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Invited Article

The local field in uniaxial liquid crystals

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Analysis of the various models for the local field shows that most of them give similar Lorenz–Lorentz formulae for nematic liquid crystals. They differ only in the way they define parameters such as the structural anisotropy. Because of the arbitrariness of the model parameters, the structural anisotropy values in the Lorenz–Lorentz equation for liquid crystals can be better determined with the help of experiment. The results of absorption dichroism measurements for this purpose are analysed in some detail.

1. Introduction

Optical methods are very valuable for molecular and structural studies of liquid crystals. For example, measurements of the refractive indices of liquid crystals are frequently analysed to yield information about the degree of orientational order and the polarizabilities of the constituent molecules. Moreover, the special optical properties are the reason for the technological interest in them. However, the relationship between the refractive indices of a nematic and its microscopic structure is not straightforward. A quantitative evaluation of the results of optical experiments requires a knowledge of the difference between the local field $\mathbf{E}^l$ of a light wave, experienced by a molecule, and the macroscopic or Maxwell field $\mathbf{E}$ in the medium, that is a knowledge of the local field correction factor f, connecting the amplitudes of these fields, $\mathbf{E}^l = f\mathbf{E}$.

The local field expression given by Lorentz [1],

$$f = \tfrac{1}{3}(\varepsilon + 2), \tag{1}$$

is only valid for cubic crystals with point polarizabilities at the sites of the lattice (ε is the dielectric permittivity). Even for isotropic liquids this expression is only approximately valid: the intermolecular correlations have to be taken into account. Moreover, the non-uniformity of the local field leads to contributions of higher multipole interactions. For liquids consisting of anisotropic molecules such corrections become very complicated. These problems have been treated in many papers devoted to the investigation of the local field in isotropic liquids [2]. Similar studies exist for liquid crystals. Orientational and orientational–translational correlations of the molecules resulting from intermolecular forces have been analysed [3–5]. The effects of the non local character of the molecular polarizability and the peculiarities of its distribution over the molecular volume, its renormalization due to interactions with the nearest surroundings, have also been treated [6]. However, it seems impossible now to take all these factors systematically into account. The reason for this lies in the complexity of the mesogenic molecules in combination with the presence of internal degrees of freedom. In consequence various semi-empirical models have become very popular in treating the local field problem.

In these models the authors try to account for the main feature of liquid crystals, namely their translational disorder and anisotropy. This includes not only the anisotropy of the molecular polarizability and of the orientational distribution, but also the anisotropy of the intermolecular distances, the so-called structural anisotropy. Actually, the question relating to the local field can be stated in two parts. First, which of the theories should be preferred and secondly, even if we find the preferred theory, how can we determine the model parameters describing the structural anisotropy? This article focuses on these two problems.

Later we shall analyse some models for the local field in uniaxial liquid crystals with the aim of making their advantages and potential for the description of the interaction of light with liquid crystals explicit. As we shall see, the only acceptable methods with which to determine the model parameters and the local field anisotropy are experimental. The plan of the article is as follows: first, we consider the analogues of the Lorenz–Lorentz equation for liquid crystals. Then we discuss the relative merits and limitations of the various assumptions that have to be made in order to determine the model parameters. Finally, we present experimental methods for the determination of the local field anisotropy. The article is not meant to be a general review of existing local field models and theories. Furthermore, we deal only with non-polar compounds or the high-frequency limit. Since our emphasis is on the long range structural anisotropy, we shall not discuss models in which this effect is neglected (see, for example, [7]). We shall not pay much attention to the agreement or disagreement of the various theories with experiment; often those 'experimental' results are obtained with the help of similar or other theories, and there are many reasons for any type of agreement to be fortuous. Consequently, the models are discussed from the point of view of their possible theoretical justification.

2. Generalization of the Lorenz–Lorentz equation for liquid crystals

2.1. *Lattice theories*

There are two ways to calculate the local field in a liquid crystal. The first is to use formulae obtained originally for anisotropic crystals. Another way is to introduce the anisotropy of the liquid-crystalline phase into models developed for isotropic liquids.

