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A THEORY OF THE DIELECTRIC LOSS IN THE ALIGNED NEMATIC MESOPHASE

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A theory of dielectric absorption and dispersion in the nematic phase is developed which does not rely on the use of a nematic "director". The major features of the spectrum are reproduced by using the fact that the autocorrelation functions $\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{v}(t) \rangle$ and $\langle \boldsymbol{v}(t) \cdot \boldsymbol{\mu}(0) \rangle$ are no longer symmetry disallowed when the overall sample is anisotropic, as in the aligned nematic. Here $\boldsymbol{\mu}$ is the dipole vector of the diffusing molecule and $\boldsymbol{v}$ the centre of mass *linear* velocity.

1. Introduction

The theory of molecular dynamics in liquid crystalline mesophases[1]) has been based on the existence of the nematic director potential which cannot easily be given a molecular origin. In this sense therefore there is a need to attempt to explain the observable (for example dielectric[2])) properties of the mesophase on purely molecular terms. The purpose of this short paper is to develop a theory of the dielectric properties of the aligned nematic by considering the interaction of molecular rotation with translation[3]).

2. Theory

In an isotropic molecular liquid the symmetry laws[4]) of time reversal parity and reflection imply that the autocorrelation functions

$$\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{v}(0) \rangle \quad \text{and} \quad \langle \boldsymbol{v}(t) \cdot \boldsymbol{\mu}(0) \rangle$$

vanish for all $t \geqslant 0$. Here $\boldsymbol{\mu}$ is the dipole vector and $\boldsymbol{v}$ the centre of mass velocity. However, in an aligned nematic these laws no longer apply[4]) because the specimen is no longer isotropic. If we consider isotropic diffusion on the Debye model[5]) this implies that the Langevin equation[6]) governing the system may be written[7]) as

$$\dot{\boldsymbol{\mu}} = -\gamma_{\mu}\boldsymbol{\mu} - \gamma_{\mu v}\boldsymbol{v} + \boldsymbol{\Gamma}(t), \tag{1}$$

$$\dot{\boldsymbol{v}} = -\gamma_{v\mu}\boldsymbol{\mu} - \gamma_{v}\boldsymbol{v} + \boldsymbol{F}(t). \tag{2}$$

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Here the matrix

$$\gamma = \begin{bmatrix} \gamma_\mu & \gamma_{\mu v} \\ \gamma_{v\mu} & \gamma_v \end{bmatrix} \tag{3}$$

represents the friction term governing both the reorientation and translation of the molecule under consideration. Γ and F are the usual stochastic torque and force terms. Solving eqs. (1) and (2) for the orientational autocorrelation function we have:

$$\frac{\langle \mu(t) \cdot \mu(0) \rangle}{\langle \mu(0) \cdot \mu(0) \rangle} = \hat{\mathcal{L}}_a^{-1}\left[\frac{p + \gamma_v}{(p + \gamma_v)(p + \gamma_\mu) - \gamma_{\mu v}\gamma_{v\mu}}\right] \rightarrow \hat{\mathcal{L}}_a^{-1}(p + \gamma_\mu)^{-1}, \tag{4}$$

when $\gamma_{\mu v} = \gamma_{v\mu} = 0$. In the aligned nematic phase the orientational autocorrelation function is exponential only when rototranslational interaction is negligible. The dielectric spectrum from eq. (4) is, neglecting all internal field corrections[8]),

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_p)\omega \int_0^\infty \langle u(t) \cdot u(0) \rangle \cos \omega t \, dt,$$

$$\epsilon'(\omega) = \epsilon_0 - (\epsilon_0 - \epsilon_p)\omega \int_0^\infty \langle u(t) \cdot u(0) \rangle \sin \omega t \, dt, \tag{5}$$

so that

$$\epsilon''(\omega) = \frac{(\epsilon_0 - \epsilon_p)\omega[\omega^2\gamma_\mu + \gamma_v(\gamma_v\gamma_\mu - \gamma_{\mu v}\gamma_{v\mu})]}{[\gamma_v\gamma_\mu - \gamma_{\mu v}\gamma_{v\mu} - \omega^2]^2 + \omega^2[\gamma_\mu + \gamma_v]^2}. \tag{6}$$

