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A. Kozak [a b] , J. K. Moscicki [a c] & G. Williams [b]

[a] Institute of Physics, Jagiellonian University, 31-059 Krakow, Reymonta 4, Poland

[b] University College of Swansea, Department of Chemistry, Singleton Park, Swansea, SA2 8PP, UK

[c] Cornell University, Baker Laboratory of Chemistry, Ithaca, NY, 14853-1301, U.S.A.
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On Dielectric Relaxation in Liquid Crystals

A. KOZAK†‡, J. K. MOSCICKI†§ and G. WILLIAMS‡

† *Institute of Physics, Jagiellonian University, 31-059 Krakow, Reymonta 4, Poland;* ‡ *University College of Swansea, Department of Chemistry, Singleton Park, Swansea SA2 8PP, UK;* § *Cornell University, Baker Laboratory of Chemistry, Ithaca, NY 14853-1301, U.S.A.*

A general expansion of the orientational distribution function in terms of the Wigner matrix is employed in order to calculate dipole moment correlation functions in liquid crystals. It is shown that the qualitative interpretation of dielectric relaxation spectra of liquid crystals is possible without explicit characterization of the molecular motions involved. Thus, a wide range of stochastic motions can be considered within the framework of the model. A fundamental influence of the orientational order of molecules in the liquid-crystalline state on the qualitative form of dielectric spectra is emphasized.

INTRODUCTION

A number of experimental methods are used to study rotational motions of molecules in the condensed matter. These include dielectric relaxation (DR) spectroscopy, which usually gives information on the rotational mobility of molecules, or molecular fragments, having a permanent electric dipole moment.[1] The method is particularly useful in studies of liquid-crystalline substances, which are predominantly built of rigid, elongated polar species or fragments.

Liquid-crystalline materials possess a significant anisotropy of their molecular and bulk properties. It is well known experimentally that dielectric relaxation spectra of liquid-crystalline phases of elongate molecules have rich structures, dependent on how the molecules are oriented with respect to a measuring electric field.[2] For a monodomain sample of a thermotropic liquid crystal, usually prepared mechanically, or by external application of electric and magnetic fields, the dielectric relaxation spectrum for the probing electric field parallel to the (nematic) director (an average direction of the long molecular axis) is composed of two relaxation domains well-separated in frequency; one of them usually is in the range of low MHz, and the second in the range of low GHz frequencies.[2] On an Argand plot of $\varepsilon''(\omega)$ (the dielectric loss factor) against $\varepsilon'(\omega)$ (the dielectric permittivity), where $\omega = 2\pi f$, is the angular frequency of the probing electric field, the low frequency relaxation can be described by the ideal Debye equation, while the high frequency relaxation by the Cole-Cole relationship.[2]

For the probing field perpendicular to the director, the most frequently observed spectrum in thermotropic liquid crystals is a broad single domain at low GHz. Measurements performed on unoriented samples show presence of two dispersion regions, one at low MHz and the other at low GHz frequencies.[2b]

DR-spectra very similar in character were also observed in polymer liquid crystals: thermotropic[3-5] and rod-like lyotropic.[6]

It is believed that dielectric relaxation in liquid crystals is associated with reorientations of permanent molecular dipole moments. A number of different theories of dielectric relaxation in thermotropic liquid crystals have been proposed in the past.[7-10] All these theories are based on assumption about the character of the molecular reorientations involved. A common approach is to use a general expansion of the orientational probability distribution functions. As a result, all models predict four basic modes active in the dielectric relaxation in liquid crystals. Accordingly, observed dispersion regions can be associated with the following molecular reorientations: the low MHz region with the *end-over-end* reorientation of a molecule via either diffusion[7,8,10] or jump processes,[9] the microwave *(GHz)* domains, with diffusional reorientation about the long axis and/or the diffusional fluctuations of the direction of the long axis about the director.[8] Although the theories properly predict a simple Debye relaxation for the low frequency domain, they do not explain the distribution of relaxation times observed at high frequencies.