The first route has been taken by Maier and Saupe [8]. They supposed that molecules in a nematic phase are distributed over a simple lattice, and followed Neugebauer's development [9]. The local field at any point within the polarized liquid crystal is obtained by summing the electric fields due to the induced dipoles situated at all the lattice sites and the external field. To calculate the contribution from the induced dipoles, Neugebauer drew a sphere around a particular particle (see figure 1). As in the Lorentz model, the radius of the sphere is chosen to be large in comparison with the average distance between two neighbouring dipoles, and this distance must be sufficiently larger than the distance between the positive and negative charges of one particle. This allows the physical dipoles of finite size to be replaced by point dipoles. The dipoles outside the Lorentz sphere can be dealt with as if they fill the space uniformly, using the result for the cavity field from electrostatics of continuous media. The contribution of the dipoles within the sphere to the field at the centre, which in the isotropic case is equal to zero, depends on the type of lattice and may

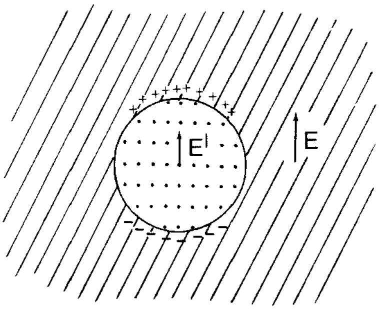

Figure 1. Neugebauer model for the calculation of the local field factor. The local field **E**′ differs from the macroscopic field **E** due to the charges induced at the surface of the cavity by the field **E** and due to the contribution of the induced dipoles inside the sphere.

be calculated in any particular case. For uniaxial liquid crystals the principal axes of the molecular polarizability tensor, averaged over all possible orientations, are parallel to those of the dielectric permittivity tensor. The Maier–Saupe–Neugebauer model then leads to a simple relation for the factor f, connecting the local and macroscopic fields, namely

$$f_{xx} = \tfrac{1}{3}[n_x^2 + 2 + a(n_x^2 - 1)], \quad f_{zz} = \tfrac{1}{3}[n_z^2 + 2 - 2a(n_z^2 - 1)], \tag{2}$$

where a is determined by the parameters of the crystalline lattice, and the n_i denote the principal components of the refractive index of the mesophase. As we are only concerned with the high frequency limit, $n_i^2 = \varepsilon_{ii}$.

A more straightforward way to calculate the induced dipole contribution to the local field was proposed by Born and Huang [10]. In their method for evaluating the lattice sum they have no need to postulate a cavity model. Introducing the Lorentz-factor tensor **L**, Dunmur [11, 12] has rewritten their result in a more convenient form and extended it to liquid crystals. For uniaxial liquid crystals the **L** tensor is diagonal with respect to the principal axes, and the local field factor may be written as

$$f_{ii} = 1 + L_{ii}(\varepsilon_{ii} - 1). \tag{3}$$

Consequently, the generalized Lorenz–Lorentz equation takes the form

$$\frac{\varepsilon_{ii} - 1}{1 + L_{ii}(\varepsilon_{ii} - 1)} = 4\pi\varrho\langle\alpha_{ii}\rangle, \tag{4}$$

where ϱ and $\boldsymbol{\alpha}$ are the number density and the molecular polarizability tensor, while the brackets denote an average over the molecular orientations.

The best model of the dielectric properties of a material has to reproduce the results from an exact microscopic theory. For molecular crystals the lattice model is exact, and the Lorentz factor tensor can be calculated precisely for any particular lattice. However liquid crystals are macroscopically anisotropic fluids which have only short range translational order. Therefore in the absence of a microscopic theory of such fluids, the cavity/continuum model of the internal field probably is physically more appealing. So we shall now analyse the cavity models developed for isotropic liquids.

