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A theory of dielectric relaxation in anisotropic systems

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There is no complete theory of dielectric relaxation for liquid crystals, in particular, or for anisotropic polar dielectrics, in general. Here we develop a relation between the complex frequency-dependent permittivity tensor and the autocorrelation matrix for the net permanent dipole moment of an ellipsoidal cavity within the dielectric. The relevant equations are derived for both non-polarizable and polarizable molecules. The choice of the cavity geometry and simple reductions of the macroscopic autocorrelation matrix to that for a single particle are discussed.

1. INTRODUCTION

The characteristic behaviour of liquid crystals and other anisotropic systems is governed by the strong orientation-dependent forces between the constituent molecules. As a consequence of these forces the molecules in a liquid crystal mesophase tend to lie with their long axes parallel to a particular direction, called the director. The reorientational process in such a system therefore differs from that in an isotropic medium by the presence of torques which favour molecular alignment parallel to the director. One of the most direct methods for investigating the consequences of an orientation-dependent torque is dielectric relaxation and several studies of nematogens have been reported (Maier & Meier 1961 *a, b*; Axmann 1966; Weiss & Axmann 1966; Rondelez, Diguët & Durand 1971). The complex permittivity is found to exhibit a single dispersion at high frequencies in the isotropic phase of the nematogen. However, the permittivity for the nematic mesophase contains a low-frequency dispersion in addition to a dispersion at frequencies comparable to that for the isotropic phase. The high-frequency absorption is associated with rotation about the molecular long axis and this motion is essentially unaffected by the transition from the isotropic to the nematic phase. In contrast, the rotation of the long axis is severely hindered by the orienting torques in the nematic phase and this produces the shift of the absorption to lower frequencies.

However, although the origin of the two dispersions is qualitatively understood there is no precise relation between the frequency-dependent complex permittivity and the autocorrelation function of the net dipole moment of the system. One of the earliest attempts to interpret dielectric relaxation in liquid crystals was based on an extension of the Debye model for isotropic media to an anisotropic system (Meier & Saupe 1966). This theory contained a number of simplifying assumptions which

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have since been removed (Martin, Meier & Saupe 1971) but the new theory is still subject to all of the failings of the Debye analysis. In addition it is limited to the diffusion model for molecular reorientation and it is difficult to incorporate other models of rotational motion. The theory proposed by Nordio, Rigatti & Segre (1973*a*) does not suffer from this limitation, instead it is open to criticism because the relation between the complex permittivity and the dipole moment autocorrelation function, obtained by Glarum (1960), is simply assumed to apply for an anisotropic liquid crystal.

The absence of any complete theory of dielectric relaxation in anisotropic systems is not too surprising when viewed against the plethora of theories developed for isotropic media. However, the situation for such systems was considerably clarified by Glarum (1960) and Cole (1965), who have applied the Kubo formalism to the problem. The details of this treatment have been criticized and new relations between the complex permittivity and the net dipole moment autocorrelation function proposed (Fatuzzo & Mason 1967; Scaife 1967). Both calculations were then extended to include polarizable molecules (Klug, Kranbuehl & Vaughan 1969; Hill 1972). Glarum (1972) has since attempted to justify his original result and has been supported in this by Cole (1973). More recently Titulaer & Deutch (1974) have discussed the problem for nonpolarizable molecules by using linear response theory and have justified this approach by more detailed arguments based on the fluctuation-dissipation theorem. Their analysis is particularly transparent and shows that the Fatuzzo–Mason result is correct while that obtained by Glarum describes a different system.

In this paper we shall employ the linear-response formalism, as prescribed by Titulaer & Deutch, to derive a relation between the frequency-dependent permittivity tensor of a polar anisotropic system and the autocorrelation matrix for the net dipole moment of a small region embedded in the dielectric material. In the following section we shall restrict our attention to non-polarizable molecules while in §3 we attempt to allow for the molecular polarizability. The difficult task of relating the macroscopic to the molecular autocorrelation functions is discussed in §4 and the two simplest relations described. Finally we would emphasize that although the relations obtained in this paper were intended for liquid crystalline systems they should be generally applicable to anisotropic systems.

