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Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

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To cite this Article Dunmur, D. A.(2005) 'The determination of molecular parameters from dielectric measurements on nematic liquid crystals', *Liquid Crystals*, 32: 11, 1379 – 1387

To link to this Article: DOI: 10.1080/02678290500124684

URL: <http://dx.doi.org/10.1080/02678290500124684>

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The determination of molecular parameters from dielectric measurements on nematic liquid crystals

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(Received 15 October 2004; accepted 10 December 2005)

The physical properties of liquid crystal phases (mesophases) depend in a very sensitive manner on the structure of the constituent liquid crystal-forming molecules (mesogens). Thus a small change in molecular structure can result in a dramatic change in the corresponding liquid crystal properties. The dielectric responses of materials reflect the electric properties of molecules, and so analysis of dielectric measurements on liquid crystals in terms of molecular properties should lead to the development of structure/property relationships for such mesophases. This paper explores the problems of determining molecular parameters from dielectric measurements on nematic liquid crystals. Specifically, the difficulties in defining the internal electric field and knowing the value of the order parameter are addressed. Experimental results on a range of liquid crystals show that short range correlations are important in determining both the dielectric and optical response of nematic liquid crystals. It is concluded therefore that more sophisticated molecular theories, which take account of molecular shape and volume, need to be developed before reliable structure/property relationships can be established for liquid crystals.

1. Introduction

This collection of papers, entitled *A Chemical Physics Approach to Liquid Crystals*, is a tribute to Geoffrey Luckhurst, one of the founding editors of *Liquid Crystals*, on his sixty-fifth birthday. The theme of chemical physics is appropriate since it embraces all his contributions to the liquid crystal literature. Almost all of Luckhurst's papers have been concerned with the interpretation of physical measurements on liquid crystals in terms of molecular properties. This is the essence of chemical physics, which provides the link between the physical properties of materials and the structure and properties of the constituent molecules.

The interpretation of physical measurements on liquid crystals requires a suitable theory for the response being measured in terms of observables, and then, if information on molecular parameters is required, a molecular statistical theory. To assist in this interpretation, molecular simulations are often useful, which can model observable properties making assumptions about molecular interactions and properties. Ultimately the success of molecular theories and molecular modelling of properties should be the prediction of macroscopic properties of liquid crystals from the molecular structure of constituent molecules. If this were achieved, then it would be possible to design a molecule that would possess desired liquid crystal behaviour in terms

of phases and properties. However even reaching this objective would not satisfy the demands made by applications of liquid crystals, which rely on the collective behaviour of complex mixtures of many components. In addition, a knowledge of the interaction of liquid crystals with aligning surfaces and electrodes is also required; this cannot, even in principle, be predicted just from molecular properties.

In the context of this paper, which focuses on the dielectric response of nematic liquid crystals, the molecular properties of interest are the polarizability tensor and dipole moment. If non-linear dielectric response is included, then non-linear polarizabilities will also contribute to the measured properties. These molecular properties measure the response of a molecule to an external electric field, and can be defined from quantum mechanics in terms of the molecular charge distribution, including both the nuclear and electronic contributions to the Hamiltonian H :

$$H = H_0 - \mu_\alpha E_\alpha. \quad (1)$$

Here H_0 is the Hamiltonian in the absence of an electric field \mathbf{E} , while the dipole operator μ is defined as a sum over the position vectors of electronic (e_i) and nuclear charges (q_i):

$$\mu_\alpha = \mu_{\text{electronic}} + \mu_{\text{nuclear}} = \sum e_i r_{i\alpha} + \sum q_i R_{i\alpha}. \quad (2)$$

A repeated suffix implies summation over all possible cartesian components. The Hamiltonian contains the electric field explicitly, since we are interested in electric properties, although it can be formulated in terms of the scalar potential and vector potential if desired. The dipole moment vector is a simple expectation value for the ground electronic state of the molecule, and a sum over the contributions from nuclear charges:

$$\mu_\alpha = \langle o | e r_\alpha | o \rangle + \sum q_i R_{i\alpha} \quad (3)$$

while the optical polarizability is a sum over all electronic states (n) of transition moments $\langle o | \mu_\alpha | n \rangle$, excluding the ground state, where Δ_{no} is the energy difference between ground and excited states ($U_n - U_o$):

$$\alpha_{\alpha\beta} = 2 \sum_{n \neq o} \frac{\langle o | e r_\alpha | n \rangle \langle n | e r_\beta | o \rangle}{\Delta_{no}} + 2 \sum_{v \neq o} \frac{\langle o | \sum_i q_i R_{i\alpha} | v \rangle \langle v | \sum_i q_i R_{i\beta} | o \rangle}{\Delta_{vo}} \quad (4)$$