2.2. *Cavity theories*

First, the extension of the Onsager model by de Jeu and Bordewijk [13] should be mentioned. They approximate a molecule by an anisotropic homogeneously polarizable

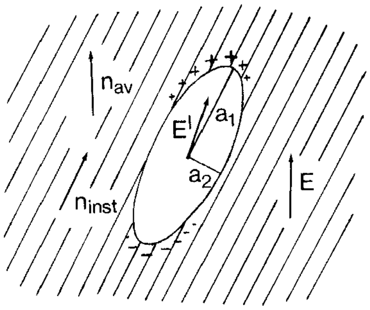

Figure 2. The model of molecular arrangement resulting from the de Jeu–Bordewijk consideration. $\mathbf{n}_{inst}$ and $\mathbf{n}_{av}$ indicate the instantaneous and average orientations of the director.

spheroid filling the cavity in the anisotropic homogeneously polarized continuum (see figure 2). They did not succeed in deriving an expression for the local field factor from a molecular model of a liquid crystal. Based on experimental data, the authors require the local field to be independent of the macroscopic dielectric anisotropy. As a result, they obtain an expression for the local field factor similar to equation, (3),

$$f_{ii} = 1 + \Omega_i(\varepsilon_{ii} - 1), \tag{5}$$

where the principal values of **L** are now identified with the depolarization factors of a dielectric prolate spheroid with an axial ratio a_1/a_2 equal to that of the molecular repulsive core (see figure 2); thus

$$\Omega_i = \frac{a_1 a_2^2}{2}\int_0^{\infty} \frac{dv}{(v + a_i^2)(v + a_2^2)\sqrt{[(v + a_1^2)]}} \tag{6}$$

or

$$\Omega_z = \frac{1 - l^2}{2l^3}\left[\ln\frac{1 + l}{1 - l} - 2l\right], \tag{7}$$

where

$$l = \sqrt{\left[1 - \left(\frac{a_2}{a_1}\right)^2\right]}, \quad \Omega_x = \tfrac{1}{2}(1 - \Omega_z).$$

The range of the depolarization factors is $0 \leqslant \Omega_z \leqslant \frac{1}{3}$ when $0 \leqslant a_2/a_1 \leqslant 1$. The analysis of de Jeu's result shows that such a local field acts on a molecule only in the case of total orientational correlation of the molecules in a nematic liquid crystal, which is the case when orientational disorder is due to the variation of the director orientation (cf. $\mathbf{n}_{inst}$ on figure 2).

Perhaps the work by Segre [14] is based on a much more realistic model (in this paper the less successive approaches by Petrov and Kuznetsov are criticized). Following Onsager, he has solved the electrostatic problem for a partly oriented anisotropic spheroid in a uniaxial dielectric continuum (see figure 3). His result for the local field factor may be written as

$$\left.\begin{aligned} f_{xx} &= \tfrac{1}{3}[\varepsilon_{xx} + 2 + (m_{zz} - m_{xx})S(\varepsilon_{xx} - 1)], \\ f_{zz} &= \tfrac{1}{3}[\varepsilon_{zz} + 2 - 2(m_{zz} - m_{xx})S(\varepsilon_{zz} - 1)], \end{aligned}\right\} \tag{8}$$

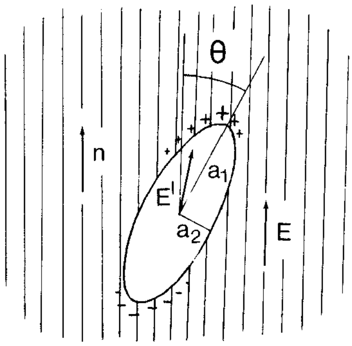

Figure 3. The Segre model for the calculation of the local field. The order parameter is defined as $S = \langle \frac{1}{2}(3\cos^2\theta - 1)\rangle$.

i.e. unlike de Jeu's model, the depolarization anisotropy of the Onsager cavity $(m_{zz} - m_{xx})S$ is proportional to the second rank orientational order parameter S. The proportionality coefficient equals the anisotropy of the depolarization factors of the cavity, defined as the repulsive core of the intermolecular pair potential $(m_{ii} = -\Omega_i)$.