2. NON-POLARIZABLE MOLECULES

The system which we shall consider is sketched in figure 1. It is composed of an ellipsoidal cavity surrounded by an infinite dielectric continuum; we shall return to the choice of this geometry in the final section. The permittivity of the material inside and outside the cavity is anisotropic and the principal axes of both permittivity tensors are parallel to the major axes of the ellipsoid. To be quite general the complex permittivity $\epsilon^{(2)}$ of the material inside the cavity is taken to be different from that $\epsilon^{(1)}$ of the surrounding continuum. Finally, in defining the system we shall

ignore ferroelectric and piezoelectric effects and, for the moment, the polarizabilities of the constituent molecules. We now wish to derive a relation between the frequency-dependent permittivity of the system and the fluctuations in the instantaneous dipole moment of the cavity $\mathbf{m}(t)$. This calculation is, as we have noted, a relatively straightforward extension of the treatments for isotropic systems based on the linear response theory and we shall follow closely the formalism employed by Titulaer & Deutch (1974). The philosophy of these calculations is to obtain, and then equate, two expressions for the ensemble average of the net dipole moment for the cavity $\langle \mathbf{m}(t) \rangle_{E^\infty}$ when a time-dependent electric field $\mathbf{E}^\infty(t)$ is applied to the system. One expression is derived with the aid of linear response theory while the other follows from a standard electrostatic calculation of the polarization $\mathbf{P}(t)$.

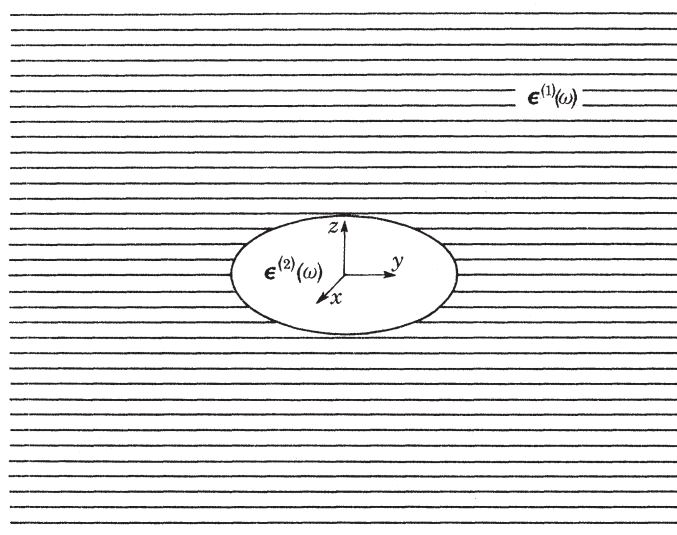


FIGURE 1. The anisotropic system comprises an ellipsoidal cavity with a complex permittivity tensor $\epsilon^{(2)}(\omega)$ surrounded by an infinite polar dielectric with a complex permittivity tensor $\epsilon^{(1)}(\omega)$.

We start with linear response theory which gives the net dipole at a time t as

$$\langle \mathbf{m}(t) \rangle_{E^\infty} = - (1/kT) \int_0^\infty \dot{\Phi}(t') \cdot \mathbf{E}^c(t-t') dt', \quad (1)$$

where the angular brackets, with an E^∞ subscript, denote an ensemble average in the presence of the applied field. \mathbf{E}^c is the electric field which would exist in the cavity in the absence of any interaction with the permanent electric dipoles—that is, inside the empty cavity; more detailed calculations based on the fluctuation-dissipation theorem would appear to justify the use of this field (Titulaer & Deutch 1974). The autocorrelation matrix $\Phi(t)$ is defined in terms of the instantaneous electric dipole moment of the cavity as

$$\Phi(t) = \langle \mathbf{m}(0) \mathbf{m}(t) \rangle, \quad (2)$$

where the brackets without the subscript denote an ensemble average in the absence of the applied field. The autocorrelation matrix is symmetric because the dynamic process responsible for the fluctuations in \mathbf{m} is taken to be stationary and microscopically symmetric under time reversal. The electric field inside the empty cavity is related to the oscillating field $\mathbf{E}^\infty(t)$ applied at large distances from the cavity by

