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A refined model of dielectric relaxation in uniaxial liquid crystals

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A refined approach to dielectric relaxation in uniaxial liquid crystals based on the linear response concept is presented. The model is based on the expansion of the conditional probability function in terms of the probability function evolution operator eigenfunctions (instead of the Wigner functions). As a result, the time dependence of the expansion coefficients $a^j_{lm}(t)$ is not, in general, a single exponential Wigner matrix element autocorrelation function.

1. Introduction

Dielectric relaxation spectra of classical thermotropic liquid crystals usually consists of two well-separated domains for measurements parallel to the order director, and two less obviously separated domains for a perpendicular experimental geometry [1]. Theoretical models which have been proposed to explain the observed spectra have considered a number of different particular mechanisms of molecular rotational motions responsible for the relaxation [2–6]. The most renowned of them, a theory of rotational diffusion by Nordio *et al.* [2], was successfully applied to analyse experimental data by Parneix [1 a] in what has been by all means the most complete experimental study of dielectric relaxation in classical thermotropic liquid crystals.

In a previous paper [7] we outlined a model of dielectric relaxation in uniaxial liquid crystals based on the Kubo linear response theory [8]. The proposed model followed the original idea of Nordio *et al.* [2]; however, we avoided the necessity of specifying mechanisms for the molecular motions involved. As a result, it was shown in [7] that a commonly observed characteristic of dielectric relaxation spectra in liquid crystals should be associated with the structure of the phase (symmetry of a pseudo potential acting on a molecule), rather than a particlar mechanism of the motion. In a sense [7] also offered unified explanation of similar results obtained from different existing models of dielectric relaxation in liquid crystals [2–6].

The development of such a universal approach to dielectric relaxation was necessitated by the synthesis of a new class of liquid-crystalline materials, i.e. the side chain polymer liquid crystals in recent years. Surprisingly, despite the very complicated molecular structure of these polymers, observed dielectric relaxation spectra qualitatively resemble those of classical monomer liquid crystals [1 c, 9–12]. Clearly, steric hindrance prevents a simple reorientation of the side chain mesogenic unit about its long or short axes in the polymer. Reorientations of the unit, if any, are possible only as a result of highly cooperative motions involving both rotation and translation of the unit and of the neighbouring environment. Therefore, any particular assumption about the mechanism of the reorientation in the polymer liquid crystals is doubtful.

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The results of [7] have been used in semiquantitative analysis of experimental data for side chain polysiloxanes [9, 10]. However, despite its apparent success, [7] needs refinement. In the course of the model development a few simplifying assumptions were made, and they will be eliminated in the present paper. The first, the (orientational) conditional probability function $P(\Omega/\Omega_0; t)$, was assumed to be expandable in the basis of Wigner functions (cf. later). This assumption often seems to be justified, but in general, the Wigner functions may not be eigenfunctions of the evolution operator of the probability function. As a consequence of the above assumption, [7] predicted relaxation modes as single exponential correlation functions. The second, the restriction that $P(\Omega/\Omega_0; t)$ has to converge to $P(\Omega)$, the (stationary) distribution function at long times,

$$P(\Omega/\Omega_0; t) \xrightarrow[t \to \infty]{} P(\Omega),$$

has not been considered. As shown later, the above condition enforces important selection rules on the probability function expansion coefficients. For clarity of presentation, in the following section we redevelop the model incorporating the previously mentioned changes and improvements.

2. Theory

In order to investigate how the stochastic rotational dynamics of molecules influences the dielectric spectra of liquid crystals, we apply the linear response concept [2]. Because of the complexity of the local field problem, which has yet to be solved, we make a simplifying assumption by writing a relation between the complex dielectric permittivity, $\hat{\varepsilon}_k(\omega)$, and the correlation function as

$$\hat{\varepsilon}_k(\omega) - \varepsilon_k(\infty) = G_k L_{i\omega}\{-\dot{\gamma}_k(t)\}, \tag{1}$$

where G_k, the total local field factor, is assumed frequency independent, $\gamma_k(t)$ is the unnormalized correlation function of the k component of the dipole moment, ω is the angular frequency, and $\varepsilon_k(\infty)$ denotes the high frequency limit of the dielectric constant, $L_{i\omega}$ denotes the Laplace transform. Neglecting the frequency dependence of the local field factor, we inevitably lose some of the fine details of the cooperative motions leading to dielectric relaxation which are responsible for the detailed frequency dependence of each dielectric relaxation process. However, in [7] and in the present work we are primarily concerned with the complexity of the dielectric spectra of liquid crystals, and we believe that for this purpose the assumption is justified. Hence, the following discussion will be restricted to the behaviour of the dipole moment autocorrelation function [13].