2.3. *Comparison of the different approaches*

As we can see comparing the relations (2), (5) and (8), very different approaches to the local field problem, based on different models, result in formally identical expressions if it is assumed that

$$-a = -(m_{zz} - m_{xx})S = \Omega_z - \Omega_x = L_{zz} - L_{xx}. \tag{9}$$

Moreover, the molecular statistical theory of nematics also gives similar expressions for the local field factor [3, 5] when orientational fluctuations are ignored

$$f_{ii} = \tfrac{1}{3}(n_i^2 + 2) + \eta_{ii}(n_i^2 - 1) \tag{10}$$

(an alternative expression is discussed in the Appendix). In [5] it is shown that it is possible to construct inside a polarized anisotropic fluid a surface with the property that the contribution of the dipoles within the volume bounded by this surface to the electric field at the origin is zero. The shape of this generalized Lorentz cavity and the associated local field factors are connected with the radial distribution function. More recently, a simple model [16] (see also figure 4), incorporating only steric intermolecular repulsions, predicted the anisotropy of the local field to be very nearly proportional to the orientational order parameter, in good agreement with Segre's predictions

$$\eta_{xx} \approx \frac{2}{5}\left(\frac{k-1}{k+2}\right)S, \quad \eta_{zz} \approx -\frac{4}{5}\left(\frac{k-1}{k+2}\right)S, \tag{11}$$

where $k = a_1/a_2$ is the molecular length-to-breadth ratio. Hence we can conclude that formally the results of different models and molecular statistical approaches are similar to that given by equation (3).

The relationship between the continuum and lattice models has been discussed by Dunmur and Munn [17]. They have calculated the dielectric properties of a simple model, treating the molecules as sphero-cylinders arranged on a trigonal lattice with one molecule in the primitive unit cell. Their results indicate that for axial ratios up

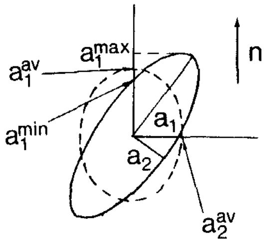

Figure 4. Illustration of the lowering of the averaged cavity anisotropy due to orientational disorder (according to the steric repulsion model [16]).

to five the assumption of an ellipsoidal cavity for a molecule in a fluid gives the same value for the local field as fixing the molecule on a regular lattice with the same spatial anisotropy.

Of course, these results should only be considered as models, and their predictions only approach the exact results. To derive molecular polarizabilities from the refractive index data we have to take into account the local orientational and translational ordering, the real distribution of the electron density over the molecular volume, the contributions of many body interactions and, probably, some other effects. However, it has been shown [3] that the effect of pair correlations can be formulated as a renormalization of the molecular polarizability. It may be hoped that this is the case for other contributions too. When we only analyse the long range effects of the dipole–dipole interactions, the problem is reduced to choosing the appropriate cavity or lattice.

3. Approximations to determine the model parameters

3.1. *Exact molecular statistical results*

From the viewpoint of molecular statistics, the factor

$$\tau = -\tfrac{1}{3}(L_{zz} - L_{xx})$$

which characterizes the structural anisotropy is determined by the anisotropy of the pair distribution function. In the absence of orientational correlations this relation can be written in the form [5]

$$\tau = \frac{1}{4\pi}\int \ln(R_c(\hat{r}))(3r_i^2 - 1)d\Omega, \tag{12}$$

where $\hat{r}$ is a unit vector in the laboratory fixed coordinate system with components r_i; $d\Omega$ is the angular volume element and $R_c(\hat{r})$ is the distance from the origin to a point on the surface of the generalized Lorentz cavity in the direction $\hat{r}$. The equation of this surface is [5]

$$\ln(R_c(\hat{r})) = \ln b - \int_0^b \frac{g(r\hat{r})dr}{r} + \int_b^\infty \frac{(1 - g(r\hat{r}))}{r}dr, \tag{13}$$

where $g(r\hat{r})$ is the radial distribution function and b is an arbitrary constant. Using the well-known properties of this function, equation (13) may be rewritten in the form more suitable for analysis, but less easy for computation,

$$\tau = -\frac{1}{4\pi}\int\int \frac{g(r\hat{r})}{r}dr(3xx - 1)d\Omega. \tag{14}$$

However, it is rather difficult to calculate the pair distribution function even for isotropic liquids consisting of symmetrical molecules. For liquid crystals a proper theory is completely absent. Even if a microscopic theory of anisotropic fluids existed, the cavity shape would not necessarily be expressible as an analytic function. It is desirable therefore to determine the structural anisotropy of the mesophase on the basis of some additional approximations and models.