$$\mathbf{E}^c(t) = \mathbf{T}^o(\omega) \cdot \mathbf{E}^\infty(t), \quad (3)$$

where the field

$$\mathbf{E}^\infty(t) = \mathbf{E}^\infty e^{i\omega t}. \quad (4)$$

The tensor \mathbf{T}^o is diagonal within the principal coordinate system x, y, z of the permittivity tensors and, for the remainder of the paper, we shall find it convenient to work in this coordinate system. The principal components of $\mathbf{T}^o(\omega)$ are evaluated in the appendix and found to be

$$\mathbf{T}^o(\omega) \equiv \frac{\boldsymbol{\varepsilon}^{(1)}(\omega)}{\boldsymbol{\varepsilon}^{(1)}(\omega) - \mathbf{n}(\omega) \cdot \{\boldsymbol{\varepsilon}^{(1)}(\omega) - \mathbf{1}\}}, \quad (5)$$

where $\mathbf{n}(\omega)$ is the depolarization or shape tensor which is defined in the appendix.

Accordingly

$$\langle \mathbf{m}(t) \rangle_{E^\infty} = \frac{1}{kT} \mathcal{L} \{ -\dot{\boldsymbol{\Phi}}(t') \} \cdot \mathbf{T}^o \cdot \mathbf{E}^\infty(t), \quad (6)$$

where \mathcal{L} denotes the Laplace transform

$$\mathcal{L} \{ -\dot{\boldsymbol{\Phi}}(t') \} = \int_0^\infty -\dot{\boldsymbol{\Phi}}(t') e^{-i\omega t'} dt'. \quad (7)$$

This calculation is only valid when the associated wavelength of the oscillating electric field is large compared with the cavity dimensions. In practise this condition is easily satisfied in all dielectric studies of polar liquid crystals.

The polarization within an ellipsoidal cavity is uniform and so the induced dipole moment calculated from electrostatics is simply

$$\langle \mathbf{m}(t) \rangle_{E^\infty} = V \mathbf{P}(t), \quad (8)$$

where V is the volume of the cavity. The polarization vector is related to the permittivity of the material and the electric field $\mathbf{E}(t)$ inside the cavity by

$$\mathbf{P}(t) = \frac{1}{4\pi} \{ \boldsymbol{\varepsilon}^{(2)}(\omega) - \mathbf{1} \} \cdot \mathbf{E}(t). \quad (9)$$

The relation between $\mathbf{E}(t)$ and the applied electric field is analogous to that given in equation (3); in fact,

$$\mathbf{E}(t) = \mathbf{T}(\omega) \cdot \mathbf{E}^\infty(t), \quad (10)$$

where, as we show in the appendix,

$$\mathbf{T}(\omega) \equiv \frac{\boldsymbol{\varepsilon}^{(1)}(\omega)}{\boldsymbol{\varepsilon}^{(1)}(\omega) - \mathbf{n}(\omega) \cdot \{ \boldsymbol{\varepsilon}^{(1)}(\omega) - \boldsymbol{\varepsilon}^{(2)}(\omega) \}}. \quad (11)$$

Consequently the induced dipole moment is

$$\langle \mathbf{m}(t) \rangle_{E^\infty} = \frac{V}{4\pi} \{ \boldsymbol{\varepsilon}^{(2)}(\omega) - \mathbf{1} \} \cdot \mathbf{T}(\omega) \cdot \mathbf{E}^\infty(t). \quad (12)$$

Since the equality of the two equations for $\langle \mathbf{m}(t) \rangle_{E^\infty}$ must be satisfied for any applied electric field $E^\infty(t)$ then

$$\frac{1}{kT} \mathcal{L} \{ -\dot{\Phi}(t') \} = \frac{V}{4\pi} \{ \boldsymbol{\epsilon}^{(2)}(\omega) - \mathbf{1} \} \cdot \mathbf{T}(\omega) \cdot \mathbf{T}^o(\omega)^{-1}. \quad (13)$$