These equations are valid for isotropic rotational diffusion but for use in the aligned nematic have to be generalised further. Some examples of the dielectric loss from eq. (5) have been calculated and it can be seen that the usual Debye peak is split into two components, which is roughly what is observed in the aligned nematic.

Consider the generalised Favro equation,

$$\frac{\partial}{\partial t} P(\Omega, t \mid \Omega_0, 0) = \int_0^t M_j D_{jk}(t - s) M_k P(\Omega, s \mid \Omega_0, 0) \, ds \tag{7}$$

for rotational diffusion where p is the conditional probability density function for the space (Ω) of Euler angles. M_j and M_k are differential operators defined by:

$$M = u \times \nabla_u. \tag{8}$$

Here u is a unit vector fixed in the frame of a rigid asymmetric rotator along the resultant permanent dipole moment μ. In eq. (7) D_{jk} represents the rotational diffusion tensor and sums over repeated indices are understood.

From the rototranslational equivalent of eq. (7) we need to extract the correlation functions of experimental interest in a dielectric experiment on an aligned nematogen. These have been defined by Nordio et al. as 1) $\langle \mu_Z(t)\mu_Z(0)\rangle$ and 2) $\langle \mu_X(t)\mu_X(0)\rangle$ *in the laboratory frame*. These are related to the a.c.f.'s in the molecule frame (for the symmetric top for example) by

$$\langle \mu_Z(t)\mu_Z(0)\rangle = \langle D^1_{00}(0)D^{1*}_{00}(t)\rangle \mu_z^2 + \langle D^1_{01}(0)D^{1*}_{01}(t)\rangle(\mu_x^2 + \mu_y^2), \tag{9}$$

$$\langle \mu_X(t)\mu_X(0)\rangle = \langle D^1_{10}(0)D^{1*}_{10}(t)\rangle \mu_z^2 + \langle D^1_{11}(0)D^{1*}_{11}(t)\rangle(\mu_x^2 + \mu_y^2)$$

where μ_x, μ_y and μ_z are components of μ in the molecule frame, and μ_X and μ_Z in the laboratory frame (XYZ) whose Z-axis is in the direction of the optical axis of the liquid crystal. D are the usual Wigner coefficients linking (xyz) and (XYZ). The components of $\mu(t)$ in the Z and X directions are given by

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

$$\mu_X(t) = \frac{1}{\sqrt{2}} \sum_p (-1)^p [D^1_{1,-p}(t) - D^1_{\bar{1},-p}(t)]\mu'^{(1,p)}, \tag{10}$$

where the irreducible spherical tensor components $\mu'^{(1,p)}$ are, in terms of the components μ_x, μ_y and μ_z in the molecule frame

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

$$\mu'^{(1,\pm 1)} = \mp \frac{1}{\sqrt{2}}(\mu_x \pm i\mu_y). \tag{11}$$

The problem is therefore to solve for the tensor a.c.f. $\langle u^{\mathrm{T}}(0)u(t)\rangle$ in the molecule frame and convert to $\langle \mu_Z(t)\mu_Z(0)\rangle$ and $\langle \mu_X(t)\mu_X(0)\rangle$ using eqs. (9) to (11).

