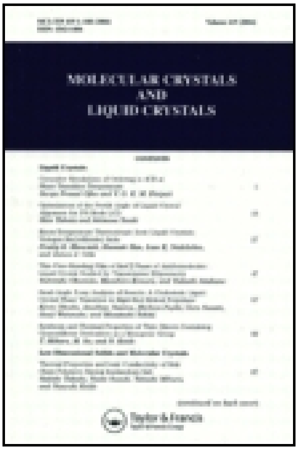

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DIELECTRIC RELAXATION THEORY IN NEMATIC LIQUIDS†

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The dipole relaxation behaviour in liquid crystals as a function of the molecular ordering has been interpreted theoretically. The decay function of the electric dipole polarization has been calculated in terms of the correlation function of the Wigner rotation matrices. The orientational potential energy function has been expanded as a series of Legendre polynomials, and the contributions of the various terms investigated.

1. INTRODUCTION

Dielectric dispersion in nematic liquid crystals, macroscopically oriented by a magnetic field, occurs at very different frequency regions when the electric field is parallel and perpendicular to the orientational axis of the mesophase [1–3]. An anomalously large temperature shift of the relaxation frequency is especially observed when the electric field is parallel to the direction of preferred alignment. This effect has been ascribed [4] to the hindrance of the reorientations of the long molecular axis, due to the strong orienting forces acting in the nematic state.

In recent studies [5] we have examined theoretically molecular rotational diffusion in the liquid crystalline state to interpret relaxation effects in magnetic resonance experiments.

The understanding of any relaxation process requires knowledge of the correlation function of the time-dependent variables associated with the process. The treatment proposed for the magnetic relaxation can be

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adapted in a general way to the study of different kinds of relaxation phenomena. Therefore its extension to the dielectric case provides a test of the assumptions underlying the theory, especially those concerning the nature of the orienting forces in a nematic mesophase.

Martin *et al.* [6] have developed the interpretation of Meier and Saupe [4] by extending the Debye theory of dipole relaxation to nematic liquids. The present approach, based on the evaluation of the time correlation function of the fluctuating molecular dipole components, is mathematically more general and makes allowance in a very simple way for various forms of the orienting potential and the effects of the diffusion tensor.

2. DIELECTRIC RELAXATION

The basic theoretical interpretation of the dielectric relaxation phenomenon is founded on the work of Debye [7] who investigated the behaviour of the orientational part of the polarization in dipolar molecules dissolved in non-polar solvents in an oscillating electric field. The central result of the Debye's theory is the expression for the frequency dependence of the complex dielectric susceptibility:

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega T}, \tag{1}$$

where the macroscopic relaxation time T is related to the characteristic relaxation time τ of the molecular dipoles through the relation

$$T = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\tau. \tag{2}$$

Recent developments [8, 9] based on the Kubo's linear response theory [10], which take into account the dipole–dipole and induced dipole–dipole interactions in a condensed phase, lead to the expression [9]

$$\begin{aligned} \frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} &= \{1 + [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)][L(-\dot{\gamma}_e)^{-1} - 1]\}^{-1}, \\ L(-\dot{\gamma}_e) &= 1 - i\omega \int_0^\infty \gamma_e(t)\exp(-i\omega t)dt, \end{aligned} \tag{3}$$

where $\gamma_e(t)$ is the normalized correlation function of the component of the molecular dipole $\bar{\mu}$ in the direction of the electric field. If the correlation function can be expressed as a single exponential decay, the frequency dependence of ϵ is the same as in equation (1), with

$$T = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty}\tau.$$

When $\gamma_e(t)$ is a sum of exponential decays, the expression for ϵ is a series of terms having the same form as (1), with different dispersion amplitudes and relaxation times.

3. CORRELATION FUNCTION IN NEMATIC MESOPHASE

In the liquid crystalline state the dielectric susceptibility $\epsilon(\omega)$ is an axially-symmetric second rank tensor. The optical axis of the mesophase is the symmetry axis. The dependence of the static principal values of $\epsilon(\omega)$ upon the degree of order has been discussed by Maier and Meier [11]. We shall consider the effect of the molecular ordering on the correlation function $\gamma_e(t)$ when an electric field is directed parallel or perpendicular to the direction of preferential alignment.