In equation (4) for the total polarizability an additional term is included to account for the so-called atomic polarization. This can be represented as a sum over the vibrational states (v) of a molecule, assuming that the Born–Oppenheimer approximation is valid, and usually contributes less than 5% to the total polarizability. The frequency dependence of the polarizability could be included, but for simplicity has been neglected here. The definitions of molecular properties given above are within the dipole approximation. That is to say, the electric field is assumed to be uniform over the molecule, and the property can be represented as a dipole or polarizability acting at a point within the molecule. It is also assumed that the molecule is isolated in vacuum, so that any intermolecular interactions are unimportant. The choice of axis system is arbitrary, but the polarizability tensor can be diagonalized, which defines a principal axis system within the molecule; of course in general the dipole moment direction does not coincide with any of the principal axes.

With the constraints noted, the relative electric permittivity (ϵ) of a low density gas can be written in terms of the polarizability and dipole moment as:

$$(\epsilon - 1) = \frac{N}{\epsilon_0} \left[\bar{\alpha} + \frac{\mu^2}{3k_B T} \right] \quad (5)$$

where N is the molecular number density, T is the absolute temperature, and $\bar{\alpha} = \frac{1}{3} \alpha_{\alpha\alpha}$ is the isotropic polarizability.

The electric permittivity and magnetic permeability are defined by Maxwell's equations, and so relate the

response of a medium to the Maxwell field. This is not the same as the externally applied field, and depends on the electrode configuration, sample shape and on the electromagnetic properties of the medium. The solutions to these problems for isotropic media are known. A further complication arises if it is desired to express the measured dielectric properties in terms of molecular parameters. The electric field experienced by a molecule is not the same as either the externally applied field or the Maxwell field. The latter represents an average of the field within the medium, taking account of both the externally applied field and the polarization within the medium. To describe the response of a molecule within a dielectric medium, it is necessary to introduce another field, the local field or internal field, which is an average over a volume element within the sample, but which excludes the molecule. Again, these subtleties are well understood and documented [1] for isotropic media. Thus there exists a theoretical framework to express the dielectric properties of isotropic condensed phases in terms of molecular parameters. Of course the effects of intermolecular interactions must be included in the statistical description of the molecular response. In condensed phases such effects can be avoided if the dielectric response of the molecules of interest is measured in solution, using a suitable solvent, and the results extrapolated to infinite dilution.

Liquid crystals are not isotropic and clearly intermolecular interactions strongly influence their phase behaviour and properties. The interpretation of physical measurements on liquid crystals in terms of molecular properties is therefore a difficult problem. In this paper, various aspects of the problem will be critically examined, and progress in formulating a complete molecular theory of the dielectric properties of nematic liquid crystals will be discussed. Different approaches to the determination of molecular parameters will be reviewed for a variety of liquid crystal systems. The purpose of the paper is to provide a basis from which attempts to interpret the dielectric properties of liquid crystals can be critically assessed, and to resolve some of the apparent conflicts of interpretation that exist in the literature.

2. Dielectric properties of nematic liquid crystals

For the purposes of this paper we shall regard refractive indices, and hence the optical properties of liquid crystals, as a high frequency dielectric response. While this assumption is certainly not valid in materials for which the relative magnetic permeability is significantly different from unity, it can be adopted for liquid crystals without error. Thus the components of the high frequency (optical) permittivity tensor can be replaced

by the square of the principal refractive indices. This relation is correct for the principal axes, but on rotating the axes, the refractive indices do not transform as a second rank tensor: there are no off-diagonal refractive indices. The range of frequencies over which the dielectric properties of liquid crystals can be studied extends from 0 to 10^{15} Hz. Below about 10^{10} Hz, the dielectric response can be measured using various capacitance bridge methods [2], but at higher frequencies, more specialized techniques are necessary [3]. For optical frequencies, it is normal to measure the refractive indices directly using refractive or interference methods. The frequency dependence of the dielectric permittivity contains information on the dynamics of the system, from collective relaxations at low frequencies to relaxation of single molecules or segments of molecules at high frequencies. The frequency dependences of infrared and visible refractive indices are due to molecular vibrations and electronic absorptions, respectively.