By definition:

$$\langle u(t)u^{\mathrm{T}}(0)\rangle = \int u(\Omega)u^{\mathrm{T}}(\Omega_0)P(\Omega, t \mid \Omega_0, 0)P_{\mathrm{eq}}(\Omega_0)\,\mathrm{d}\Omega_0\,\mathrm{d}\Omega \tag{12}$$

and therefore from (7) and (12)

$$\frac{\partial}{\partial t}\langle u(t)u^{\mathrm{T}}(0)\rangle = \int\int \mathrm{d}\Omega\,\mathrm{d}\Omega_0 \int_0^t u(\Omega)u^{\mathrm{T}}(\Omega_0)\boldsymbol{M}^{\dagger}\boldsymbol{D}(t-s)\boldsymbol{M} \times P(\Omega, s \mid \Omega_0, 0)P_{\mathrm{eq}}(\Omega_0)\,\mathrm{d}s \tag{13}$$

and

$$\frac{\partial}{\partial t}\langle u_i(t)u_n(0)\rangle = \int_0^t D_{jk}(t-s)\int \mathrm{d}\Omega_0 P_{eq}(\Omega_0)u_n(\Omega_0)$$

$$\times \int \mathrm{d}\Omega u_i(\Omega)M_jM_kP(\Omega, s \mid \Omega_0, 0). \tag{14}$$

Dropping (for convenience) the explicit Ω-dependence and integrating by parts:

$$\int \mathrm{d}\Omega u_iM_jM_kP = \int \mathrm{d}\Omega u_i\epsilon_{jlm}u_l\nabla_m\epsilon_{kpq}u_p\nabla_qP$$

$$= \int \mathrm{d}\Omega u_iu_l\epsilon_{jlm}\epsilon_{kpq}(\nabla_q\delta_{mp} + u_p\nabla_m\nabla_q)P$$

$$= \int \mathrm{d}\Omega P\epsilon_{jlm}\epsilon_{kpq}(-\nabla_q\delta_{mp} + \nabla_m\nabla_qu_p)u_iu_l$$

$$= \int \mathrm{d}\Omega P\epsilon_{jlm}\epsilon_{kpq}[-u_i\delta_{lq}\delta_{mp} - u_l\delta_{iq}\delta_{mp} + u_p\{\delta_{qi}\delta_{lm} + \delta_{lq}\delta_{mi}\}$$

$$+ u_l\{\delta_{iq}\delta_{mp} + \delta_{qp}\delta_{mi}\} + u_i\{\delta_{lq}\delta_{mp} + \delta_{qp}\delta_{ml}\}]$$

$$= \int \mathrm{d}\Omega P\epsilon_{jlm}\epsilon_{kpq}[u_p\{\delta_{qi}\delta_{lm} + \delta_{lq}\delta_{mi}\} + u_l\delta_{qp}\delta_{mi} + u_i\delta_{qp}\delta_{ml}].$$

Using the property $\epsilon_{rtt} = 0$ of the Ricci tensor, we have

$$\int \mathrm{d}\Omega u_iM_jM_kP = \int \mathrm{d}\Omega P\epsilon_{jli}\epsilon_{kpl}u_p$$

$$= \int \mathrm{d}\Omega Pu_p\{\delta_{ik}\delta_{jp} - \delta_{jk}\delta_{ip}\}.$$

Now, returning to eq. (14),

$$\frac{\partial}{\partial t}\langle u_i(t)u_n(0)\rangle = \int_0^t D_{jk}(t-s)\int \mathrm{d}\Omega_0 P_{eq}(\Omega_0)u_n(\Omega_0)$$

$$\times \int \mathrm{d}\Omega u_p(\Omega)\{\delta_{ik}\delta_{jp} - \delta_{jk}\delta_{ip}\}$$

$$= \int_0^t \{D_{ji}(t-s)\langle u_j(s)u_n(0)\rangle - D_{jj}\langle u_i(t)u_n(0)\rangle\}\,\mathrm{d}s,$$

so that

$$\frac{\partial}{\partial t}\langle \boldsymbol{u}(t)\boldsymbol{u}^{\mathrm{T}}(0)\rangle = \int_0^t (\boldsymbol{D}^{\mathrm{T}}(t-s) - \mathbf{1}\,\mathrm{Tr}[\boldsymbol{D}(t-s)])\langle \boldsymbol{u}(t)\boldsymbol{u}^{\mathrm{T}}(0)\rangle\,\mathrm{d}s,$$