Let (XYZ) be a laboratory coordinate system with the Z-axis in the direction of the optical axis of the liquid crystal; (xyz) a molecular coordinate system with the z-axis in the direction of the long molecular axis; $(\alpha\beta\gamma)$ the time fluctuating Euler angles relating the two systems. The components of $\mu(t)$ in the Z and X directions are given by

$$\mu_Z(t) = \sum_p (-1)^p D_{0,-p}{}^1(t)\mu'^{(1,p)},$$

$$\mu_X(t) = \frac{1}{\sqrt{2}}\sum_p (-1)^p [D_{-1,-p}{}^1(t) - D_{1,-p}{}^1(t)]\mu'^{(1,p)},$$

where $D_{lm}{}^j(\alpha\beta\gamma)$ are the Wigner rotation matrix elements [12] and the irreducible spherical tensor components $\mu'^{(1,p)}$ are, in terms of the molecular components $\mu_x,\ \mu_y,\ \mu_z$:

$$\mu'^{(1,0)} = \mu_z,$$

$$\mu'^{(1,\pm 1)} = \mp\frac{1}{\sqrt{2}}(\mu_x \pm i\mu_y).$$

Therefore the problem is reduced to calculate the correlation functions of the Wigner matrices

$$\langle D_{lm}{}^1(0)D_{l'm'}{}^{1^*}(t)\rangle = \int d\Omega_0 D_{lm}{}^1(\Omega_0)P(\Omega_0)\int d\Omega D_{l'm'}{}^{1^*}(\Omega)P(\Omega_0,\Omega;\ t)$$

according to the assumption that the molecular motion is a stationary Markoff process [13].

The distribution function $P(\Omega)$ and the joint probability function $P(\Omega_0,\Omega;\ t)$ are obtained by solving the diffusion equation for molecules subjected to a nematic pseudo-potential V_{N} [5]

$$
\begin{aligned}
&\nabla_{\Omega^2} f + \frac{1}{kT}\,\mathrm{div}[f \text{ grad } V_{\mathrm{N}}],\\
&= \nabla_{\Omega^2} f + \frac{1}{2kT}[\nabla_{\Omega^2} f\, V_{\mathrm{N}} + f(\nabla_{\Omega^2} V_{\mathrm{N}}) - V_{\mathrm{N}}(\nabla_{\Omega^2} f)],\\
&= \mathsf{R}f = \frac{1}{D_\perp}\frac{\partial f}{\partial t}.
\end{aligned}
$$

If the orientating pseudopotential is expressed as a series expansion of Legendre polynomials [5, 14] $V_{\mathrm{N}}/kT = \sum \lambda_n P_n(\cos\ \beta)$ then the general solution of the diffusion equation has the form

$$
\begin{aligned}
f(\Omega, t) &= \sum a_{klm}(0)\exp(D_\perp {\alpha_{lm}}^k t)\psi_{klm}(\Omega),\\
\psi_{klm}(\Omega) &= \sum {X_{jk}}^{lm} {D_{lm}}^j(\Omega).
\end{aligned}
\tag{4}
$$

The matrices X and the roots α_k are obtained by solving, for each set of indices (lm), the eigenvalue problem

$$\mathsf{X}^{-1}\mathsf{R}\mathsf{X} = \boldsymbol{\alpha}.$$

The matrix elements of the operator R in the linear space of the Wigner functions are

$$
\begin{aligned}
{R_{jj'}}^{lm} = &-[j(j+1) + (D_\parallel/D_\perp - 1)m^2]\delta_{jj'}\\
&-\tfrac{1}{2}\sum_n \lambda_n[j(j+1) - j'(j'+1)\\
&+ n(n+1)]C(n, j', j;\ 0, l)C(n, j', j;\ 0, m).
\end{aligned}
\tag{5}
$$