The quantities that may be obtained from the frequency dependence of the electric permittivity of materials are the strengths and characteristic frequencies for absorption of electromagnetic radiation. These in turn can be related to molecular properties and dynamics. This paper is focused primarily on time-independent molecular properties, and so the interpretation of molecular dynamics in liquid crystal phases will not be discussed in detail. However the variation of the dielectric permittivity with frequency is of relevance, since the strength of an absorption can be related to particular molecular parameters, such as dipole components or polarizability components. It is usual to express the frequency dependence of the components of the complex permittivity $\varepsilon(\omega)_{(j)}$ as a sum over the dielectric strengths associated with each absorption, thus:

$$\varepsilon(\omega)_{(j)} - n_{(j)}^2 = \sum_k \delta\varepsilon_k(\omega)_{(j)} - \frac{i\sigma(\text{d.c.})_{(j)}}{\varepsilon_0\omega} \quad (6)$$

In this expression the high frequency part of the permittivity, represented as the square of the appropriate principal refractive index $n_{(j)}^2$, is assumed to be independent of frequency. The frequency dependence of the dielectric strengths is given by an appropriate line-shape function, the most convenient of which is the Havriliak–Negami function:

$$\delta\varepsilon_k(\omega)_{(j)} = \frac{\delta\varepsilon_{k(j)}}{\left[1 + (i\omega\tau_{k(j)})^{\alpha_k(j)}\right]^{\beta_{k(j)}}}. \quad (7)$$

For a particular component (j) of the permittivity,

the strength of each absorption (k) is $\delta\varepsilon_{k(j)}$, and the absorption is centred on a frequency $[\tau_{k(j)}]^{-1}$. Departures from a Lorentzian-line-shape for each absorption are determined by the exponents α_k and β_k .

A useful way to formulate the dielectric response of a material is to use the Kubo formalism [4], which relates the linear response of a system to an average of property fluctuations, represented as an appropriate correlation function. This has been thoroughly investigated for the dielectric response of isotropic fluids, and in a paper published in 1975, Luckhurst and Zannoni [5] extended the treatment for isotropic fluids to anisotropic fluids. They considered a uniaxial ellipsoidal sample of anisotropic fluid with a complex permittivity $\varepsilon^{(2)}(\omega)$ immersed in an infinite dielectric having a different complex permittivity $\varepsilon^{(1)}(\omega)$. It was assumed that the principal axes of both permittivity tensors were coincident along the axes of the ellipsoidal sample. Using an expression for the cavity field in an anisotropic dielectric, Luckhurst and Zannoni obtained a relation between the correlation function for the dipole polarization and the dielectric properties of the system, assuming that the molecules within the ellipsoidal sample are non-polarizable. For a single component system, $\varepsilon^{(1)}(\omega)$ equal to $\varepsilon^{(2)}(\omega)$, this relation is:

$$\frac{\left\{\varepsilon(\omega)_{(j)} - 1\right\} \left[\varepsilon(\omega)_{(j)} - \Omega(\omega)_{(j)} \left\{\varepsilon(\omega)_{(j)} - 1\right\}\right] \varepsilon(0)_{(j)}}{\left\{\varepsilon(0)_{(j)} - 1\right\} \left[\varepsilon(0)_{(j)} - \Omega(0)_{(j)} \left\{\varepsilon(0)_{(j)} - 1\right\}\right] \varepsilon(\omega)_{(j)}} = \int_0^\infty -\frac{d}{dt} [\Phi(t)_{(j)}] \exp(-i\omega t) dt \quad (8)$$

where $\Phi(t)_{(j)}$ is the j th principal component of the normalized correlation matrix for the dipole moment $m(t)_{(j)}$ of the cavity:

$$\Phi(t)_{(j)} = \langle m(0)_{(j)} m(t)_{(j)} \rangle / \langle m(0)_{(j)} m(0)_{(j)} \rangle. \quad (9)$$