$$\frac{\partial}{\partial t}\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle = \int_0^t \{\mathrm{Tr}[\boldsymbol{D}^{\mathrm{T}}(t-s)]\langle \boldsymbol{u}(t)\boldsymbol{u}^{\mathrm{T}}(0)\rangle - \boldsymbol{1}\mathrm{Tr}[\boldsymbol{D}(t-s)]\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle\}\,\mathrm{d}s. \tag{15}$$

Perrin's well known results can be obtained from eq. (15) by dropping the time dependence of the tensor $\boldsymbol{D}$ (i.e. dropping memory effects), and assuming further that $\boldsymbol{D}$ is diagonal, i.e. that:

$$[p + \mathrm{Tr}\,\boldsymbol{D}]\boldsymbol{1} - \boldsymbol{D}^{\mathrm{T}} = \begin{bmatrix} p + D_{22} + D_{33} & 0 & 0 \\ 0 & p + D_{11} + D_{33} & 0 \\ 0 & 0 & p + D_{11} + D_{22} \end{bmatrix} \tag{16}$$

In this case the solution to eq. (15) in p space is

$$\langle \boldsymbol{u}(t)\boldsymbol{u}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{u}(0)\boldsymbol{u}^{\mathrm{T}}(0)\rangle^{-1} = \mathscr{L}_{\mathrm{a}}^{-1}[(p + \mathrm{Tr}\,\boldsymbol{D})\boldsymbol{1} - \boldsymbol{D}^{\mathrm{T}}]^{-1}, \tag{17}$$

Perrin's equation. In this form eq. (17) is a description of orientational motion in a macroscopically isotropic sample. In the aligned nematic condition it is possible that $\langle \boldsymbol{u}^{\mathrm{T}}(0)\boldsymbol{v}(t)\rangle \neq 0$ so that we consider the rototranslational generalisation of the eq. (17):

$$\begin{bmatrix} \langle \boldsymbol{u}(t)\boldsymbol{u}^{\mathrm{T}}(0)\rangle & \langle \boldsymbol{v}(t)\boldsymbol{u}^{\mathrm{T}}(0)\rangle \\ \langle \boldsymbol{u}(t)\boldsymbol{v}^{\mathrm{T}}(0)\rangle & \langle \boldsymbol{v}(t)\boldsymbol{v}^{\mathrm{T}}(0)\rangle \end{bmatrix} \begin{bmatrix} \langle \boldsymbol{u}(0)\boldsymbol{u}^{\mathrm{T}}(0)\rangle & \boldsymbol{0} \\ \boldsymbol{0} & \langle \boldsymbol{v}(0)\boldsymbol{v}^{\mathrm{T}}(0)\rangle \end{bmatrix}^{-1}$$

$$= \mathscr{L}_{\mathrm{a}}^{-1}\begin{bmatrix} \boldsymbol{\alpha}(p) & \boldsymbol{\beta}(p) \\ \boldsymbol{\gamma}(p) & \boldsymbol{\delta}(p) \end{bmatrix}^{-1}, \tag{18}$$

where

$$\boldsymbol{\alpha}(p) = \begin{bmatrix} p + D_{22}^{(u)} + D_{33}^{(u)} & 0 & 0 \\ 0 & p + D_{11}^{(u)} + D_{33}^{(u)} & 0 \\ 0 & 0 & p + D_{11}^{(u)} + D_{22}^{(u)} \end{bmatrix},$$

$$\boldsymbol{\beta}(p) = \begin{bmatrix} D_{11}^{(uv)} & 0 & 0 \\ 0 & D_{22}^{(uv)} & 0 \\ 0 & 0 & D_{33}^{(uv)} \end{bmatrix},$$

$$\gamma(p) = \begin{bmatrix} D_{11}^{(vu)} & 0 & 0 \\ 0 & D_{22}^{(vu)} & 0 \\ 0 & 0 & D_{33}^{(vu)} \end{bmatrix},$$

$$\delta(p) = \begin{bmatrix} p + D_{11}^{(v)} & 0 & 0 \\ 0 & p + D_{22}^{(v)} & 0 \\ 0 & 0 & p + D_{33}^{(v)} \end{bmatrix}.$$