Let the z axis of the molecular frame $\{x, y, z\}$ be the long axis of the molecule, and the Z axis of the laboratory frame $\{X, Y, Z\}$ be the director axis, **n**, of a liquid-crystalline phase. The molecular motion is assumed to be the stochastic stationary Markov process [14] for which the eulerian angles $\Omega = (\alpha, \beta, \gamma)$ of the molecular frame with respect to [2, 7] form a three dimensional stochastic variable. Therefore, a knowledge of the first conditional (orientational) probability distribution function and the stationary distribution function is necessary for calculation of a correlation function of interest. The conditional and stationary probability distribution function should be continuous almost everywhere (in mathematical sense), since employing the assumption of continuity, the (orientational) probability distribution function can be always expanded in terms of any orthogonal and complete set of functions.

Assuming that the probability distribution function, $P(\Omega, t)$, fulfills the equation of evolution

$$\frac{\partial}{\partial t} P(\Omega, t) = \mathbb{D}(\Omega) P(\Omega, t), \tag{2}$$

where $\mathbb{D}$ is the evolution operator for $P(\Omega, t)$. In contrast to [7], we expand $P(\Omega, t)$ in terms of eigenfunctions of $\mathbb{D}$ instead of Wigner matrix elements

$$P(\Omega, t) = \sum_{jlm} b^j_{lm}(t) \Psi^j_{lm}(\Omega) \tag{3}$$

where $b^j_{lm}(t) = b^j_{lm}(0) \exp(\alpha^j_{lm} t)$, and α^j_{lm} are eigenvalues of $\mathbb{D}$. As $P(\Omega, t)$ should be the conditional probability distribution function, the initial condition, $\Omega \equiv \Omega_0$ at $t = 0$, has to be imposed

$$P(\Omega, 0) = \delta(\Omega - \Omega_0), \tag{4}$$

where is the position of the molecule at the initial time. Assuming the completeness of the set of $\Psi^j_{lm}(\Omega)$ functions, we can write [15]

$$\delta(\Omega - \Omega_0) = \sum_{KLM} \Psi^K_{LM}(\Omega) \Psi^{K*}_{LM}(\Omega_0). \tag{5}$$

Substitution of equation (4) into this equation and comparison of the result with equation (3) for $t = 0$, yields

$$b^j_{lm}(0) = \Psi^{j*}_{lm}(\Omega_0), \tag{6}$$

where the use of the orthogonality of the base $\{\Psi^K_{LM}(\Omega)\}$ was made. The conditional probability distribution can be now written as

$$P(\Omega/\Omega_0) = \sum_{jlm} a^j_{lm}(t) \Psi^{j*}_{lm}(\Omega_0) \Psi^j_{lm}(\Omega), \tag{7}$$

where $a^j_{lm}(t)$ are the normalized time dependent coefficients of the expansion; $a^j_{lm}(t) = \exp(\alpha^j_{lm} t)$.

We recall at this point, that in [7] we expanded $P(\Omega/\Omega_0)$ in terms of Wigner functions. Usually such a procedure is justified but since the Wigner function may not be in the general case the eigenfunction of $\mathbb{D}$, the time dependence of the expansion coefficients may not be of a single exponent function.

Since Wigner functions form also the base set of functions in the space of eulerian angles, $\Psi^j_{lm}(\Omega)$ can be expanded in the following way:

$$\Psi^j_{lm}(\Omega) = \sum_{MNJ} W^{jMN}_{lmJ} \frac{\sqrt{(2J+1)}}{\sqrt{(8)}\pi} D^J_{MN}(\Omega). \tag{8}$$

Hence,

$$P(\Omega/\Omega_0) = \sum_{\substack{MNJ \\ LKI \\ jlm}} a^j_{lm}(t) W^{jMN}_{lmJ} W^{jLK*}_{lmI} \frac{\sqrt{(2J+1)}\sqrt{(2I+1)}}{8\pi^2} D^{I*}_{LK}(\Omega_0) D^J_{MN}(\Omega). \tag{9}$$

Also the one particle stationary orientational probability distribution function is similarly expanded in terms of Wigner functions [1]

$$P(\Omega_0)=\sum_j \frac{2j+1}{8\pi^2}\bar{P}_j D^j_{00}(\Omega), \tag{10}$$

where $\bar{P}_j=\langle P_j(\beta)\rangle$ is the liquid-crystalline phase (orientational) order parameter of j rank, and $P_j(\beta)$ is the Legendre polynomial of j order.