$\Omega(\omega)_{(j)}$ is the depolarization tensor, which takes account of both the anisotropy of the permittivity in the cavity field—hence its frequency dependence—and the shape anisotropy of the ellipsoidal cavity. It is given by the expression:

$$\Omega(\omega)_{(j)} = \frac{abc}{2(\varepsilon_{xx}\varepsilon_{yy}\varepsilon_{zz})^{\frac{1}{2}}} \int_0^\infty \frac{ds}{\left[s + R_{(j)}^2\right] R} \quad (10)$$

$$R_{(j)} \equiv R_x, R_y, R_z = \frac{a}{\varepsilon_{xx}^{\frac{1}{2}}}, \frac{b}{\varepsilon_{yy}^{\frac{1}{2}}}, \frac{c}{\varepsilon_{zz}^{\frac{1}{2}}} \text{ and}$$

$$R^2 = (s + R_x^2)(s + R_y^2)(s + R_z^2)$$

where a, b, c are the semi-axes of the shape ellipsoid,

and $R_{(j)}$ is the scaled semi-axis of the ellipsoidal cavity. Equation (10) enables the electric field in a cavity in an anisotropic dielectric to be determined. The dummy integration variable s is defined for a hypothetical ellipsoid having semi-axes a , b , c scaled by the square root of the principal permittivities [5]. In order to apply the theory outlined above to interpret dielectric properties it is necessary to specify the shape anisotropy of the cavity. Various possibilities have been considered, for example the shape anisotropy can reflect the overall anisotropy of the sample, or can simply be the shape anisotropy of a constituent molecule.

If the molecules of the sample are allowed to be polarized, there is an additional contribution to the internal field from the reaction field. That is, the induced polarization in the sample can induce an additional polarization in the surrounding dielectric, and hence react back on the sample itself. Some care is required to apply the reaction field, since it cannot change the polarization of the sample due to permanent dipoles. If the latter happened, there would be a polarization catastrophe, where positive feedback from the reaction field would ultimately result in a ferroelectric state. The reaction field in an anisotropic cavity has been calculated by Urano and Inoue [6] and independently by Dunmur [7]. It can be used to extend the theory of the dielectric properties of anisotropic fluids but, as we shall see, this is probably an irrelevance for liquid crystals.

The theory of anisotropic dielectrics outlined above can be applied to any system, so it was of interest to see how it might apply to molecular crystals. For such a system, only the high frequency response (refractive indices) need be considered, since the permanent dipoles are fixed on the lattice sites. The key elements of the comparison are the anisotropic cavity and reaction fields. These can be calculated as referenced above from the anisotropy in the permittivity and an assumed cavity shape. On the other hand, for a crystal it is possible to calculate the internal field directly using the methods of Born and Bradburn [8] and Ewald [9]. A comparison of results provides some guidance on the significance of the cavity shape for anisotropic dielectric fluids. The first point to emerge was that the anisotropy of the cavity and reaction fields for lattices reflects the long range anisotropy of the radial distribution. As a result of studying a number of molecular crystals of elongated molecules such as phenanthrene, naphthalene and anthracene, for which accurate single crystal refractive indices are available, it became clear that the point polarizability model for the molecules was inappropriate. By adopting a distributed polarizability it was possible to obtain excellent correspondence between the

continuum cavity and reaction field model with that based on dipole lattice sums for an isotropic depolarization tensor. The conclusion from this work [10], was that the anisotropy of the depolarization factor represented a long range anisotropy in the radial distribution. Such a long range anisotropy does not exist, at least in nematic liquid crystals, and it is appropriate to use an isotropic depolarization tensor. However the effects of the local anisotropy do manifest themselves as a requirement to adopt a distributed polarizability for the molecule, which is clearly associated with its electronic structure.

3. Molecular parameters from dielectric properties

The molecular properties that contribute to dielectric properties have already been identified as the molecular dipole moment and the polarizability. However for liquid crystals, as seen in equations (11) and (12) below, these are convoluted with the order parameter. This was originally introduced by Tsvetkov [11] as a molecular parameter, although it can also be regarded as a macroscopic variable defined in terms of the macroscopic anisotropy of a liquid crystal phase [12]. The molecular order parameter requires that a unique axis can be defined within the molecule, the long axis, which specifies the orientation of the molecule with respect to the liquid crystal director. Since both the dipole moment and polarizability components of a molecule depend on orientation, then the angles between the long molecular axis and the dipole direction and the principal axes of the polarizability must also be specified or determined from some model. These will enter the appropriate molecular expressions for the electric permittivity and refractive indices. For calamitic nematic liquid crystals, the major axis of the polarizability is always assumed to be coincident with the long molecular axis. If the molecules depart from axial symmetry, then additional angles are necessary to specify the orientation of a molecule with respect to the director, and appropriate biaxial order parameters [13] are introduced to specify the average orientations of these minor axes. Flexible molecules have internal degrees of freedom, so that any molecular axis may fluctuate, and measured properties will include averages over these internal coordinates. Internal order parameters [14] or shape parameters [15] have been introduced to account for the effects of molecular flexibility.