It is convenient to consider the structural anisotropy effect on the local field factor tensor after transforming the equations connecting the components of the tensors **L** and **f** (for example, equations (3)) to the corresponding expressions for the mean value

$$\bar{f} = \tfrac{1}{3}(f_{zz} + 2f_{xx})$$

and the local field tensor anisotropy

$$\delta f = \tfrac{1}{3}(f_{zz} - f_{xx})$$

[18]:

$$\bar{f} = 1 + 4\pi\bar{L}\bar{\chi} + 8\pi\delta L\delta\chi, \tag{15}$$

$$\delta f = 4\pi(\bar{L}\delta\chi + \bar{\chi}\delta L + \delta\chi\delta L), \tag{16}$$

where χ is the dielectric susceptibility tensor. Here and later the overbar and prefix δ denote the average value and the anisotropy respectively. Taking the relationship between the dielectric susceptibility and permittivity into account we have

$$\bar{f} = \tfrac{1}{3}(\bar{\varepsilon} + 2) + 2\delta\varepsilon\tau, \tag{17}$$

$$\delta f = \tfrac{1}{3}\delta\varepsilon + (\bar{\varepsilon} - 1)\tau + \delta\varepsilon\tau. \tag{18}$$

It should be noted that these formulae are valid independently of the model used to calculate τ.

According to X-ray diffraction results [19], the mean distance between the centres of molecules in nematics along the director is larger than that in the perpendicular direction, and therefore $\tau < 0$. We can see from equation (17) that both the structural anisotropy τ and the optical anisotropy $\delta\varepsilon$ contribute to the mean value of the tensor f. τ dependent terms are always negative in the nematic phase of non-polar liquid crystals and tend to zero when approaching the phase transition to the isotropic liquid. On the other hand, the anisotropy in the tensor f may be positive or negative depending on the values of $\delta\varepsilon$ and τ. The effect of varying the local field anisotropy with the wavelength of light is essential for the interpretation of absorption dichroism measurements for pure liquid crystals and their solutions.

3.2. *Different model approximations*

First of all we discuss the model proposed by Vuks [20]. The analysis of experimental data lead him to the assumption that the local field in an anisotropic medium can be effectively independent of the direction and is equal to $\tfrac{1}{3}(\bar{\varepsilon} + 2)\mathbf{E}$. From equation (18) it is clear that the local field can be isotropic in two cases: (1) $\delta\varepsilon = \tau = 0$, giving

$$f_{zz} = f_{xx} = \bar{f} = \tfrac{1}{3}(\bar{\varepsilon} + 2); \tag{19}$$

this corresponds to the case of an isotropic liquid when the correlation of neighbouring molecules is ignored; (2) $\delta\varepsilon \neq 0$, $\tau = \tau_k$, where

$$\tau_k = \frac{\delta\varepsilon}{3(\bar{\varepsilon} - 1 + \delta\varepsilon)}; \tag{20}$$

while δf vanishes in this case, the local field factor

$$f_{zz} = f_{xx} = \bar{f} = \tfrac{1}{3}(\bar{\varepsilon} + 2) - \frac{2\delta\varepsilon^2}{3(\bar{\varepsilon} - 1 + \delta\varepsilon)} \tag{21}$$

differs from that proposed by Vuks. It is clear from equation (20) that the local field in liquid crystals can be isotropic for such a mesophase structure that $\tau = \tau_k$. In other words, this is the case when the structural and optical anisotropies compensate for each other. It is worth noting that the value of τ only changes with temperature while τ_k depends also on the wavelength of light because of the dispersion of the refractive indices. Therefore the local field in a liquid crystal can be isotropic for some specific wavelength. As the dispersion of refractive indices for liquid crystals is relatively small in the visible region far from the absorption bands, these relations may be approximately valid in a sufficiently wide spectral interval. The temperature dependence of τ_k and τ, obtained with different methods, is illustrated in table 1.