The null elements in (18) come from the fact that, e.g.

$$\langle v(0)u^{\mathrm{T}}(0)\rangle = \int_{\Gamma_0} v(\Gamma_0)u^{\mathrm{T}}(\Gamma_0)P_{\mathrm{eq}}(\Gamma_0)\,\mathrm{d}\Gamma_0$$

$$= \frac{1}{T}\int_0^T v(t)u^{\mathrm{T}}(t)\,\mathrm{d}t = 0.$$

Finally therefore:

$$\mathscr{L}_{\mathrm{a}}(\langle u_x(t)u_x(0)\rangle) = \frac{\langle u_x(0)u_x(0)\rangle(p + D_{11}^{(v)})}{[(p + D_{22}^{(u)} + D_{33}^{(u)})(p + D_{11}^{(v)}) - D_{11}^{(vu)}D_{11}^{(uv)}]},$$

$$\mathscr{L}_{\mathrm{a}}(\langle u_y(t)u_y(0)\rangle) = \frac{\langle u_y(0)u_y(0)\rangle(p + D_{22}^{(v)})}{[(p + D_{11}^{(u)} + D_{33}^{(u)})(p + D_{22}^{(v)}) - D_{22}^{(uv)}D_{22}^{(vu)}]},$$

$$\mathscr{L}_{\mathrm{a}}(\langle u_z(t)u_z(0)\rangle) = \frac{\langle u_z(0)u_z(0)\rangle(p + D_{33}^{(v)})}{(p + D_{11}^{(u)} + D_{22}^{(u)})(p + D_{33}^{(v)}) - D_{33}^{(uv)}D_{33}^{(vu)}}.$$

It remains to link these components with the observables $\langle u_X(t)u_X(0)\rangle$ and $\langle u_Z(t)u_Z(0)\rangle$ in the laboratory frame. It is already clear, however, that the consideration of O/T coupling produces in general dielectric spectra composed of a number of peaks for the asymmetric top without using the idea of director potential. Only two of these are usually resolved experimentally. Increasing the symmetry of the nematic molecule under consideration will of course reduce the number of D elements and the number of theoretical loss peaks.

It is of interest to pursue this discussion into the field of induced birefringence (e.g. the Kerr-effect) because this can be used to investigate the nematic to isotropic transition region in detail. The theory of Kerr-effect transients involves the higher order correlation functions $\langle(u(t)\cdot u(0))^n\rangle$.

The same approach may be used to compute higher order two-time cor-

relation functions:

$$\frac{\partial}{\partial t}\langle u_n(0)u_s(0)u_i(t)u_f(t)\rangle = \int \mathrm{d}s\{D_{jk}(t-s)\langle u_n(0)u_s(0)u_l(s)u_p(s)\rangle\epsilon_{lij}\epsilon_{kpf}$$
$$+ \epsilon_{lfj}D_{jk}(t-s)\epsilon_{kpi}\langle u_n(0)u_s(0)u_l(s)u_p(s)\rangle + D_{pf}(t-s)\langle u_n(0)u_s(0)u_p(s)u_i(s)\rangle$$
$$- 2D_{jj}(t-s)\langle u_n(0)u_s(0)u_i(s)u_f(s)\rangle + D_{pi}(t-s)\langle u_n(0)u_s(0)u_f(s)u_p(s)\rangle\},$$