The first molecular theory of the dielectric properties of nematics was formulated by Maier and Meier in 1961 [16], and the corresponding Maier and Meier equations express the components of the dielectric permittivity, parallel and perpendicular to the director, in terms of

the molecular dipole moment, mean polarizability, the polarizability anisotropy and the order parameter. Although the molecular order parameter was introduced by Tsvetkov in 1942, it was not until 1958 that Maier and Saupe [17] produced a molecular theory that predicted the temperature dependence of the order parameter. This has become known as the Maier–Saupe Mean Field Theory, but it must be pointed out that the first molecular field theory was actually published by Grandjean [18] in 1917, and his results are essentially the same as those of Maier and Saupe.[†]

For uniaxial nematic liquid crystals, the Maier and Meier equations for parallel and perpendicular components of the permittivity (ϵ_{\parallel} , ϵ_{\perp}) are:

$$\epsilon_{\parallel} - 1 = \epsilon_0^{-1} N h F \left\{ \bar{\alpha} + \frac{2}{3} \Delta \alpha S + \frac{F}{3 k_B T} [\mu_{\text{eff}}^{\parallel}]^2 \right\} \quad (11)$$

$$\epsilon_{\perp} - 1 = \epsilon_0^{-1} N h F \left\{ \bar{\alpha} - \frac{1}{3} \Delta \alpha S + \frac{F}{3 k_B T} [\mu_{\text{eff}}^{\perp}]^2 \right\}. \quad (12)$$

In these equations an isotropic internal electric field has been assumed, such that:

$$h = \frac{3\bar{\epsilon}}{2\bar{\epsilon} + 1} \quad \text{and} \quad F = \frac{(2\bar{\epsilon} + 1)(\bar{n}^2 + 2)}{3(2\bar{\epsilon} + \bar{n}^2)} \quad (13)$$

and S is the Tsvetkov order parameter for a uniaxial liquid crystal. The effective mean square moments parallel and perpendicular to the director can be written as:

$$[\mu_{\text{eff}}^{\parallel}]^2 = g_1^{\parallel} [\mu_{\ell}^2(1 + 2S) + \mu_t^2(1 - S)] \quad (14)$$

$$[\mu_{\text{eff}}^{\perp}]^2 = g_1^{\perp} \left[\mu_{\ell}^2(1 - S) + \mu_t^2 \left(1 + \frac{1}{2} S \right) \right] \quad (15)$$

where μ_{ℓ} and μ_t are, respectively, the components of the molecular dipole moment along and perpendicular to the molecular long axis. The g -factors take account of specific dipole–dipole interactions, and are discussed below.

Equations (11) and (12) give the relationship between measured components of the electric permittivity and the molecular parameters of dipole moment, mean polarizability $\bar{\alpha}$, polarizability anisotropy $\Delta\alpha$ and order parameters. Additionally the density (number of molecules per unit volume) must be specified, and correction factors h and F for the internal field evaluated from some model. While the qualitative behaviour of the

permittivity can mostly be explained in terms of these equations, they do not provide a quantitative theory of dielectric behaviour. The sign of the dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) is largely determined by the angle β between the molecular dipole moment and the long axis of the molecule:

$$\Delta\epsilon = \frac{N h F S}{\epsilon_0} \left[\Delta\alpha + \frac{\mu^2}{2 k_B T} (3 \cos^2 \beta - 1) \right]. \quad (16)$$

Thus if the dipole is predominantly perpendicular to the alignment axis, then the dielectric anisotropy is negative. In some liquid crystals there is a balance between the positive polarizability anisotropy, and the contribution of the dipole moment, so that the dielectric anisotropy can change sign with temperature. The temperature dependence of the dielectric anisotropy is determined primarily by variation of the order parameter with temperature.