Since the right hand side of equation (13) is diagonal within the principal coordinate system shared by $\boldsymbol{\epsilon}^{(2)}(\omega)$, $\mathbf{T}^o(\omega)$ and $\mathbf{T}(\omega)$ then the time derivative of the auto-correlation matrix and hence the matrix itself must be diagonal within the same coordinate system because $\Phi(t)$ contains no time-independent terms. That is the fluctuations in the components of the electric dipole moment \mathbf{m} along different principal axes are uncorrelated. The volume of the cavity appears as an arbitrary factor in equation (13) but it can be removed in the following way. We first take the limit of equation (13) as the frequency of the applied field tends to zero; this gives

$$\frac{1}{kT} \Phi(0) = \frac{V}{4\pi} \{ \boldsymbol{\epsilon}^{(2)}(0) - \mathbf{1} \} \cdot \mathbf{T}(0) \cdot \mathbf{T}^o(0)^{-1}, \quad (14)$$

where

$$\Phi(0) = \langle \mathbf{m}(0) \mathbf{m}(0) \rangle, \quad (15)$$

and $\boldsymbol{\epsilon}(0)$ denotes the appropriate static permittivity tensor. On eliminating the volume from equation (13) we find

$$\mathcal{L} \{ -\dot{\Phi}^N(t') \} = \frac{\{ \boldsymbol{\epsilon}^{(2)}(\omega) - \mathbf{1} \} \cdot \mathbf{T}(\omega) \cdot \mathbf{T}^o(\omega)^{-1}}{\{ \boldsymbol{\epsilon}^{(2)}(0) - \mathbf{1} \} \cdot \mathbf{T}(0) \cdot \mathbf{T}^o(0)^{-1}}, \quad (16)$$

where $\Phi^N(t')$ is the normalized autocorrelation matrix defined by

$$\Phi^N(t') = \Phi(t') \cdot \Phi(0)^{-1}. \quad (17)$$

It should, however, be remembered that this procedure does not eliminate the dependence on the shape of the cavity because the \mathbf{T} tensors are partly determined by $\mathbf{n}(\omega)$ which, in turn, is a function of the relative dimensions of the ellipsoid. Substituting explicit expressions for the tensors \mathbf{T} and \mathbf{T}^o gives the following relation between the diagonal elements of the permittivity tensors and the autocorrelation matrix:

$$\begin{aligned} \mathcal{L} \{ -\dot{\Phi}_{xx}^N(t') \} \\ = \frac{[\epsilon_{xx}^{(2)}(\omega) - 1][\epsilon_{xx}^{(1)}(\omega) - n_{xx}(\omega)\{\epsilon_{xx}^{(1)}(\omega) - 1\}][\epsilon_{xx}^{(1)}(0) - n_{xx}(0)\{\epsilon_{xx}^{(1)}(0) - \epsilon_{xx}^{(2)}(0)\}]}{[\epsilon_{xx}^{(2)}(0) - 1][\epsilon_{xx}^{(1)}(0) - n_{xx}(0)\{\epsilon_{xx}^{(1)}(0) - 1\}][\epsilon_{xx}^{(1)}(\omega) - n_{xx}(\omega)\{\epsilon_{xx}^{(1)}(\omega) - \epsilon_{xx}^{(2)}(\omega)\}]}, \end{aligned} \quad (18)$$

with analogous expressions for the other diagonal elements. This is the desired result; it does, of course, reduce to that obtained by Titulaer & Deutch (1974) for the corresponding isotropic system when the permittivity tensors tend to scalars and the cavity becomes spherical.

We shall now consider three particular cases of this general result. In a single component system the permittivities of the material inside and outside the cavity will be identical; then equation (18) reduces to

$$\mathcal{L} \{ -\dot{\Phi}_{xx}^N(t') \} = \frac{\{\epsilon_{xx}(\omega) - 1\}[\epsilon_{xx}(\omega) - n_{xx}(\omega)\{\epsilon_{xx}(\omega) - 1\}]\epsilon_{xx}(0)}{\{\epsilon_{xx}(0) - 1\}[\epsilon_{xx}(0) - n_{xx}(0)\{\epsilon_{xx}(0) - 1\}]\epsilon_{xx}(\omega)}, \quad (19)$$

