. This eliminates the complicated mathematical analysis which arises from the Fokker-Planck equation. Our approach is based on a well-defined method (that of Morita [13] or the effective eigenvalue [9]) of reducing the  $n$ th order characteristic equation of the system to one of the first order. The relaxation of the polarization components is thus characterized by a single effective eigenvalue or weighted decay rate so allowing a precise definition of the term 'relaxation time of the polarization' when an external potential is present. The effective eigenvalues  $\lambda_{\parallel}$  and  $\lambda_{\perp}$  give precise information on the initial decay of the polarization components.

Equation (36) is in qualitative agreement with available experimental data (see, for example, [16]) and with previous theoretical estimates [1, 15, 17], from which it follows that the relaxation time  $\tau_{\parallel}$  increases and  $\tau_{\perp}$  decreases in nematic liquid crystals as compared to the Debye relaxation time in the isotropic phase.

The effective eigenvalue may be defined in the context of the Sturm–Liouville equation as [9]

$$\lambda_{\text{eff}} = \frac{\sum_k \lambda_k C_k}{\sum_k C_k}, \quad (45)$$

where  $\lambda_k$  and  $C_k$  are the eigenvalues and their corresponding weight coefficients (amplitudes). We reiterate that it is usually very difficult to evaluate  $\lambda_{\text{eff}}$  from this formula using the Sturm–Liouville equation as a knowledge of the law of formation of the eigenvalues and their corresponding amplitudes is required. The approach we have used in this paper just as in [9] does not attempt to calculate  $\lambda_{\text{eff}}$  by explicitly calculating the eigenvalue spectrum as required by equation (45) rather it gives  $\lambda_{\text{eff}}$  in terms of the equilibrium average  $S$ . It should be noted that a global characterization of the polarization decay is given by the relaxation times  $T_{\parallel}$  and  $T_{\perp}$ , defined as

$$T_{\gamma} = \frac{\int_0^{\infty} \langle \mu_{\gamma}(t) \rangle dt}{\langle \mu_{\gamma}(0) \rangle}, \quad (\gamma = \parallel, \perp).$$

As noted in [9] this correlation time also includes contributions from all the eigenvalues, but it gives no information on possible different time regimes of relaxation. The behaviour of  $T_{\gamma}$  and  $\tau_{\gamma}$  is sometimes similar. In fact, if a single eigenvalue dominates the relaxation of the polarization,  $T_{\gamma} = \tau_{\gamma}$ . However if different time scales are involved, the behaviour of  $T_{\gamma}$  and  $\tau_{\gamma}$  can be different [9] and in this case  $\tau_{\gamma}$  gives precise information on the initial relaxation of the polarization.

In view of the difficulties associated with the Sturm–Liouville equation it is often assumed that the longest relaxation time of the distribution function accurately represents that of the polarization. This is true only if a single eigenvalue determines the relaxation process. In all other cases the reciprocal of the effective eigenvalue yields a more accurate description of the relaxation process since it includes the weighted contributions from all the other eigenvalues associated with the relaxation. Note that equation (28) was originally given by Meier [18] for the special case of a  $\cos^2 \vartheta$  potential.

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