Finally, since we are considering a stationary Markov process, so

$$P(\Omega/\Omega_0;t)\xrightarrow[t\to\infty]{} P(\Omega). \tag{11}$$

Until this point, considerations were quite general, and had not yet involved the symmetry of a liquid-crystalline phase. Since we restrict our attention to uniaxial nematic and smectic phases with point symmetry, the symmetry implies the same symmetry on $P(\Omega_0)$ and, thus, subscript j has to take even values ($j=2k$). Therefore, for uniaxial liquid crystals equation (11) gives in the limit

$$\sum_{\substack{MNJ\\LKI\\jlm}} a^j_{lm}(\infty)W^{jMN}_{lmJ}\,W^{jLK*}_{lmI}\,\frac{\sqrt{(2J+1)}\sqrt{(2I+1)}}{8\pi^2}D^{I*}_{LK}(\Omega_0)D^J_{MN}(\Omega)$$
$$=\frac{1}{8\pi^2}\sum_k(4k+1)\bar{P}_{2k}D^{2k}_{00}(\Omega). \tag{12}$$

From equation (12) it follows that:

(i) the left hand side of equation (12) has to be Ω_0 independent, so all α^j_{lm} have to be negative or equal to 0;

(ii) since equation (4) should be simultaneously fulfilled, only $\alpha^0_{00}=0$, and the following rules are imposed on superscripts and subscripts, and expansion coefficients: $L=M=l$, $K=N=m$, and $W^{000}_{00I}=W^{000}_{000}\delta_{I0}$.

This leads us to the final form of the conditional probability distribution function

$$P(\Omega/\Omega_0)=\sum_{\substack{jlm\\JI}} a^j_{lm}(t)W^{lm}_{jJ}\,W^{lm*}_{jI}\,\frac{\sqrt{(2J+1)}\sqrt{(2I+1)}}{8\pi^2}D^{I*}_{lm}(\Omega_0)D^J_{lm}(\Omega), \tag{13}$$

or, in more compact form

$$P(\Omega/\Omega_0;t)=\sum_{nklm}\Phi^{ln}_{mk}(t)D^{l*}_{mk}(\Omega_0)\,D^n_{mk}(\Omega), \tag{14}$$

where

$$\Phi^{ln}_{mk}(t)=\sum_j a^j_{mk}(t)W^{mk}_{jn}\,W^{mk*}_{jl}\,\frac{\sqrt{(2l+1)}\sqrt{(2n+1)}}{8\pi^2}, \tag{15}$$

and $W^{lm}_{jJ}\equiv W^{jlm}_{lmJ}$.

We are ready now to calculate the dipole moment correlation functions. As usual, the dipole moment in the molecular frame is conviently expressed in terms of components of the first rank irreducible spherical tensor [7, 16]

$$\mu^{(1,0)}=\mu_z \quad\text{and}\quad \mu^{(1\pm1)}=\frac{1}{\sqrt{2}}\mp(\mu_x\pm i\mu_y). \tag{16}$$

The components of the dipole moment in the laboratory frame are then expressed by components in the molecular frame in the following manner [7]:

$$\mu_Z=\sum_k D^1_{0k}(\Omega)\mu^{(1,k)} \quad \text{and} \quad \mu_X=\frac{1}{\sqrt{2}}\sum_k [D^1_{-1k}(\Omega)-D^1_{1k}(\Omega)]\mu^{(1,k)}. \tag{17}$$

By definition, correlation functions of these components are:

$$\langle\mu^*_Z(0)\mu_Z(t)\rangle=\int \mu^*_Z(\Omega_0)\mu_Z(\Omega)P(\Omega/\Omega_0)P(\Omega_0)\,d\Omega\,d\Omega_0 \tag{18 a}$$

$$\langle\mu^*_X(0)\mu_X(t)\rangle=\int \mu^*_X(\Omega_0)\mu_X(\Omega)P(\Omega/\Omega_0)P(\Omega_0)\,d\Omega\,d\Omega_0, \tag{18 b}$$

respectively, and can be explicitly calculated using the orthogonality relations for the Wigner functions [15]:

$$\begin{aligned}\langle\mu_Z(0)\mu^*_Z(t)\rangle={}&\langle D^1_{00}(\Omega_0)D^{1*}_{00}(\Omega)\rangle\cdot\mu_z^2\\&+[\langle D^1_{0-1}(\Omega_0)D^{1*}_{0-1}(\Omega)\rangle+\langle D^1_{01}(\Omega_0)D^{1*}_{01}(\Omega)\rangle]\cdot(\mu_x^2+\mu_y^2)/2,\end{aligned} \tag{19 a}$$