The expression for $P(\Omega_0, \Omega;\ t)$ obtained from equation (4) with the initial condition $f(\Omega, 0) = \delta(\Omega - \Omega_0)$ [5], is

$$P(\Omega_0, \Omega;\ t) = \sum (2i+1){X_{ki}}^{-1(lm)}{X_{jk}}^{(lm)} \exp\ (D_\perp {\alpha_{lm}}^k t){D_{lm}}^{i^*}(\Omega_0){D_{lm}}^j(\Omega).$$

The angular distribution function $P(\Omega)$ is immediately obtained from $P(\Omega_0,\ \Omega;\ t)$ as a limit for $t \to \infty$ [13]. From the structure of the matrices R^{lm} it can be seen that for $l = m = 0$ the lowest root ${\alpha_{00}}^0$ vanishes for any value of the parameters λ_n. It follows that ${X_{0i}}^{-1} = {X_{00}}^{-1}\delta_{0i}$. Therefore we have:

$$P(\Omega) = {X_{00}}^{-1}\sum X_{j0}{D_{00}}^j(\Omega).$$

The required correlation functions are therefore

$$
\begin{aligned}
\langle {D_{lm}}^1(0){D_{lm}}^{1^*}(t)\rangle &= \tfrac{1}{3}\sum(2i+1){X_{ki}}^{-1(lm)}{X_{1k}}^{(lm)} \exp\ (D_\perp {\alpha_{lm}}^k t)\\
&\quad \times \langle {D_{lm}}^1(0){D_{lm}}^{i^*}(0)\rangle,\\
&= \tfrac{1}{3}\sum(2j+1){X_{ki}}^{-1(lm)}{X_{1k}}^{(lm)} \exp\ (D_\perp {\alpha_{lm}}^k t)\\
&\quad \times \langle {D_{00}}^j\rangle C(j, 1, i; 0, l)C(j, 1, i; 0, m),
\end{aligned}
$$

where

$$\langle D_{00}{}^{j}\rangle = X_{00}{}^{-1}X_{j0}/(2j+1).$$

It is easily verified that for $t = 0$ the correlation function reduces to $\langle |D_{lm}{}^{1}|^{2}\rangle$ and for $t = \infty$ it goes to $\langle D_{lm}{}^{1}\rangle^{2}$, as required by the ergodic properties of the random stationary processes [10].

Cross-correlation terms vanish owing to the orthogonality of the Wigner functions. Furthermore, from the symmetry properties of the Clebsch–Gordan coefficients [12] the following equalities hold:

$$\langle D_{lm}{}^{1}(0)D_{lm}{}^{1^*}(t)\rangle = \langle D_{l-m}{}^{1}(0)D_{l-m}{}^{1^*}(t)\rangle = \langle D_{-l-m}{}^{1}(0)D_{-l-m}{}^{1^*}(t)\rangle.$$

For spherical molecules, $D_{\|}/D_{\perp} - 1 = 0$ and

$$\langle D_{lm}{}^{1}(0)D_{lm}{}^{1^*}(t)\rangle = \langle D_{ml}{}^{1}(0)D_{ml}{}^{1^*}(t)\rangle.$$

Finally we obtain

$$\begin{aligned}\langle \mu_Z(0)\mu_Z(t)\rangle &= \langle D_{00}{}^{1}(0)D_{00}{}^{1^*}(t)\rangle \mu_z{}^{2} + \langle D_{01}{}^{1}(0)D_{01}{}^{1^*}(t)\rangle(\mu_x{}^{2} + \mu_y{}^{2}),\\ \langle \mu_X(0)\mu_X(t)\rangle &= \langle D_{10}{}^{1}(0)D_{10}{}^{1^*}(t)\rangle \mu_z{}^{2} + \langle D_{11}{}^{1}(0)D_{11}{}^{1^*}(t)\rangle(\mu_x{}^{2} + \mu_y{}^{2}).\end{aligned} \tag{6}$$