Such a picture of dielectric relaxation is quite acceptable as long as one considers low molecular mass thermotropic liquid crystals. However, very similar dielectric relaxation spectra are observed also in thermotropic polymer side-chain liquid crystals,[3-5] where steric hindrances prevent a simple reorientation of a side-chain mesogenic unit about its long or short axes. Reorientation of the unit, if any, is possible only as a result of highly cooperative motions involving both rotations and translations of the unit and in the neighboring environment. Because of such a complexity of motions, DR-spectra of polymer liquid crystals are significantly broader and shifted to lower frequencies in comparison with the thermotropic liquid crystals.[2b,3-5] Therefore, any particular assumption about the reorientation mechanism in polymer liquid crystals is doubtful.

Recently we have undertaken theoretical studies of a possible description of dielectric relaxation in liquid crystals, *without* prior specification of the character of motions involved in the process. The basic concepts of our approach have been presented in Reference 5, but the derived results were adapted for a particular use and, therefore, presented in a less general form. Thus, it is the main objective of this paper to present a generalized theory within the framework of the linear response concept.[11] For simplicity, we neglect the intra-molecular motions assuming that a liquid crystalline molecule reorients as a rigid unit. It will be shown that a qualitative interpretation of dielectric relaxation spectra of liquid crystalline phases with the point symmetry of elongated mesogenic molecules (or units), like nematics and high temperature smectics,[12] is possible without specifying the character of the stochastic motions involved. Although the theory presented does not explicitly take into account discrete processes, such stochastic motions can also be considered.[13]

THEORY

In order to investigate dielectric spectra of liquid crystals in terms of the stochastic rotational dynamics of molecules, we apply the linear response theory.[11] Following Luckhurst and Zannoni,[14] a direct relation between the complex dielectric permittivity and the (auto) correlation functions of the principal components of the dipole moment of a liquid crystalline molecule, can be written as:

$$\frac{[\varepsilon_k(\omega) - \varepsilon_k(\infty)]\{\varepsilon_k(\omega) - n_k(\omega)[\varepsilon_k(\omega) - \varepsilon_k(\infty)]\}\varepsilon_k(0)}{[\varepsilon_k(0) - \varepsilon_k(\infty)]\{\varepsilon_k(0) - n_k(0)[\varepsilon_k(0) - \varepsilon_k(\infty)]\}\varepsilon_k(\omega)} = \mathcal{L}_{i\omega}\{-\dot{\Phi}_k(t)\} , \quad (1)$$

where $\varepsilon_k(\omega)$ and $n_k(\omega)$ $(k = \parallel, \perp)$ are the complex electric permittivity and the reaction field factor, and $\omega = 0$ and $\omega = \infty$ denote respectively frequencies much below and above the relaxation domain. $\Phi_k(t)$ is the normalized correlation function of the k-component of the dipole moment and $\mathcal{L}_{i\omega}$ denotes the Laplace transform. Since a problem of the local field is not finally solved,[1,14] many authors restricted their investigations to the behavior of the dipole moment correlation function,[1,2,8] In such a case, Equation (1) takes a form:

$$\varepsilon_k(\omega) - \varepsilon_k(\infty) = G_k \mathcal{L}_{i\omega}\{-\dot{\gamma}_k(t)\} , \quad (2)$$

Where G_k is the total local field factor and assumed frequency independent, the $\gamma_k(t)$ is the unnormalized correlation function of the appropriate component of the dipole moment.

Usually, a particular model of stochastic dynamics is necessary in order to calculate the appropriate probability distribution functions.[7-9] An advantage of the present approach is the absence of any assumption about the particular mechanism of molecular motions and, thus, about the reorientation of dipole moments.

Let us consider a homogeneously ordered sample of a liquid crystalline phase, which from now will be referred to a momodomain sample. Let the z-axis of the molecular frame $(mf[x,y,z])$ be the long axis of the molecule and the Z-axis of the domain (laboratory) frame (DF[X,Y,Z]) be along the nematic director ($\hat{n}$) of the liquid crystalline phase. Let us next assume that the molecular motion is a stochastic stationary Markov process[16] for which a set of Eulerian angles $\Omega = (\alpha, \beta, \gamma)$ of mf with respect to DF[17] forms a three-dimensional stochastic variable. Then, the only information necessary to calculate correlation functions are (i) the first conditional probability distribution function and (ii) the stationary distribution function.[16] Next, we assume that the conditional and stationary probability distribution functions are continuous almost everywhere (in mathematical sense).[18]