for a system with permittivity $\epsilon(\omega)$. This result is the anisotropic analogue of the Fatuzzo–Mason equation derived for a spherical cavity in an isotropic medium. We may also obtain the anisotropic equivalent of the Glarum equation, for isotropic systems, simply by setting the permittivity of the infinite continuum equal to the static permittivity $\epsilon(0)$ of the material inside the cavity (Glarum 1960). We then find from equation (18)

$$\mathcal{L}\{-\dot{\Phi}_{xx}^N(t')\} = \frac{\{\epsilon_{xx}(\omega) - 1\}\epsilon_{xx}(0)}{\{\epsilon_{xx}(0) - 1\}[\epsilon_{xx}(0) - n_{xx}\{\epsilon_{xx}(0) - \epsilon_{xx}(\omega)\}]}, \quad (20)$$

where the depolarization tensor \mathbf{n} is now frequency independent. Finally we may obtain a Debye-like equation by removing the material from the surrounding continuum and setting $\epsilon^{(1)}(\omega)$ equal to $\mathbf{1}$; this gives

$$\mathcal{L}\{-\dot{\Phi}_{xx}^N(t')\} = \frac{\{\epsilon_{xx}(\omega) - 1\}[1 - n_{xx}\{1 - \epsilon_{xx}(0)\}]}{\{\epsilon_{xx}(0) - 1\}[1 - n_{xx}\{1 - \epsilon_{xx}(\omega)\}]}. \quad (21)$$

However, we would emphasize that the only result with any relevance for dielectric studies of real anisotropic systems would appear to be equation (19). In the following section we shall see how this result might be modified to allow for the polarizability of real molecules.

3. POLARIZABLE MOLECULES

In principle, the material filling the ellipsoidal cavity should be composed of polarizable molecules each with a permanent electric dipole moment. However, in the calculation we shall find it convenient to adopt Fröhlich's model for this material and therefore represent it as a continuous medium with a frequency-independent permittivity $\epsilon^{(2)}(\infty)$ containing point dipoles embedded in it (Böttcher 1973). The permittivity $\epsilon^{(2)}(\infty)$ is to be identified with the limiting high frequency permittivity of the material. We shall now calculate the contribution $\langle \mathbf{m}^\mu(t) \rangle_{E^\infty}$ made by these point dipoles to the net dipole moment of the cavity induced by the applied electric field. According to linear response theory this contribution is given by equation (1) provided $\mathbf{E}^c(t)$ is equated with the Fröhlich field—that is, the field inside the cavity when it is filled with the continuous dielectric of permittivity $\epsilon^{(2)}(\infty)$. This field is related to the applied electric field $\mathbf{E}^\infty(t)$ by

$$\mathbf{E}^c(t) = \mathbf{T}^\infty(\omega) \cdot \mathbf{E}^\infty(t), \quad (22)$$

where

$$\mathbf{T}^\infty(\omega) = \frac{\boldsymbol{\epsilon}^{(1)}(\omega)}{\boldsymbol{\epsilon}^{(1)}(\omega) - \mathbf{n}(\omega) \cdot \{\boldsymbol{\epsilon}^{(1)}(\omega) - \boldsymbol{\epsilon}^{(2)}(\infty)\}}. \quad (23)$$

The autocorrelation matrix is unchanged and is determined solely by the fluctuations in the instantaneous dipole moment caused by the reorientation of the point dipoles. The ensemble average $\langle \mathbf{m}^\mu(t) \rangle_{E^\infty}$ is therefore given by equation (6) but with $\mathbf{T}^0(\omega)$ replaced by $\mathbf{T}^\infty(\omega)$. This average dipole moment may also be calculated from equation (8) provided we know that part of the polarization $\mathbf{P}_{\text{or}}(t)$ which

originates from the point dipoles. We shall identify this contribution as the difference between the total polarization, given in equation (9), and the induced polarization caused by the continuum with permittivity $\epsilon^{(2)}(\infty)$ in the cavity:

$$\mathbf{P}_{\text{in}}(t) = \frac{1}{4\pi} \{\epsilon^{(2)}(\infty) - \mathbf{1}\} \cdot \mathbf{E}(t). \quad (24)$$