$$\begin{aligned}\langle\mu_X(0)\mu^*_X(t)\rangle 1={}&[\langle D^1_{-10}(\Omega_0)D^{1*}_{-10}(\Omega)\rangle+\langle D^1_{10}(\Omega_0)D^{1*}_{10}(\Omega)\rangle]\cdot\mu_z^2/2\\&+[\langle D^1_{1-1}(\Omega_0)^{1*}_{1-1}(\Omega)\rangle+\langle D^1_{-11}(\Omega_0)D^{1*}_{-11}(\Omega)\rangle\\&+(\langle D^1_{11}(\Omega_0)D^{1*}_{11}(\Omega)\rangle+\langle D^1_{-1-1}(\Omega_0)D^{1*}_{-1-1}(\Omega)\rangle]\cdot(\mu_x^2+\mu_y^2)/4.\end{aligned} \tag{19 b}$$

Correlation functions $\langle D^1_{KL}(\Omega_0)D^{1*}_{KL}(\Omega)\rangle$ can be easily calculated using a formula for the triple integral of Wigner functions [15]

$$\begin{aligned}\langle D^1_{KL}(\Omega_0)D^{1*}_{IJ}(\Omega)\rangle&=\int D^1_{KL}(\Omega_0)D^{1*}_{IJ}(\Omega)P(\Omega/\Omega_0)P(\Omega_0)\,d\Omega\,d\Omega\\&=\sum_{\substack{ln\\mkj}}\frac{(2j+1)}{8\pi^2}\Phi^{ln}_{mk}(t)\bar{P}_j\int D^1_{KL}(\Omega_0)D^{1*}_{IJ}(\Omega)D^j_{00}(\Omega_0)D^{1*}_{mk}(\Omega_0)D^n_{mk}(\Omega)\,d\Omega\,d\Omega_0\\&=\sum_{\substack{ln\\mkj}}\frac{(2j+1)8\pi^2}{(2n+1)(2l+1)}\Phi^{ln}_{mk}(t)\bar{P}_j\delta_{1n}\delta_{mI}\delta_{kJ}C^{lm}_{j01k}C^{lk}_{j01L}\\&=\sum_{jk}\frac{(2j+1)8\pi^2}{(2l+1)3}\Phi^{l1}_{IJ}(t)\bar{P}_jC^{lI}_{j01K}C^{lJ}_{j01L}\end{aligned} \tag{20}$$

where C^{IJ}_{klmn} are the Clebsch–Gordon coefficients. Thus, finally, the dipole moment component correlation functions take the form

$$\langle\mu_z(0)\mu_z(t)\rangle=A_{00}(t)\mu_l^2+A_{01}(t)\mu_t^2 \tag{21 a}$$

and

$$\langle\mu_x(0)\mu_x(t)\rangle=A_{10}(t)\mu_l^2+A_{11}(t)\mu_t^2. \tag{21 b}$$

Substitution of equations (21) into equation (1) yields final results for the complex dielectric permittivity of the liquid-crystalline phase

$$\hat{\varepsilon}_{\parallel}(\omega)-\varepsilon_{\parallel}(\infty)=\frac{G_{\parallel}}{3kT}[\mu_l^2F^l_{\parallel}(\omega;S)+\mu_t^2F^t_{\parallel}(\omega;S)] \tag{22 a}$$

and

$$\hat{\varepsilon}_{\perp}(\omega)-\varepsilon_{\perp}(\infty)=\frac{G_{\perp}}{3kT}[\mu_{\mathrm{l}}^{2}F_{\perp}^{\mathrm{l}}(\omega;S)+\mu_{\mathrm{t}}^{2}F_{\perp}^{\mathrm{t}}(\omega;S)], \tag{22b}$$

where subscripts $\|$ and $\perp$ denote two basic geometries of an experiment: the probing electric field either parallel or perpendicular to the director axis, respectively. $F(\omega;S)$ are Fourier transforms of linear combinations of appropriate correlation functions of Wigner natrices (cf. equation (19)); μ_{l} and μ_{t} denote the longitudinal and transverse components of the molecular dipole moment, $\mu_{\mathrm{l}}^2=\mu_z^2$ and $\mu_{\mathrm{t}}^2=\mu_x^2+\mu_y^2$, respectively.

It has to be emphasized once again, that these results are obtained without any assumption about the mechanism of reorientation, solely benefiting from the point symmetry of the phase.