Employing the assumption of continuity, we can always expand the (orientational) probability distribution function in terms of any orthogonal and complete set of functions. Therefore, assuming that the probability distribution function, $P(\Omega,t)$, fulfills the equation of evolution:

$$\frac{\partial}{\partial t} P(\Omega, t) = \Re_\Omega P(\Omega, t) , \tag{3}$$

where $\Re_\Omega$ is the evolution for $P(\Omega, T)$, we expand $P(\Omega, T)$ in terms of Wigner matrix elements[19]:

$$P(\Omega, t) = \sum_{jlm} b^j_{lm}(t) \mathcal{D}^j_{lm}(\Omega) . \tag{4}$$

Since $P(\Omega, t)$ should be the conditional probability distribution function, the initial condition has to be imposed:

$$P(\Omega, 0) = \delta(\Omega - \Omega_o) , \tag{5}$$

Ω_o being the position of the molecule at the initial time. Because of the completeness of the set of Wigner functions one can write[19]:

$$\delta(\Omega - \Omega_o) = \sum_{KLM} \frac{2K+1}{8\pi^2} \mathcal{D}^K_{LM}(\Omega) \mathcal{D}^{K*}_{LK}(\Omega_o) . \tag{6}$$

Substitution of Equation (6) into Equation (5) and comparison with (4) for $t = 0$ yields

$$b^j_{lm}(0) = \frac{2j+1}{8\pi^2} \mathcal{D}^j_{lm}(\Omega_o) , \tag{7}$$

where we benefited from the orthogonality of Wigner functions. The conditional probability distribution can be now written as:

$$P(\Omega / \Omega_o) = \sum_{jlm} a^j_{lm}(t) \frac{2j+1}{8\pi^2} \mathcal{D}^{j*}_{lm}(\Omega_o) \mathcal{D}^j_{lm}(\Omega) , \tag{8}$$

where $a^j_{lm}(t)$ are normalized correlation functions of $\mathcal{D}^j_{lm}(\Omega)$:

$$a^j_{lm}(t) = \frac{\langle \mathcal{D}^{j*}_{lm}(\Omega_o) \mathcal{D}^j_{lm}(\Omega) \rangle}{\langle \mathcal{D}^{j*}_{lm}(\Omega_o) \mathcal{D}^j_{lm}(\Omega_o) \rangle} , \tag{9}$$

so $a^j_{lm}(0) = 1$. Similarly, the one-particle stationary orientational probability distribution function can be expanded[18]:

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

where $\mathcal{P}_j = \langle P_j(\beta) \rangle$ is the jth orientational order parameter of the liquid crystalline phase and $P_j(\beta)$ is the Legendre polynomial of the order of j. Until this point our considerations have been quite general. We limit now our attention to liquid crys-

talline phases with the point symmetry, what implies the same symmetry of $P(\Omega_o)$ and, thus, subscript j has to take only even values.

We can now calculate the correlation functions of interest. Components of the dipole moment in mf can be conveniently expressed in terms of components of the first rank irreducible spherical tensor[8,15]:

$$\mu^{(1,0)} = \mu_z \quad \text{and} \quad \mu^{(1,\pm 1)} = \mp \frac{1}{\sqrt{2}} (\mu_x \pm {}^i\mu_y). \tag{11}$$

The components of the dipole moment in DF are then expressed by the components in mf in the following manner[5]:

$$\mu_Z(\Omega) = \sum_k \mathcal{D}^1_{0k}(\Omega)\mu^{(1,k)} ,$$

$$\mu_X(\Omega) = \sum_k [\mathcal{D}^1_{-1k}(\Omega) - \mathcal{D}^1_{1k}(\Omega)]\mu^{(1,k)} . \tag{12}$$

Autocorrelation functions of these components are defined as:

$$\langle \mu_Z^*(0)\mu_Z(t) \rangle = \int \mu_Z^*(\Omega_o)\mu_Z(\Omega)P(\Omega/\Omega_o)P(\Omega_o)d\Omega d\Omega_o$$

$$\langle \mu_X^*(0)\mu_X(t) \rangle = \int \mu_X^*(\Omega_o)\mu_X(\Omega)P(\Omega/\Omega_o)P(\Omega_o)d\Omega d\Omega_o \tag{13}$$

and can be explicitly calculated using the orthogonality relations and the formula for the triple integrals of Wigner functions[15]:

$$\langle \mu_Z^*(0)\mu_Z(t) \rangle = \sum_{\substack{ki \\ jJ \, ml}} \left[\frac{(2J+1)(2j+1)}{64\pi^4} a^J_{ml}(t)\overline{P}_j \mu^{(1,k)*}\mu^{(1,i)} \times \right.$$

$$\left. \int \mathcal{D}^{1*}_{0k}(\Omega)\mathcal{D}^1_{0i}(\Omega)\mathcal{D}^j_{00}(\Omega_o)\mathcal{D}^{J*}_{ml}(\Omega_o)\mathcal{D}^J_{ml}(\Omega)d\Omega d\Omega_o \right]$$

$$= \sum_{\substack{ki \\ jJ \, ml}} (2j+1)a^j_{ml}(t)\overline{P}_j \mu^{(1,k)*}\mu^{(1,i)}\delta_{1J}\delta_{0m}\delta_{il}C^{10}_{j0Jm}C^{1k}_{j0Jl}$$

$$= \sum_{jkl}(2j+1)a^1_{0l}(t)\overline{P}_j \mu^{(1,k)*}\mu^{(1,l)}C^{10}_{j010}C^{1k}_{j01l}$$

$$= \frac{1}{3}\sum_{lk}a^1_{0l}(t)\mu^{(1,k)*}\mu^{(1,l)}(C^{10}_{0010}C^{1k}_{001l} + 5\overline{P}_2 C^{10}_{2010}C^{1k}_{201l}$$

$$= \frac{1}{3}\left\{ a^1_{00}(t)(1+2S)\mu_z^2 + [a^1_{01}(t) + a^1_{0-1}(t)](1-S)(\mu_x^2 + \mu_y^2)/2 \right\} \tag{14}$$

where C are the Clebsch-Gordan coefficients, and $S = \bar{\mathcal{P}}_2$ is the nematic order parameter. Thus, the correlation function can be written in the form:

$$\langle \mu_Z^*(0)\mu_Z(t)\rangle = \frac{1}{3}[(1 + 2S)A_{00}(t)\mu_z^2 + (1 - S)A_{01}(t)(\mu_x^2 + \mu_y^2)] \, . \qquad (15)$$

Similar calculation yields the correlation function for the X-component:

$$\langle \mu_X^*(0)\mu_X(t)\rangle = \frac{1}{3}[(1 - S)A_{10}(t)\mu_z^2 + (1 + S/2)A_{11}(t)(\mu_x^2 + \mu_y^2)] \, , \qquad (16)$$

where:

$$A_{00}(t) \ = \ a_{00}^1(t) \, , \qquad\qquad\qquad\qquad (17)$$

$$A_{01}(t) \ = \ (a_{01}^1(t) + a_{0-1}^1)/2 \, , \qquad\qquad (18)$$

$$A_{10}(t) \ = \ (a_{10}^1(t) + a_{-10}^1)/2 \, , \qquad\qquad (19)$$

$$A_{11}(t) \ = \ a_{11}^1(t) + a_{1-1}^1 + a_{-11}^1(t) + a_{-1-1}^1 \, , \qquad (20)$$

and $a_{lm}^j(t)$ are the normalized correlation functions of $\mathcal{D}_{lm}^j(\Omega)$, cf. Equation (9).

Respective substitution of Equations (15) and (16) to Equation (2) finally yields formulas for the complex dielectric permittivity of the liquid crystalline phase:

$$\varepsilon_{\|}(\omega) - \varepsilon_{\|}(\infty) = \frac{G_{\|}}{3kT}[(1 + 2S)\mu_l^2 \mathcal{F}_{\|}^l(\omega) + (1 - S)\mu_t^2 \mathcal{F}_{\|}^t(\omega)] \, , \qquad (21)$$

and

$$\varepsilon_{\perp}(\omega) - \varepsilon_{\perp}(\infty) = \frac{G_{\perp}}{3kT}[(1 - S)\mu_l^2 \mathcal{F}_{\perp}^l(\omega) + (1 + S/2)\mu_t^2 \mathcal{F}_{\perp}^t(\omega)] \, , \qquad (22)$$

where subscripts $\|$ and $\perp$ denote measurements with the electric field either parallel or perpendicular to the director axis, respectively. $\mathcal{F}(\omega)$ are Fourier transforms of linear combinations of the appropriate correlation functions of Wigner matrices, and μ_l and μ_t denote the longitudinal and transverse components of the molecular dipole moment, $\mu_l^2 = \mu_z^2$ and $\mu_t^2 = (\mu_x^2 + \mu_y^2)/2$, respectively. It has to be emphasized that these results are obtained without any assumption about a mechanism of reorientation, instead relying solely on the point symmetry of the phase.