For many liquid crystals, especially those containing strongly polar molecules, the temperature dependence of the dielectric anisotropy is not as predicted by the Maier and Meier equations. The dielectric anisotropy may be nearly independent of temperature, while there is an increment in the mean permittivity at the nematic to isotropic transition. These features can be interpreted as due to short range angular correlations between the dipolar molecules, which can be quantitatively represented in terms of Kirkwood correlation factors, defined by:

$$g_1^j = 1 + V^{-1} \int G_1(\mathbf{r})_{(j)} d\mathbf{r} \quad (17)$$

where V is the volume of the sample, and $G_1(\mathbf{r})_{(j)}$ is the j -component of the normalized angular correlation matrix, given by:

$$G_1(\mathbf{r})_{(j)} = \langle \mu_j(0) \mu_j(\mathbf{r}) \rangle / \langle \mu_j(0) \mu_j(0) \rangle. \quad (18)$$

For isotropic fluids, the Kirkwood correlation factor can be simply interpreted as the ensemble average of the cosine of the angle (θ_{pair}) between the dipole moment vectors on interacting pairs of molecules, i.e.

$$g_1^{\text{isotropic}} = 1 + \langle \cos \theta_{\text{pair}} \rangle. \quad (19)$$

Simple theories have been developed for dipole–dipole correlation in nematics, which predict that calamitic molecules with strong longitudinal dipoles should exhibit short range antiferroelectric order, while such molecules having perpendicular dipoles have short range ferroelectric order [19]. These predictions are in fact confirmed by experimental results [20, 21].

Thus for static permittivities, there is a theoretical framework which can relate molecular properties to

[†]To recognize the earlier work, it is proposed that future references to the Mean Field or Molecular Field Theory should describe it as the Maier–Saupe–Grandjean Theory.

the measured macroscopic quantities. However, the quantitative interpretation is strongly model-dependent, to the extent that prediction of dielectric properties from molecular parameters is extremely difficult, if not impossible. Another perspective is to regard the molecular parameters as being representative of both the molecules and their liquid crystal environment. This introduces the idea of 'dressed properties', which may be more useful in the description of condensed phases.

If dielectric measurements of liquid crystals are available as a function of frequency, additional parameters become accessible, which are characteristic of the constituent molecules. The parameters that are used to interpret dielectric relaxation spectra are the respective strengths of the absorption, characteristic relaxation times and the exponents α and β ; see equation (7). The latter do not have any simple physical meaning, except to indicate the extent to which the local environment changes the dipolar relaxation from a simple exponential time dependence. A Debye-like relaxation is characterized with $\alpha = \beta = 1$. The total strength of the dielectric absorption is given as a sum of contributions from different dipole relaxations in the molecule. These can be associated with different dipole components parallel and perpendicular to the alignment axis of the molecule, which relax at different frequencies. For flexible molecules, different dipolar groups within the molecule may relax with different characteristic frequencies, and these will give rise to separate contributions to the dielectric spectrum. The separate strengths for the different contributions can all be analysed by corresponding terms in the Maier and Meier equations; for flexible molecules different dipolar groups will be expected to have different order parameters. In practice, it is usually possible to separate contributions to the dielectric spectra from the relaxations associated with parallel and perpendicular components of the molecular dipole, since these occur at widely different frequencies. For liquid crystal molecules which have a number of dipolar groups it is not usually possible to analyse their dielectric spectra in terms of separable contributions from the different groups. However for a special class of flexible dimeric mesogens having different dipolar groups attached to a linking chain, Luckhurst and co-workers [22] have demonstrated that the dielectric spectra of liquid crystal dimers can be analysed to give information about different dipolar moieties within the molecule. The strengths of the contributing absorptions change with temperature, which is an indication of changes in the overall molecular shape induced primarily by the corresponding changes in the degree of orientational order.

The quantities which describe the dynamics of relaxation processes are the relaxation times and their temperature dependence. The latter is usually represented as an Arrhenius function, with appropriate activation energies. Neither the relaxation times nor the activation energies for liquid crystals can be interpreted in terms of simple molecular properties, since they are strongly dependent on the molecular environment. However, it is possible to relate the rotational relaxation time for end-over-end reorientation of a rigid molecule in a nematic liquid crystal (τ_{\parallel}) to the relaxation time (τ_0) the molecule would have in a hypothetical isotropic fluid under the same external conditions [23]. This is the extension of the Debye theory of rotational relaxation in simple fluids to rotational relaxation in the presence of an orienting potential of mean torque. If the potential of mean torque U has the form [24]:

$$U(\theta) = -\sigma k_B T \cos^2 \theta \quad (20)$$

where θ is the angle between the director and the alignment axis of the molecule, assumed to be rod-like and rigid, and $\sigma k_B T$ is the height of the potential barrier for a π -rotation, then the ratio of relaxation times (g_t , the retardation factor) for the presence and absence of the potential is given by:

$$g_t = \frac{\tau_{\parallel}}{\tau_0} = \frac{\exp(\sigma)}{\sigma}. \quad (21)$$