This gives
$$\mathbf{P}_{\text{or}}(t) = \frac{1}{4\pi} \{\epsilon^{(2)}(\omega) - \epsilon^{(2)}(\infty)\} \cdot \mathbf{E}(t), \quad (25)$$

where the electric field in the cavity is obtained from equation (10) and so

$$\langle \mathbf{m}^\mu(t) \rangle_{E^\infty} = \frac{V}{4\pi} \{\epsilon^{(2)}(\omega) - \epsilon^{(2)}(\infty)\} \cdot \mathbf{T}(\omega) \cdot \mathbf{E}^\infty(t). \quad (26)$$

When this is identified with the same contribution calculated from linear response theory we find

$$\frac{1}{kT} \mathcal{L} \{-\dot{\Phi}(t')\} = \frac{V}{4\pi} \{\epsilon^{(2)}(\omega) - \epsilon^{(2)}(\infty)\} \cdot \mathbf{T}(\omega) \cdot \mathbf{T}^{\infty-1}(\omega), \quad (27)$$

and removal of the cavity volume by means of the procedure adopted in §2 gives

$$\mathcal{L}\{-\dot{\Phi}^N(t')\} = \frac{[\epsilon^{(2)}(\omega) - \epsilon^{(2)}(\infty)] \cdot \mathbf{T}(\omega) \cdot \mathbf{T}^{\infty-1}(\omega)}{[\epsilon^{(2)}(0) - \epsilon^{(2)}(\infty)] \cdot \mathbf{T}(0) \cdot \mathbf{T}^{\infty-1}(0)}. \quad (28)$$

When the material inside and outside the cavity have the same permittivity $\epsilon(\omega)$ then its elements are related to those of the normalized autocorrelation matrix by, for example,

$$\mathcal{L}\{-\dot{\Phi}_{xx}^N(t')\} = \frac{[\epsilon_{xx}(\omega) - \epsilon_{xx}(\infty)] [\epsilon_{xx}(\omega) - n_{xx}(\omega) \{\epsilon_{xx}(\omega) - \epsilon_{xx}(\infty)\}] \epsilon_{xx}(0)}{[\epsilon_{xx}(0) - \epsilon_{xx}(\infty)] [\epsilon_{xx}(0) - n_{xx}(0) \{\epsilon_{xx}(0) - \epsilon_{xx}(\infty)\}] \epsilon_{xx}(\omega)}. \quad (29)$$

This is our final result, which attempts to allow for the molecular polarizability; it should be compared with the relation given in equation (19). In essence this result is the anisotropic analogue of the equation obtained by Klug *et al.* (1969) for a spherical cavity in an isotropic system.

It is also possible to see what assumptions are implied by Nordio, Rigatti & Segre's use of the Glarum–Cole equation

$$\mathcal{L}\{-\dot{\Phi}^N(t')\} = \frac{\{\epsilon(\omega) - \epsilon(\infty)\} 3\epsilon(0)}{\{\epsilon(0) - \epsilon(\infty)\} \{2\epsilon(0) + \epsilon(\omega)\}}, \quad (30)$$

for the components of the permittivity tensor in their dielectric studies of nematic liquid crystals (Nordio, Rigatti & Segre 1973*a, b*). This result may be obtained from equation (28) but only by making the unrealistic assumption that the permittivity tensor for the material surrounding the cavity is frequency independent and equal to the static tensor $\epsilon(0)$. In addition, it is necessary to set the components of the depolarization tensor equal to $\frac{1}{3}$ which is incompatible with an anisotropic permittivity and implies a spherical cavity.

4. MOLECULAR AUTOCORRELATION FUNCTIONS

When the equations developed in §§2 and 3 are applied to nematic or smectic A liquid crystals there will be some simplification of the relations because of the $D_{\infty h}$ symmetry exhibited by these mesophases. There are in fact just two equations for the components of the complex permittivity parallel and perpendicular to the director. However, even when the complete frequency dependence of the permittivity has been measured it is still not possible to determine the autocorrelation matrix, by taking the Fourier transform, because the depolarization tensor depends on the relative dimensions of the sample cavity which are arbitrary. This dependence on the geometry of the sample is an unsatisfactory feature of the analysis but one which also occurs for isotropic media (Bordewijk 1973; Deutch 1973). However, it does not present a major problem when the cavity contains many molecules for then its shape is immaterial and it is expedient to choose a spherical sample since the depolarization tensor $\mathbf{n}(\omega)$ is independent of its size. Consequently the relationship between the permittivity tensor and the autocorrelation matrix for the net dipole moment of the spherical cavity is completely defined. However, we are now faced with the alternative problem of relating this macroscopic autocorrelation matrix to that for a single particle. In general, the molecular and macroscopic correlation matrices are related by