It is also useful to calculate the DR-spectrum from an unoriented or partially oriented liquid crystalline sample, since measurements on such samples have been performed for low and high molecular mass thermotropic liquid crystals in the phase.[3,5,23] To do so, we follow the approach proposed by Attard.[25] Let us then assume that (i) a sample is in a liquid crystalline state but it has a polydomain nature, (although a polydomain is a very crude approximation of a liquid crystalline

phase, the local direction of the director persists over sufficiently long distances to justify the assumption for the present needs), (ii) the domains are orientationally disordered, so the sample is macroscopically unoriented, (iii) the orientational distribution of molecules within a domain is homogeneous and this distribution is not influenced by the disorder of domains, and (iv) the macroscopic disorder of domains does not influence the molecular dynamics of a single molecule.

The DR-spectrum is detected in the laboratory frame and thus, it results from projection of the correlation functions of different components of the dipole moment onto this frame. In order to calculate the spectrum for a polydomain sample, we introduce the following convention of coordinate systems. Let the Z-axis of the laboratory frame (LF) be parallel to the probing electric field and the z-axis of the local frame within each domain (DF) be along the director of the domain. The molecular frame remains defined as before. Since each domain is considered a monodomain, the relations between the first rank spherical tensor elements of the dipole moment in the molecular and the domain frame are the same as developed above for monodomain samples, and can be used in a straightforward way. However, the appropriate relations between LF and DF have to be established.

Let $\mathcal{O}$ denote a set of Euler angles between DF and LF, and $u^{(1,k)}$ the first rank spherical tensor elements of the molecular dipole moment in DF (not in $mf!$). The Z-component of the dipole moment in LF can be then written as ($cf.$ Equation (12)):

$$\mu_Z = \mu_{LF}^{(1,0)} = \sum_k \mathcal{D}_{0k}^j(\mathcal{O})u^{(1,k)} \, , \tag{23}$$

so the correlation function of this component is:

$$\langle \mu_Z^*(0)\mu_Z(t)\rangle = \sum_{lk} \langle \mathcal{D}_{0k}^{1*}(\mathcal{O})\mathcal{D}_{0k}^1(\mathcal{O})\rangle_{dir} \langle u^{(1,k)*}(0)u^{(1,l)}(t)\rangle$$

$$= \frac{1}{3}\sum_{jkL}(2j+1)\overline{P}_j \langle \mathcal{D}_{0k}^{1*}(\mathcal{O})\mathcal{D}_{0k}^1(\mathcal{O})\rangle_{dir} C_{j01k}^{1k} C_{j01L}^{1L} a_{kL}^1(t)u^{(1,L)*}u^{(1,L)} \tag{24}$$

Utilizing results for a monodomain sample we obtain

$$\langle \mu_Z^*(0)\mu_Z(t)\rangle = \frac{1}{3}\langle \mathcal{D}_{00}^{1*}(\mathcal{O})\mathcal{D}_{00}^1(\mathcal{O})\rangle_{dir} \times$$

$$\{a_{00}^1(t)(1+2S)\mu_t^2 + [a_{01}^1(t) + a_{0-1}^1(t)](1-S)\mu_t^2/2\} +$$

$$\frac{1}{3}\langle \mathcal{D}_{01}^{1*}(\mathcal{O})\mathcal{D}_{01}^1(\mathcal{O})\rangle_{dir} \times$$

$$\{a_{10}^1(t)(1-S)\mu_l^2 + [a_{11}^1(t) + a_{1-1}^1(t)](1+S/2)\mu_t^2/2\} +$$

$$\frac{1}{3}\langle \mathcal{D}_{0-1}^{1*}(\mathcal{O})\mathcal{D}_{0-1}^1(\mathcal{O})\rangle_{dir} \times$$

$$\{a_{-10}^1(t)(1-S)\mu_l^2 + [a_{-11}^1(t) + a_{-1-1}^1(t)](1+S/2)\mu_t^2/2\} \, . \tag{25}$$