3. Discussion

We note first of all that all major qualitative results of [7] are recovered in the present version of our model. The model confirms the existence of four relaxation domains in uniaxial liquid-crystalline materials, associated with the structure of the phase (the point symmetry of the potential). Consequently, our work demonstrates that the qualitative agreement of any particular model of stochastic reorientational dynamics with experiment, should not be considered as a convincing confirmation of the appropriateness of the theory but subsequent quantitative considerations are necessary.

Another very important result of [7] which survived the mathematical improvement of our model is the explicit dependence of particular terms in equations (21) upon particular eulerian angles (via correlation functions). Knowing that $D^j_{lm}(\Omega)$ functions are the matrix elements of the rotation operator:

$$\mathbb{R}(\Omega)=\exp(-i\mathbb{J}_z\gamma)\exp(-i\mathbb{J}_x\beta)\exp(-i\mathbb{J}_z\alpha), \quad i=\sqrt{-1}, \tag{23}$$

where $\mathbb{J}_x$, $\mathbb{J}_z$ are the angular momentum operators (x and z components), particular molecular reorientations can be explicitly linked to particular relaxation domains in dielectric spectra [7]. Comparing results of [7]

$$\hat{\varepsilon}_{\|}(\omega)-\varepsilon_{\|}(\infty)=\frac{G_{\|}}{3kT}[(1+2S)\mu_{\mathrm{l}}^{2}F'^{\mathrm{l}}_{\|}(\omega)+(1-S)\mu_{\mathrm{t}}^{2}F'^{\mathrm{t}}_{\|}(\omega)] \tag{24a}$$

and

$$\hat{\varepsilon}_{\perp}(\omega)-\varepsilon_{\perp}(\infty)=\frac{G_{\perp}}{3kT}[(1-S)\mu_{\mathrm{l}}^{2}F'^{\mathrm{l}}_{\perp}(\omega)+(1+S/2)\mu_{\mathrm{t}}^{2}F'^{\mathrm{t}}_{\perp}(\omega)], \tag{24b}$$

with equations (22), shows that the present results are less detailed, i.e. they do not carry the explicit and simple dependence of $[\hat{\varepsilon}_{\|}(\omega)-\varepsilon_{\|}(\infty)]$ and $[\hat{\varepsilon}_{\perp}(\omega)-\varepsilon_{\perp}(\infty)]$ on S, characteristic for equations (24). The form of the final results in [7] followed from an implicit assumption that $P(\Omega/\Omega_0;t)$ can be expanded in terms of Wigner functions, thus expansion coefficients being single exponent functions of time. However, through this assumption an influence of the liquid-crystalline phase symmetry on the dynamic behaviour of the molecule was neglected, and that has been eliminated in the current version of the model.

Despite previously mentioned differences between former and present results, dielectric increments, $\Delta\varepsilon_k = \varepsilon_k(0) - \varepsilon_k(\infty)$, $k = \|$ or $\perp$, calculated from either equations (22) and equations (24) give the same well-known results [1, 7]

$$\Delta\varepsilon_{\|} = \varepsilon_{\|}(0) - \varepsilon_{\|}(\infty) = \frac{G_{\|}}{3kT}[(1+2S)\mu_l^2 + (1-S)\mu_t^2] \tag{25 a}$$

and

$$\Delta\varepsilon_{\perp} = \varepsilon_{\perp}(0) - \varepsilon_{\perp}(\infty) = \frac{G_{\perp}}{3kT}[(1-S)\mu_l^2 + (1+S/2)\mu_t^2]. \tag{25 b}$$

The latter, together with the complex structure of $F_1^j(\omega; S)$'s in equations (22), offer a possible indication of non-Debye-like character of most of the relaxation domains in experimentally observed spectra.

We note also that the procedure which imposes the 'selection rules' on subscripts and superscripts in expansions of probability distribution functions, as a result of restriction

$$P(\Omega/\Omega_0; t) \xrightarrow[t \to \infty]{} P(\Omega),$$

(cf. earlier) is quite general and can be used in order to obtain a qualitative description of dielectric spectra of less symmetric liquid-crystalline phases and this will be done elsewhere.

The final remark concerns the continuity restriction imposed on probability distribution functions. Despite apparent limitations, the model can be used to describe a broad class of reorientational motions, including also molecular dynamics as jumps between some equilibrium states [4], since these are rather jumps between regions than discrete states. It is quite easy to construct an appropriate model for a continuous orientational probability distribution function which has strong and well-separated peaks, so the probability of the passage between remote regions of their domains is greater than for the nearest neighbourhood thus making our formalism applicable.

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