An attempt to account for the local field anisotropy, while interpreting the refractive index data, has been made by Saupe and Maier [8]. To determine the structural anisotropy factor they proposed to equate the average molecular polarizability in the isotropic and liquid-crystalline phases

$$\frac{1}{\varrho_{\mathrm{lc}}}\left[\frac{\varepsilon_{zz} - 1}{\varepsilon_{zz} + 2 + 6\tau(\varepsilon_{zz} - 1)} + 2\frac{\varepsilon_{xx} - 1}{\varepsilon_{xx} + 2 - 3\tau(\varepsilon_{xx} - 1)}\right] = \frac{3}{\varrho_i}\frac{\varepsilon - 1}{\varepsilon + 2}. \tag{22}$$

We do not compare the results obtained by this method with other models (see table 1), but we do want to draw attention to the problems of such a method. First, the polarizability of the molecules can change not only during the transition from the isotropic liquid to the mesophase, but within the mesophase temperature interval as well. This variation can be caused either by conformational flexibility of the mesogenic molecules [33] or directly by intermolecular forces [34]. Secondly, in deriving the analogue of the Lorenz–Lorentz equation for liquid crystals several assumptions have been made (molecular point polarizabilities or homogeneously polarizable molecules, the absence of the local order, etc.). The effect of molecular correlations, for example the pair correlations [3, 4, 35], is to change effectively the molecular polarizability. Deviations from equation (3) are small: from a comparison of the results obtained for totally correlated and uncorrelated models they have been estimated to be about 1 per cent. However this is the same order of magnitude as the difference between the refraction in an isotropic liquid and the averaged refraction $\bar{R} = (\bar{\varepsilon} - 1)/(\bar{\varepsilon} + 2)$ in the nematic phase. Thus, because the optical and structural properties are connected in expression (22) in such a way that small variations of the molecular polarizability lead to large errors in the determination of τ, this method is often unreliable.

Better results can probably be obtained if τ is estimated from the molecular geometry. For example, de Jeu [13] proposed that the axial ratio of the model ellipsoidal cavity should be equated to the molecular width-to-length ratio and hence to calculate Ω_i from equation (7). The molecular length can be determined from the geometric dimensions and the width from the volume per molecule in the mesophase. The values of τ obtained in this way for 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-methoxybenzilidene-4′-*n*-butylaniline (MBBA), which have been well studied, are equal to $-0{\cdot}107$ and $-0{\cdot}11$, respectively (the results for other compounds are given in table 1). Only a perfectly oriented nematic phase can possess such a large structural anisotropy. This particular choice for the model ellipsoid is based on the proportionality

Table 1. Temperature dependence of the structural anisotropy factor for some nematogens obtained by different methods†.