$$\Phi^N(t) = \left\{ \sum_i \langle \boldsymbol{\mu}^{(i)}(0) \boldsymbol{\mu}^{(i)}(t) \rangle + \sum_{i>j} \langle \boldsymbol{\mu}^{(i)}(0) \boldsymbol{\mu}^{(j)}(t) \rangle \right\} / \left\{ \sum_i \langle \boldsymbol{\mu}^{(i)}(0) \boldsymbol{\mu}^{(i)}(0) \rangle + \sum_{i>j} \langle \boldsymbol{\mu}^{(i)}(0) \boldsymbol{\mu}^{(j)}(0) \rangle \right\}, \quad (31)$$

where $\boldsymbol{\mu}^{(i)}$ is the permanent dipole moment of the i th molecule. We can see that the reduction of $\Phi^N(t)$ to a single particle correlation matrix is prevented by the second molecular correlation matrix in equation (31), which describes the correlation between dipole moments on different molecules. The same difficulty is encountered for isotropic fluids, and a number of solutions, varying in complexity, have been proposed; the simplest, by far, is to ignore the correlation between dipole moments on different molecules for then the net dipole moment autocorrelation function is equal to that for a single particle. Despite the extensive pairwise angular correlation which must exist for anisotropic systems the degree of dipole correlation should not be any greater than that in the corresponding isotropic phase, provided, of course, the system is neither piezoelectric or ferroelectric. We may therefore adopt the same model and so can ignore the cross correlation matrix in equation (31):

$$\Phi^N(t) = \langle \boldsymbol{\mu}(0) \boldsymbol{\mu}(t) \rangle / \langle \boldsymbol{\mu}(0) \boldsymbol{\mu}(0) \rangle; \quad (32)$$

in other words, $\Phi^N(t)$ may be equated with the single particle autocorrelation matrix.

An alternative approach is to shrink the cavity until it is of molecular dimensions and contains a single dipole. Although we are now forced to assume that all of the macroscopic relationships used in the previous derivations also hold for this molecular cavity. Given this assumption the autocorrelation matrix $\Phi^N(t)$ is identical to

the molecular dipole moment autocorrelation matrix but we must decide on the shape of the cavity. It would appear reasonable that the geometry of the cavity should reflect the symmetry of the macroscopic system and this notion has motivated our choice of an ellipsoidal cavity. Accordingly a spherical cavity would seem to be the natural shape for an isotropic dielectric and, as we have seen, such a choice removes all unknown factors from the calculation. This is not the case for an ellipsoidal cavity for the relative magnitudes of the semi-axes are still required in the depolarization tensor and their choice is somewhat arbitrary. One possible solution is to assume that the semi-axes are proportional to the probability of finding the molecule parallel to the appropriate axis. Thus for a uniaxial liquid crystal the major axis of the ellipsoid would be parallel to the director and its length would be proportional to the probability of finding the molecular long axis parallel to the director. Similarly the minor semi-axis would be proportional to the probability of finding the molecular long axis perpendicular to the director. Alternatively the relative dimensions of the cavity might be taken to reflect the anisotropy in the spatial pair distribution function for the mesophase (Dunmur 1971).