Having established the coefficient of the potential of mean torque, it is possible to evaluate the order parameter. This procedure provides a method of obtaining microscopic information from the dielectric relaxation spectra [25]. The usefulness of the results for a particular system depends on the applicability of the various assumptions inherent in the diffusion model. However some more fundamental doubts have been raised by Bates and Luckhurst [26] concerning the rotational diffusion model itself. Retardation factors determined from a molecular dynamics simulation of Gay-Berne particles are significantly different from those predicted by the rotational diffusion model using equation (21). This suggests that the reverse procedure of obtaining the coefficient of the potential of mean torque, and hence the order parameter, from measurements of the retardation factor is unlikely to be reliable.

4. Results and discussion

The interpretation of dielectric properties of liquid crystals in terms of molecular properties relies on a knowledge of the order parameter. Even allowing for

Table 1. Molecular dipole moments and Kirkwood correlation factors for selected mesogens.

Compound	Chemical Structure	Dipole moment/Debye			Kirkwood correlation factors			Ref
		μ_0	μ_t	μ_e	iso ^a	nematic ^b		
		g_{\parallel}	g_{\perp}^{\parallel}	g_{\perp}^{\perp}				
CB5		4.8			0.5			[27]
CCH5		3.8			0.6			[27]
C4CN		5.8	5.5	1.7	0.7	1.1	0.6	[21]
C3FCN		6.6	6.2	2.2	0.8	1.0	0.7	[21]
CP1		5.4	5.2	1.4	0.8	0.9	0.4	[28]
CP3		2.6	2.3	1.3	1.1	1.2	0.6	[28]
4HENO4		5.5	0.2	5.5	3.6	1.6	1.9	[20, 29]
6HENO4		6.0	0.2	6.0	3.1	1.4	1.6	[20, 29]
5HBENO4		6.4			1.9			[29]

^aValues for pure materials; except for CP1 and CP3, measured in 0.1M (approx.) xylene solutions. ^bObtained from aligned solutions in the nematic phase of I22 [Merck, 1-(*trans*-4-ethylcyclohexyl)-2-(4-ethyl-2-fluorobiphenyl)ethane].

uncertainties in the order parameter, molecular properties derived from measurements on liquid crystals show evidence of the influence of short range interactions. For example, the molecular dipole moments of mesogens have been obtained from dielectric measurements on liquid crystals, and are often significantly different from either molecular calculations or dilute solution measurements. This can be rationalized in terms of short range dipole correlations that reduce or enhance the effective dipole moment. Some selected results are given in table 1.

The effect of the orientational order and local interactions on the effective dipole moments of mesogens has been demonstrated by measurements on a number of nematic solutions. The polar mesogens of interest were dissolved in a liquid crystal solvent (I22) having a relative dielectric constant of 3 and a zero dielectric anisotropy; use of this solvent minimizes the corrections due to the anisotropic internal field. A series of measurements were made as a function of concentration and temperature of the solute mesogens, and the effects of dipole correlation were clearly

evident. However a new model for calculating the electric permittivity of nematic liquid crystals has recently been reported by Ferrarini [30], which suggests that dipole correlations may not be as important as experimental measurements indicate. These results are based on a surface tensor representation of the mesogen, and the dielectric model is a molecule-shaped cavity, having a surface charge distribution calculated from the electronic structure of the molecule. By scaling the surface charges, such that the calculated and experimental molecular dipole moments are in agreement, the model reproduces the measured electric permittivity of selected polar liquid crystals. There is no need to postulate short range dipole correlations, but the electrostatic interactions no longer represent those of a point dipole, and the molecular shape and excluded volume have been explicitly included in the dielectric theory.