PAA; T_{NI} = 408 K; τ_{max} = −0·105				MBBA; T_{NI} = 318 K; τ_{max} = −0·110						PEMBA; T_{NI} = 315 K; τ_{max} = −0·095				5CB; T = 308 K; τ_{max} = −0·107							
$(T_{NI} - T)$/K	$-\tau_k$ [21]	$-\tau_1$ [8]	$-\tau_2$	$(T_{NI} - T)$/K	$-\tau_k$ [21]	$-\tau_1$	$-\tau_2$	$-\tau_3$ [22]	$-\tau_5$	$(T_{NI} - T)$/K	$-\tau_k$	$-\tau_1$	$-\tau_2$	$(T_{NI} - T)$/K	$-\tau_k$	$-\tau_1$	$-\tau_2$	$-\tau_{2'}$ [23]	$-\tau_3$ [22]	$-\tau_4$ [24]	$-\tau_5$
2	0·039	0·014	0·043	1	0·026	0·015	0·034	0·025	0·040	0·7	0·021	0·005	0·039	1	0·028	0·008	0·044	0·050	0·029	0·067	0·044
2	0·042	0·018	0·047	3	0·031	0·016	0·040	0·031	0·046	1·7	0·023	0·010	0·044	1	0·028	0·008	0·044	0·050	0·029	0·067	0·044
6	0·044	0·019	0·050	5	0·033	0·018	0·044	0·034	0·050	3.7	0·025	0·009	0·048	5	0·034	0·017	0·054	0·063	0·039	0·070	0·056
9	0·047	0·020	0·053	7	0·035	0·020	0·047	0·037	0·054	5.7	0·027	0·015	0·051	8	0·037	0·021	0·058	0·067	0·042	0·070	0·060
12	0·049	0·021	0·056	10	0·037	0·023	0·050	0·040	0·057	7·7	0·028	0·012	0·054	10	0·038	0·022	0·060	0·070	0·043	0·068	0·063
14	0·050	0·022	0·057	13	0·039	0·023	0·053	0·041	0·060	9·7	0·029	0·015	0·056	12	0·039	0·024	—	0·074	—	—	—
17	0·051	0·023	0·060	16	0·041	0·023	0·056	0·043	0·062	11·7	0·029	0·017	0·057								
20	0·052	0·023	0·061	20	0·042	0·022	0·058	—	—	13·7	0·030	0·019	0·059								

† τ_k has been determined from equation (20); τ_1 from the condition $\alpha_l = \alpha_{lc}$ (equation (22)); τ_2 and $\tau_{2'}$ from the proportionality τ and Δn (equation (23)); τ_3 from the spherical probe absorption dichroism [39]; τ_4 from the absorption dichroism of 5CB (equation (29)); τ_5 according to the Segre model ($\tau = \tau_{max} S$). τ_{max} has been evaluated from the molecular dimensions [13, 25, 26]; Δn and ϱ from [13, 25, 27–30]; S from [31, 32]; PEMBA from 4-n-pentylphenyl ester 4′-methoxybenzoic acid.

between the magnetic susceptibility and the dielectric permittivity anisotropies determined by de Jeu, and also on the constancy of $\bar{\varepsilon}/\varrho$ at the nematic–isotropic transition. It is unlikely that these conclusions can be generalized to all nematics. It is not obvious why the molecular polarizability has to vary in such a way that the ratio $\bar{\varepsilon}/\varrho$, which is related to it via formulae (3), is constant at the phase transition. In addition, it is clear that the local field anisotropy can only be independent of the optical anisotropy of the liquid crystal to a first approximation (see equation (18)). Only in this case are the dielectric properties proportional to the magnetic ones. All of these conditions are satisfied only when all of the molecules are perfectly oriented and the director, which is homogeneous in the sample, fluctuates around its average orientation as shown in figure 2.

In the model proposed by Segre [14] the structural anisotropy of the mesophase is proportional to S and such a temperature dependence of τ is in agreement with the molecular theory [16]. We can therefore calculate τ from the molecular axial ratio and from the order parameters which have been determined by independent (for example magnetic) methods, $\tau = \tau_{\max} S$. These are given as the τ_5 in table 1 ($\tau_{\max}$ was calculated from equation (7)). It should be noted that the proportionality coefficient obtained from the simple molecular statistical theory

$$\tau_{\max} = -\frac{2}{5}\frac{k-1}{k+2}$$

(cf equation (11)) is considerably larger than that calculated from equation (7) (approximately 50 per cent for the compounds listed in table 1). However it is difficult to indicate a preference for one of these models.