4. CALCULATIONS

Humphries *et al.* [15] have presented a molecular field treatment which, starting from the interactions between the pairs of rod-like molecules composing the mesophase, provides a theoretical justification for the anisotropic pseudo-potential, derived, in a very general way, as a series expansion of Legendre polynomials. They have also shown that the temperature dependence of the orientational order for 4,4′-dimethoxy-azoxybenzene (*p*-azoxyanisole) and 4,4′-diethoxy-azoxybenzene (*p*-azoxyphenetole) can be reproduced very accurately by retaining only quadratic and quartic terms in the potential expansion. Following these authors, we shall use for the two nematogens a potential of the form

$$\begin{aligned}V_N/kT &= \lambda_2 P_2(\cos\beta) + \lambda_4 P_4(\cos\beta)\\ &= \alpha[\langle P_2\rangle P_2(\cos\beta) + \lambda\langle P_4\rangle P_4(\cos\beta)],\end{aligned} \tag{7}$$

where the parameter α is calculated for any given value of the orientational order $\langle P_2\rangle$ and the constant parameter λ is obtained from the condition of vanishing orientational Helmholtz function at the nematic–isotropic transition point. Internal consistency between the values of $\langle P_2\rangle$ and $\langle P_4\rangle$ appearing as coefficients in (7) and the corresponding values calculated from the angular distribution function derived from the potential according to the Boltzmann distribution law, is achieved by an iterative procedure.

With the values of the parameters λ_2 and λ_4 so obtained, the matrices R^{lm} have been built according to equation (5). The diagonalization has been performed on matrices of order 30, to guarantee convergence in the final results.

An inspection of the behaviour of the various eigenvalues of the matrices R^{lm} for increasing value of the nematic order, shows that in the interval of interest (0.3–0.7) only the lowest odd root $\alpha_{lm}{}^1$ determines the exponential decay of $\gamma_e(t)$. Thus, as a very good approximation, the correlation function of $D_{lm}{}^1$ can always be characterized by a single relaxation time. Figure 1 shows the dependence upon the orientational order $\langle P_2 \rangle$ of the absolute value of the lowest odd root of the matrices R^{00}, R^{01}, R^{11}, obtained from the potential used by Humphries *et al.* for *p*-azoxyanisole and *p*-azoxyphenetole.

In Figure 2 is presented the behaviour of the same roots, calculated by keeping the ratio λ_4/λ_2 constant and equal to $\pm\frac{1}{3}$ and zero. All of the values have been calculated with $D_\parallel/D_\perp = 1$: the inclusion of the diffusion tensor anisotropy into equation (5) shifts of an amount $(D_\parallel/D_\perp - 1)$ the absolute

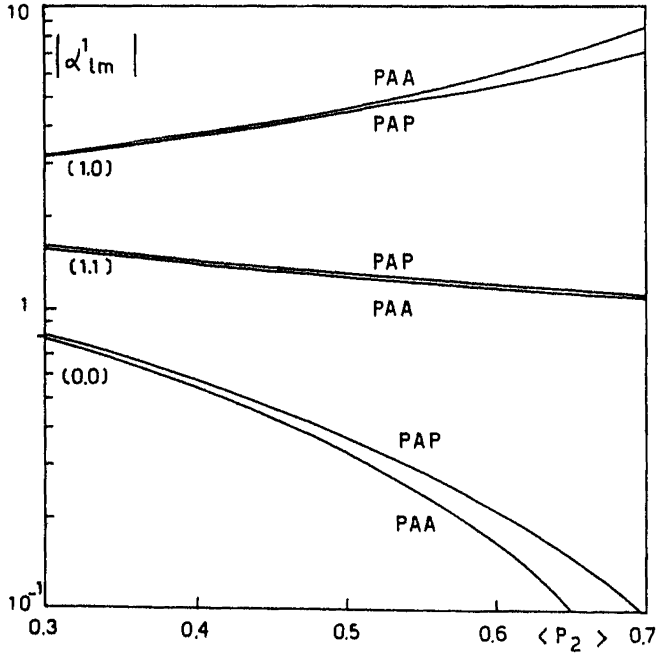

FIGURE 1 Dependence upon the orientational order $\langle P_2 \rangle$ of $\alpha_{00}{}^1, \alpha_{01}{}^1$ and $\alpha_{11}{}^1$ calculated from the potential of Humphries *et al.* for *p*-azoxyanisole (PAA) and *p*-azoxyphenetole (PAP).