The effect of molecular correlations on the effective polarizability and polarizability anisotropy of mesogens could be imagined to be even more important than short range effects on effective dipole moments. Indeed the divergence in the intensity of depolarized light scattering from isotropic fluids of mesogens as the nematic to isotropic phase transition is approached is evidence of the growth in orientational correlations between the polarizability axes of the molecules. This orientational correlation can be quantified in the same way as dipole-dipole correlations, except that the angular function is of second order in the cosine of the angle between the principal axes of the polarizability of interacting molecules. The corresponding correlation factor for isotropic fluids (g_2) can be defined as:

$$g_2 = 1 + V^{-1} \int G_2(\mathbf{r}) d\mathbf{r} \quad (22)$$

where $G_2(\mathbf{r})$ is an angular correlation for the second Legendre polynomial for molecules making an angle θ with a fixed laboratory axis:

$$G_2(\mathbf{r}) = \langle P_2[\cos\theta(0)] P_2[\cos\theta(\mathbf{r})] \rangle. \quad (23)$$

Measurements of the light scattering from solutions of mesogens indeed confirm that the effective polarizability anisotropy increases dramatically as the concentration of mesogens increases [31, 32]. This is illustrated in the figure, where g_2 is plotted as a function of concentration for a selection of mesogens in carbon tetrachloride.

Numerical values for the polarizability and polarizability anisotropy for some standard mesogens are given in table 2. The effect of angular correlations is also demonstrated if the polarizability anisotropy of mesogens determined from electric birefringence

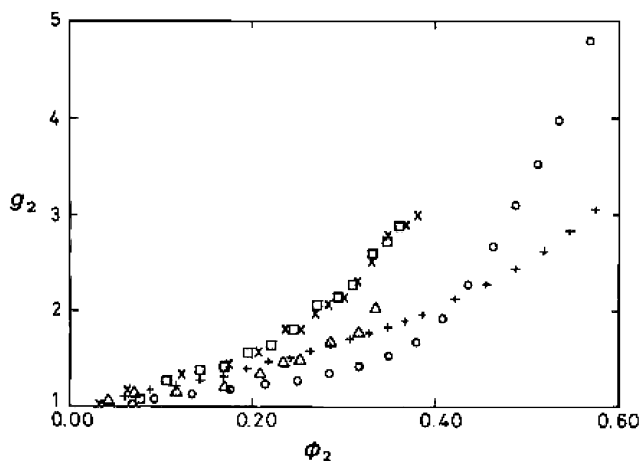


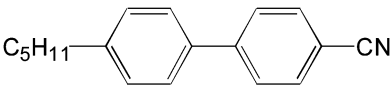
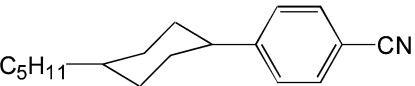
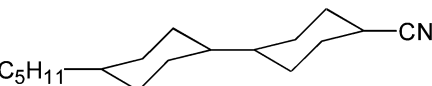
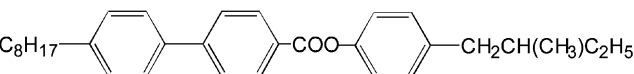
Figure. Correlation factor g_2 obtained from depolarized light scattering for solutions of mesogens in carbon tetrachloride as a function of volume fraction (ϕ_2): CE8R (racemate) \square ; CE8S \times ; CB5 $+$; biphenyl \triangle ; CCH5 \circ (from ref. [32]).

measurements on dilute solutions is compared with values derived from measurements on bulk samples [33].

5. Conclusions

It should be clear from the foregoing discussion that the molecular properties of mesogens are profoundly influenced by their environment in a liquid crystal phase. Various models exist to take account of these influences, but all the models have implicit assumptions. Almost without exception, the assumptions are that the electric properties can be represented as point properties, and furthermore that the excluded volume of the interacting molecules can be neglected. Such assumptions are not supported by the experimental results, which point to strong correlations between molecules, even if the theories on which the molecular interpretations are based ignore the effects of molecular size and shape. The interpretation of the order parameter is of fundamental importance in any discussion of molecular properties of liquid crystals. Of significance in the context of our discussion is the recent observation that retardation factors from dielectric spectroscopy were not a reliable means to obtain order parameters. A conclusion from that paper was the need to include excluded volume effects in any theory of the rotational diffusion of molecules. This conclusion is echoed here, where it seems that the specific inclusion of molecular shape and size into theories for the molecular properties of liquid crystals is necessary to advance our understanding of the dielectric properties of these materials.

Table 2. Polarizabilities and correlation factors g_2 for selected mesogens.

Compound		Polarizability/ $10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$			Ref
		α	$\Delta\alpha$	g_2^a	
CB5		37.5	20.2	1.7	[31]
PCH5		36.2	16.0		[27]
CCH5		35.5	12.1	1.3	[32]
CE8R		65.4	36.2	2.1	[32]

^aValues for a solution of 0.3 volume fraction in carbon tetrachloride [32].

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