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APPENDIX

Here we wish to derive an expression relating the electric field \mathbf{E}^c inside a dielectric ellipsoid immersed in an infinite dielectric to the applied field \mathbf{E}^∞ . The permittivity $\epsilon^{(2)}$ of the material inside the ellipsoidal cavity, like that of its surroundings $\epsilon^{(1)}$, is anisotropic and the two permittivity tensors have the same principal axes which are also parallel to the principal directions of the ellipsoid. The potential $\phi^{(2)}$ inside the cavity must satisfy Laplace's equation

$$\left\{ \epsilon_{xx}^{(2)} \frac{\partial^2}{\partial x^2} + \epsilon_{yy}^{(2)} \frac{\partial^2}{\partial y^2} + \epsilon_{zz}^{(2)} \frac{\partial^2}{\partial z^2} \right\} \phi^{(2)} = 0, \quad (\text{A } 1)$$

where the x, y, z axes are parallel to the principal axes of the permittivity tensors and the origin is at the centre of the ellipsoid. The potential $\phi^{(1)}$ outside the ellipsoid is given by the analogous equation

$$\left\{ \epsilon_{xx}^{(1)} \frac{\partial^2}{\partial x^2} + \epsilon_{yy}^{(1)} \frac{\partial^2}{\partial y^2} + \epsilon_{zz}^{(1)} \frac{\partial^2}{\partial z^2} \right\} \phi^{(1)} = 0. \quad (\text{A } 2)$$

The two potentials must satisfy certain continuity conditions at the boundary of the ellipsoid which has semi-axes a, b and c . We now scale the variables according to the following rules.

$$\left. \begin{aligned} x &= \sqrt{(\epsilon_{xx}^{(1)})} x', \\ y &= \sqrt{(\epsilon_{yy}^{(1)})} y', \\ z &= \sqrt{(\epsilon_{zz}^{(1)})} z'. \end{aligned} \right\} \quad (\text{A } 3)$$

and

With these new variables equation (A 2) for the potential outside the cavity reduces to

$$\left\{ \frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2} \right\} \phi^{(1)} = 0, \quad (\text{A } 4)$$

which is equivalent to that for a vacuum. The equation for the potential $\phi^{(2)}$ becomes

$$\left\{ \frac{\epsilon_{xx}^{(2)}}{\epsilon_{xx}^{(1)}} \frac{\partial^2}{\partial x'^2} + \frac{\epsilon_{yy}^{(2)}}{\epsilon_{yy}^{(1)}} \frac{\partial^2}{\partial y'^2} + \frac{\epsilon_{zz}^{(2)}}{\epsilon_{zz}^{(1)}} \frac{\partial^2}{\partial z'^2} \right\} \phi^{(2)} = 0, \quad (\text{A } 5)$$

while the semi-axes of the ellipsoid are changed to $a/\sqrt{\epsilon_{xx}^{(1)}}$, $b/\sqrt{\epsilon_{yy}^{(1)}}$ and $c/\sqrt{\epsilon_{zz}^{(1)}}$. The problem has therefore been reduced to one involving an ellipsoid with an anisotropic permittivity tensor $\epsilon^{(2)}/\epsilon^{(1)}$ embedded in an infinite vacuum. The electric field inside the cavity resulting from an applied field has been calculated for such a system with the result

$$\mathbf{E}^c = \mathbf{T} \cdot \mathbf{E}^\infty, \quad (\text{A } 6)$$

where, for example,

$$T_{xx} = \frac{\epsilon_{xx}^{(1)}}{\epsilon_{xx}^{(1)} - n_{xx}(\epsilon_{xx}^{(1)} - \epsilon_{xx}^{(2)})}; \quad (\text{A } 7)$$

there are analogous equations for the other two principal axes (Landau & Lifshitz 1960). The components of the depolarization tensor \mathbf{n} are related to the semi-axes of the ellipsoid; for example, the principal component in the x -direction is

$$n_{xx} = \frac{abc}{2\sqrt{\epsilon_{xx}^{(1)}\epsilon_{yy}^{(1)}\epsilon_{zz}^{(1)}}} \int_0^\infty \frac{dS}{(S + a^2/\epsilon_{xx}^{(1)})R}, \quad (\text{A } 8)$$

where

$$R^2 = (S + a^2/\epsilon_{xx}^{(1)})(S + b^2/\epsilon_{yy}^{(1)})(S + c^2/\epsilon_{zz}^{(1)}). \quad (\text{A } 9)$$

Reverting to the original coordinates leaves this result unchanged and so the field inside the ellipsoid is given by equation (A 6).

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