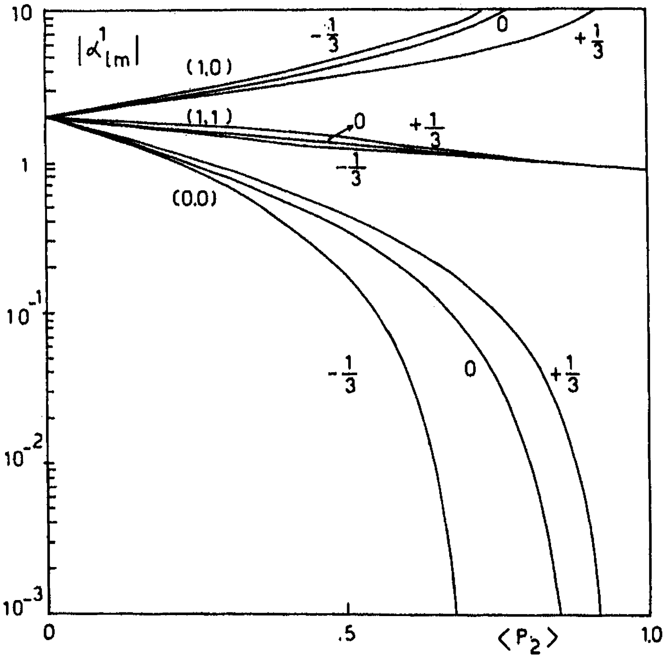

FIGURE 2 Dependence upon the orientational order $\langle P_2 \rangle$ of ${\alpha_{00}}^1, {\alpha_{01}}^1$ and ${\alpha_{11}}^1$ calculated with $\lambda_4/\lambda_2 = 0, \pm 1/3$.

value of the roots corresponding to the matrices R^{01} and R^{11}. It has the effect of increasing the difference $|{\alpha_{01}}^1 - {\alpha_{00}}^1|$ and decreasing $|{\alpha_{10}}^1 - {\alpha_{11}}^1|$.

An approximate value $D_{\parallel}/D_{\perp} = 4$ can be calculated from the molecular dimensions [16].

5. RESULTS AND DISCUSSIONS

A complete set of experimental data is available only for *p*-azoxyanisole [2,6]. Two sharp dispersion regions are observed when the electric field is parallel to the optical axis of the mesophase, whereas only one dispersion region occurs at any temperature within the nematic range when the field is applied perpendicularly.

The dipole moment vector in a *p*-azoxyanisole molecule makes an angle of approximately 60° with the long molecular axis [17]. Therefore, according to equation (6), the frequency dependence of the complex dielectric susceptibility is determined in both cases by two relaxation times. Moreover, the free rotation of the polar end groups produces an additional dispersion region overlapping the high frequency region of dispersion due to the fixed azoxy group dipole moment [4].

In general, the dispersion frequencies and intensities will be complicated functions of the calculated eigenvalues and their relative weight in the correlation function. The situation is particularly complex when the electric field is applied in the X-direction, because the values of ${\alpha_{10}}^1$ and ${\alpha_{11}}^1$ are very near and the dispersions are not resolved. A distribution of relaxation times in the same frequency region accounts for the non-vanishing β value in the Cole–Cole diagrams [2, 18].

The analysis is simplified if the dispersion regions are widely separated, and for this reason we focus our attention on the results obtained with the electric field parallel to the axis of preferred alignment of the mesophase. In this case, from the experimental values of the frequencies and intensities of the two dispersion regions corresponding to $\langle P_2 \rangle \simeq 0.55$, we obtain:

$$\omega_2/\omega_1 = 170 \quad I_2/I_1 \simeq 2.$$

If we ignore, for lack of information, the effect of the reorientation of the methoxy groups, the following results can be predicted [9]:

$$\omega_2/\omega_1 = F{\alpha_{01}}^1/{\alpha_{00}}^1 \quad I_2/I_1 = ({\mu_x}^2 + {\mu_y}^2)/{\mu_z}^2 F,$$

where $F = 3\bar{\epsilon}_0/(2\bar{\epsilon}_0 + \bar{\epsilon}_\infty)$.