$\langle \ \rangle_{dir}$ denotes an average over the *director* distribution (orientational distribution of domains). Using a formula for the product of Wigner functions,[17] it can be shown that:

$$\langle \mathcal{D}^1_{00}(\mathcal{O})\mathcal{D}^1_{00}(\mathcal{O})\rangle_{dir} = (1 + 2\langle \mathcal{D}^2_{00}\rangle_{dir}) \,, \tag{26}$$

and

$$\langle \mathcal{D}^{1*}_{0-1}(\mathcal{O})\mathcal{D}^1_{0-1}(\mathcal{O})\rangle_{dir} = \langle \mathcal{D}^{1*}_{01}(\mathcal{O})\mathcal{D}^1_{01}(\mathcal{O})\rangle_{dir} = (1 - \langle \mathcal{D}^2_{00}\rangle_{dir}) \,. \tag{27}$$

Combining Equations (25), (36) and (27), the correlation function of μ_Z is given by:

$$\langle \mu^*_Z(0)\mu_Z(t)\rangle \ = \ \frac{1}{3}(1 + 2\langle \mathcal{D}^2_{00}\rangle_{dir})\langle u^*_z(0)u_z(t)\rangle +$$
$$\frac{2}{3}(1 - \langle \mathcal{D}^2_{00}\rangle_{dir})\langle u^*_x(0)u_x(t)\rangle \,, \tag{28}$$

where $\langle \mu^*_k\mu_k\rangle$ are correlation functions of the k-component of the dipole moment in DF and are given respectively by Equations (15) and (16). The correlation function of μ_X can be calculated in the same way; however, for an unoriented sample it does not add any new information to that already obtained.

Combining Equations (21) and (14) we can write down Eq.(28) in Equation (2) and making use of Equations (21) and (22), we can write the complex dielectric permittivity of the macroscopically disordered sample:

$$\varepsilon(\omega) - \varepsilon(\infty) = \frac{1}{3}(1 + 2S_d)[\varepsilon_\|(\omega) - \varepsilon_\|(\infty)] + \frac{2}{3}(1 - S_d)[\varepsilon_\perp(\omega) - \varepsilon_\perp(\infty)] \,, \tag{29}$$

where $S_d = \langle D^2_{00}\rangle_{dir}$ is the *director* order parameter in respect to the measuring electric field (it should not be confused with the nematic order parameter, S).

DISCUSSION

An explicit dependence of particular terms in Equations (21) and (22) upon particular Euler angles enables direct qualitative interpretation of dielectric spectra of liquid crystals. Since the $\mathcal{D}^j_{lm}(\Omega)$ functions are the matrix elements of the rotation operator;

$$\mathcal{R}(\Omega) = e^{-iJ_z\gamma}e^{-iJ_x\beta}e^{-iJ_z\alpha} \,, \tag{30}$$