or

$$\frac{\partial}{\partial t}\langle u_n(0)u_s(0)u_i(t)u_f(t)\rangle = \int \mathrm{d}s\{\epsilon_{lij}\epsilon_{kpf}D_{jk}(t-s) + \epsilon_{lfj}\epsilon_{kpi}D_{jk}(t-s)$$
$$+ D_{pf}(t-s)\delta_{li} + D_{pi}(t-s)\delta_{lf} - 2D_{jj}(t-s)\delta_{li}\delta_{pf}\}$$
$$\times\langle u_n(0)u_s(0)u_l(s)u_p(s)\rangle. \tag{19}$$

Eq. (19) may be rewritten concisely as

$$\frac{\partial}{\partial t}\langle u_n(0)u_s(0)u_i(t)u_f(t)\rangle = -\int \mathrm{d}s\beta_{iflp}(t-s)\langle u_n(0)u_s(0)u_l(s)u_p(s)\rangle, \tag{20}$$

where the super-matrix β_{iflp} is defined in an obvious way by comparison of eq. (19) and eq. (20).

By solving eq. (20) we can get the $\langle(u(t)\cdot u(0))^2\rangle$ correlation function, which we need to construct the $\langle P_2(u(t)\cdot u(0))\rangle$, by simply $n=i$ and $s=f$ and performing the sums over i and f. The solution of eq. (20) in Fourier transform terms may be accomplished in the following way:

$$\langle u_n(0)u_s(0)u_i(0)u_f(0)\rangle + \mathrm{i}\omega\langle u_n(0)u_s(0)\mathscr{L}_a(u_i(t)u_f(t))\rangle$$
$$= -\hat{\beta}_{iflp}(\omega)\langle u_n(0)u_s(0)\mathscr{L}_a(u_l(t)u_p(t))\rangle \tag{21}$$

and by defining:

$$C^{(2)}_{nsif}(t) = \langle u_n(0)u_s(0)u_i(t)u_f(t)\rangle,$$
$$-C^{(2)}_{nsif}(0) = (\hat{\beta}_{iflp} + \mathrm{i}\omega\delta_{il}\delta_{fp})\hat{C}^{(2)}_{nslp}(\omega). \tag{22}$$

Eq. (22) may be reduced to a 3 dimensional matrix eqn. for pure rotational diffusion (or a super-matrix equation for rotation/translation), since it does not depend on the indices ns, and by defining an index m which sum as follows $m=1 \langle=\rangle i=1,\ f=1,\ m=2 \langle=\rangle i=z,\ f=1,\ m=3 \langle=\rangle i=2,\ f=2\ldots$. Eq. (22) may be simplified by assuming that $\hat{D}_{jk}$ is a diagonal matrix.

In this case the matrix $\hat{\beta}_{iflp}$ may be written as

$$\hat{\beta}_{iflp}(\omega) = \hat{D}_{jj}(\omega)[\delta_{if}\delta_{lp} - \delta_{fl}\delta_{pi}] + \hat{D}_{jj}(\omega)[\delta_{if}\delta_{lp} - \delta_{il}\delta_{fp}]$$
$$+ \hat{D}_{ff}(\omega)[\delta_{li}\delta_{pf}] + \hat{D}_{ii}(\omega)[\delta_{lf}\delta_{pi}] - 2D_{jj}(\omega)\delta_{li}\delta_{pf}.$$

By using the fact that we can make the permutation $i \leftrightarrow f$ without changing

$C^{(2)}_{nsij}$, eq. (22) simplifies to

$$\hat{\beta}_{ijlp}(\omega) = 2\hat{D}_{jj}(\omega)[\delta_{if}\delta_{lp} - 2\delta_{il}\delta_{pf}] + 2\hat{D}_{ii}(\omega)[\delta_{lf}\delta_{pi}]$$

which can be used to develop the r/t theory of Kerr transients in the aligned nematic phase.

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