From Figure 1 we obtain for the p-azoxyanisole, with $D_\parallel/D_\perp = 4, {\alpha_{01}}^1/{\alpha_{00}}^1 = 34$.

The ratio $({\mu_x}^2 + {\mu_y}^2)/{\mu_z}^2$ has a value of approximately 3, according to the Maier and Meier calculations [17]. The internal field factor F, that in isotropic systems can only assume values between 1 and $\frac{3}{2}$, has a value 1.2 at $\langle P_2 \rangle = 0.55$ and it is rather insensitive to molecular ordering. It should be modified to take into account the anisotropy of the medium and the molecular shape, but this seems to be a minor correction. Thus, the calculated value of ω_2/ω_1 appears too low of a factor of 4 compared with the experimental value.

$\langle P_2 \rangle$	$\lambda_4 = -\lambda_2/3$	$\lambda_1 = 0$ $\lambda_4 = 0$	$\lambda_4 = \lambda_2/3$	$\lambda_4 = 0$ $\lambda_1 = \pm\lambda_2/3$
$0 \cdot 50$	29 (47)	13 (21)	9 (16)	9 (16)
$0 \cdot 53$	44 (69)	16 (26)	10 (18)	11 (18)
$0 \cdot 57$	97 (146)	22 (34)	13 (22)	14 (23)
$0 \cdot 60$	162 (241)	30 (45)	16 (26)	17 (27)

Values of ${\alpha_{01}}^1/{\alpha_{00}}^1$ for different choices of the nematic pseudopotential and $D_\parallel/D_\perp = 1$ and 4 (in paranthesis).

However, as it can be seen from Figure 2, the ratio ${\alpha_{01}}^1/{\alpha_{00}}^1$ depends strongly upon the sign and the magnitude of the coefficient of the quartic term in the potential expansion. The values of this ratio calculated for different choices of λ_4/λ_2 in the interval 0.5−0.6 of orientational order, are presented in the table.

Satisfactory agreement with the experimental results can be reached with $\lambda_4/\lambda_2 \simeq -\frac{1}{3}$, but it is difficult to justify this value within the framework of the theory of Humphries *et al.* The corresponding value of λ_4/λ_2 deduced from their potential is approximately −1/15 in the same range of $\langle P_2 \rangle$. Thus we could not rationalize values as high as 400 for ω_2/ω_1 reported [2] in the cases of the butyloxy-, hexyloxy-, and heptyloxy-azoxybenzenes, with any reasonable choice of the anisotropy factor $D_{\|}/D_{\perp}$, if λ_4/λ_2 is kept lower than $\frac{1}{3}$ in absolute value.

It may be noted that a positive sign of λ_4/λ_2 is predicted [15] for 4,4′-diethoxy-azoxybenzene. According to our results, the separation between the two dispersion regions should be slightly less than in the case of *p*-azoxyanisole, at the same orientational order. However, dielectric relaxation data are not available for this compound.

We have also tested the effect of a linear term in the potential expansion. Although the coefficients λ_n cannot be associated with certainty to specific intermolecular interactions, it can be presumed that such a term should derive from dipole forces [19].

The introduction of a linear term, as it can be seen from the last column of the table, gives too low values of ${\alpha_{01}}^1/{\alpha_{00}}^1$, contrarily to the result we wish. This may be an argument supporting the idea that the orientational energy is dominated by dispersion forces, and the dipolar forces do not play a significant role.

In conclusion, even if the formal expansion of the pseudopotential which gives the best interpretation of the dielectric relaxation phenomena is not exactly the same of that obtained by Humphries *et al.*, both the calculations emphasize the importance of the quartic contribution to the orientational potential, as already affirmed by the electron spin resonance experiments [5, 14]. The discrepancies in the detailed form of the potential to be used, might be attributed to inherent limitations of the diffusional model, as well as to the approximations introduced in the derivation of the nematic pseudopotential.

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