where J_x and J_z are x and z components of the angular momentum operator, it is easy now to link appropriate changes of Euler angles with a particular domain of relaxation, see Figure 1.
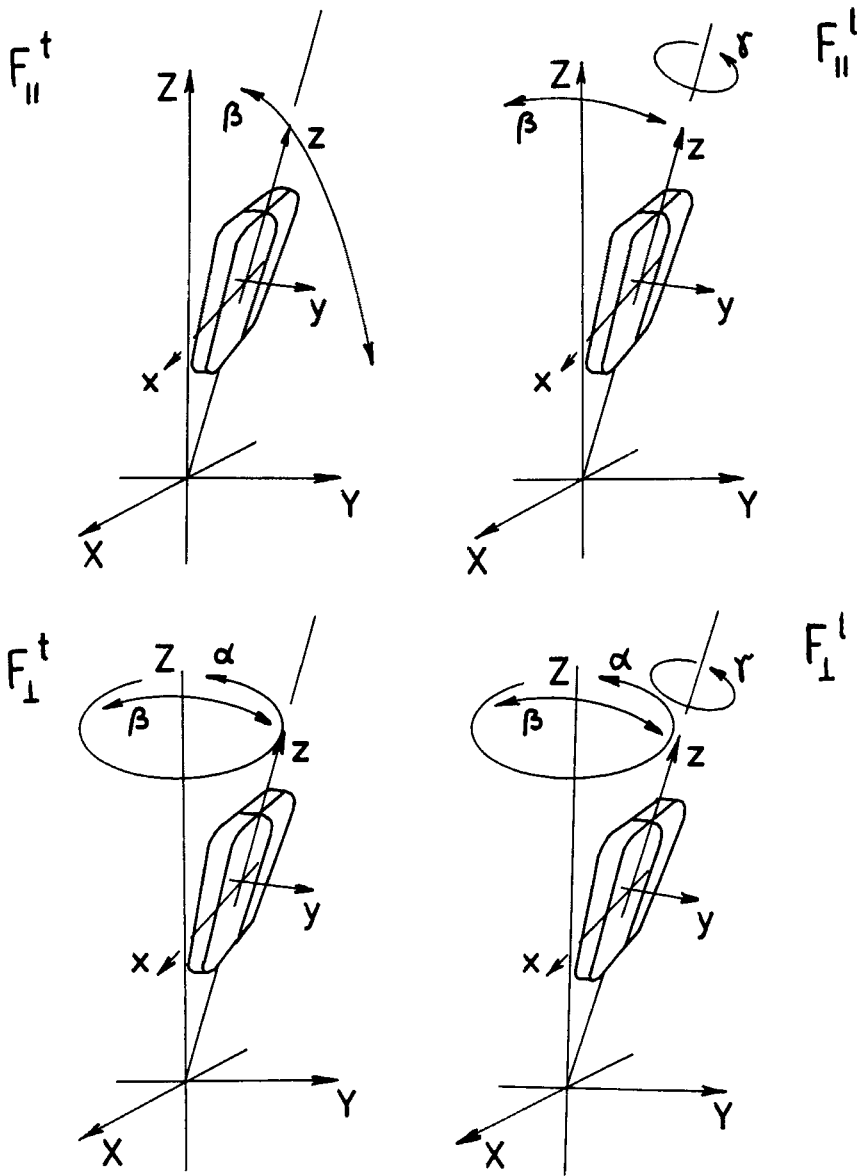
FIGURE 1   Schematic representation of the four modes active in the dielectric spectra of liquid crystals.

Let us first consider the case when the probing field is parallel to the nematic director, *cf.* Equation (21). $\mathcal{F}_\parallel^l$ is associated with reorientations of the longitudinal component of the dipole moment. Because of the amplitude of this process, this domain should be associated with large-scale reorientations of the long axis, i.e., "rotations" of the mesogenic unit about the short axis, as schematically indicated

in Figure 1a. It is in agreement with an interpretation already presented by many authors for low molecular mass thermotropic liquid crystals.[2,21,23] However, the quotation marks have been put down purposely, in order to signify that it does not need to be strictly a simple rotation about the short axis. Any significant change of the β angle with respect to LF should contribute to this relaxation domain. For example, in liquid crystalline side-chain polymers recently so vigorously studied, where polar mesogenic units are attached to the backbone chain by flexible spacers, pure rotation about the short axis is topologically restricted. There is, however, a possibility of a large scale reorientation of the long axis of the mesogenic unit, but only together with the space.[24] Such a process may also involve a section of the backbone chain.

The second domain observed in the parallel geometry described by $\mathscr{F}_{\parallel}^{t}$ results from molecular reorientation about the z-axis of the molecular frame (the long axis of molecule), which can easily be verified by the dependence of the appropriate a_{jk}^{1} correlation functions on the Euler angles, see Equation (9) and Figure 1b. The dielectric relaxation signal from reorientation of the perpendicular component (μ_{t}) of the dipole moment is "visible" in this direction, only when the long axis of the molecule is tilted with respect to the direction ($S < 1$). Rotating about the long axis, the molecule changes then a direction of the perpendicular component of the dipole moment with respect to the laboratory Z-axis, thus giving the additional relaxation domain. Since the rotation about the long axis is only slightly influenced by the presence of a liquid crystalline orienting potential, the dielectric relaxation time characteristic of this domain should be of the same order as in the isotropic phase of the material. Such correlation is indeed observed experimentally in thermotropic low molecular mass liquid crystals.[2,21,22] Again, the term "rotation" is used above in a general sense and means a stochastic change of the appropriate angle. Such changes can be quite complicated processes in polymers with mesogenic units laterally attached to side-chain spaces,[4] where the reorientation of the mesogen unit about its long axis is strongly topologically constrained.

When the measuring electric field is perpendicular to the director axis, Equation (22) also predicts the appearance of two relaxation domains, see Figures 1c and 1d. The first one, described by $\mathscr{F}_{\perp}^{t}$, results from changes of a projection of the longitudinal component of the dipole moment on the direction of the probing field,

TABLE I

Explicit form of $D_{mk}^{1}(\beta)$ functions†

$m\backslash k$	1	0	-1
-1	$(1 + \cos\beta)/2$	$-\sin\beta/\sqrt{2}$	$(1 - \cos\beta)/2$
0	$\sin\beta/\sqrt{2}$	$\cos\beta$	$-\sin\beta/\sqrt{2}$
1	$(1 - \cos\beta)/2$	$\sin\beta/\sqrt{2}$	$(1 + \cos\beta)/2$

†The explicit form of the Wigner function of our interest is: $\mathcal{D}_{mk}^{j}(\alpha,\beta,\gamma) = e^{-im\alpha}d_{mk}^{j}e^{-ik\gamma}$.

and can be associated with a sort of stochastic precession and/or fluctuations of the long molecular axis with respect to the director. Such motions are completely described by the β and γ Euler angles, see Table I and Fig. 1c.

The last term in Equation (22) cannot be clearly identified with a particular rotation of the molecule since it depends on the full set of Euler angles, see Figure 1d. However, knowing that this contribution comes from the perpendicular component of the dipole moment, we notice that the relaxation must be dominated by molecular rotation about the long axis.

An important consequence of the result in Equation (29) is the possibility of deducing the director order parameter from the DR-data. Substituting explicitly the complex dielectric permittivity, $\varepsilon = \varepsilon' - i\varepsilon''$, in Equation (29) we get:

$$S_d = \frac{3[\varepsilon'(\omega) - \varepsilon'(\infty)] - \{[\varepsilon'_{\parallel}(\omega) - \varepsilon'_{\parallel}(\infty)] + 2[\varepsilon'_{\perp}(\omega) - \varepsilon'_{\perp}(\infty)]\}}{2\{[(\varepsilon'_{\parallel}(\omega) - \varepsilon'_{\parallel}(\infty)] - [\varepsilon'_{\perp}(\omega) - \varepsilon'_{\perp}(\infty)]\}}, \qquad (31)$$

for the dielectric permittivity, and

$$S_d = \frac{3\varepsilon''(\omega) - [\varepsilon''_{\parallel}(\omega) + 2\varepsilon''_{\perp}(\omega)]}{2[\varepsilon''_{\parallel}(\omega) - \varepsilon''_{\perp}(\omega)]}, \qquad (32)$$

for the dielectric loss factor. Thus, knowing the dielectric properties of the monodomain sample, we can study the degree of order of a polydomain sample as a function of different external factors (electric or magnetic fields, pressure, flow, heat). Such studies are under way and will be reported elsewhere.[26,27]

FINAL REMARKS

The proposed model offers the qualitative interpretation of dielectric relaxation spectra of liquid crystalline materials. It clearly indicates that the existence of four relaxation domains in liquid crystalline materials should be associated with the structure of the phase (the point symmetry of the potential) rather than with a particular model of reorientational motion. Therefore, the qualitative agreement of a theory based on a particular model of stochastic reorientational dynamics with experiment should not be considered solely as convincing confirmation of the appropriateness of the theory. Subsequent quantitative considerations, in particular, of the shape of the dielectric spectrum, are necessary.

In spite of continuity restriction imposed on probability distribution functions our theory seems to be quite general. Even if one thinks of the molecular dynamics as of jumps between some states of equilibrium,[9] these are jumps between regions rather than between discrete states. It seems justified, therefore, to construct an appropriate continuous orientational probability distribution function that has strong and well-separated maxima, thus making present formalism applicable also in the case of large jumps.

The additional advantage of the theory presented here is that it enables evaluation of molecular parameters from experimental data: the order parameter S, the ratio of the dipole moment components and the local field factor ratio.[5] It is potentially significant in the applied physics and chemistry, and in technology of polymer liquid crystals, since dielectric methods are nondestructive and quite easily applicable in technological processes. For example, detection and continuous monitoring of the degree of orientation of liquid crystalline samples is essential in such applications as optical memories,[28] Fresnel zone plates[29] and nonlinear optical processing.[29]

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