With good accuracy $\Delta n \equiv (n_z - n_x) \propto S$ and Segre's model can be considered as the confirmation of the temperature dependence of Δn proposed by Averyanov and Shabanov [18]. They have suggested that the anisotropy of the Lorentz cavity is decreased compared with the molecular anisometry by a factor proportional to Δn:

$$\frac{|\tau(\Delta T)|}{\Delta n(\Delta T)} = \text{const.} \tag{23}$$

In such a case the order parameter can be obtained from the refractive indices data as

$$S = S_0(1 + \sigma), \tag{24}$$

where

$$S_0 = \frac{\Delta n(n_z + n_x)}{4\pi\varrho\Delta\alpha(\bar{f} + \delta f)},$$

$$\sigma = \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\left[9k\frac{\bar{n}^2 - 1}{n_z + n_x} + 3k\Delta n - 1\right], \quad k = \frac{|\tau|_{\max}}{\Delta n_{\max}}.$$

Here $\Delta\alpha$ is the anisotropy of the polarizability in the molecular reference system. $\tau_{\max}$ and $\Delta n_{\max}$ correspond to a perfectly ordered sample. Using equations (23) and (24), good agreement has been found between the order parameters obtained by optical methods and N.M.R. spectroscopy for compounds such as 4,4′-dimethoxyazoxybenzene (PAA) and 4,4′-diethoxyazoxybenzene (PAP) [18], 5CB and 4-*n*-heptyl-4′-cyanobiphenyl (7CB) [23, 24]. However, this assumption is not completely satisfactory because the determination of the coefficient k remains to a certain extent arbitrary. For example, the value for k of 0·381 [23] is noticeably larger than 0·319 which can be obtained by the same method from the refractive indices [29] and the molecular dimensions [30] of 5CB. The resulting uncertainty in the values for τ obtained with these ks can also be noted from table 1 (τ_2 and $\tau_{2'}$). In view of these differences in predicting the structural anisotropy parameter, the development of an independent experimental method to determine the local field anisotropy in liquid crystals is of great importance.

4. Experimental methods for the determination of the local field anisotropy

4.1. *Non-optical methods*

We begin by considering the determination of the geometric parameters of the model cavity via neutron and X-ray diffraction [21]. The analysis of neutron and X-ray diffraction patterns gives the molecular pair distribution function along the director and in the plane perpendicular to it [19, 36]. This allows us to calculate the mean intermolecular distances in these two directions. However, it is very questionable whether such mean distances can be taken as the semi-axes of the model ellipsoidal cavity. Almost all local field models which we have discussed are based on the assumption that there is no correlation between molecules. Then the mean intermolecular distances to be used are those obtained after averaging over the orientational distribution function. On the other hand diffraction patterns depict the real local packing of the molecules, and the intermolecular distances so obtained are approximately equal to the van der Waals radii [19]. Hence the cavity anisometry obtained in this way is closer to the molecular anisometry than to that of the ellipsoidal cavity postulated in the model theories. The former can only be used, perhaps, in de Jeu's theory.

Another way to deal with the pair distribution function extracted from X-ray scattering is to use equations (12) and (13) or (14) for the determination of τ. However the previous arguments apply to this case as well, since these equations have been derived in the approximation of no orientational correlations.

4.2. *Optical probing*

Another experimental method for the direct determination of the local field anisotropy is based on absorption dichroism measurements. In fact, the dichroic ratio for a partly oriented molecular system is determined by the order parameter S and the anisotropy of the local field acting on a molecule

$$N = \sigma \frac{1 - SS_\beta}{1 + SS_\beta}, \qquad (25)$$

where

$$\sigma = \frac{n_z f_{xx}^2}{n_x f_{zz}^2}, \quad N = \frac{D_x}{D_z},$$

and D is the absorption coefficient, the subscripts indicate the orientation of the light polarization relative to the nematic director. In equation (25) it is assumed that the molecules possess axial symmetry and

$$S_\beta = \tfrac{1}{2}(3\cos^2\beta - 1)$$

depends on the angle β between the transition dipole moment and the long molecular axis. If the order parameter S is zero for the molecules under consideration, but the system is still macroscopically anisotropic, the local field anisotropy can be determined directly from the absorption dichroism measurements:

$$\frac{f_{xx}}{f_{zz}} = \sqrt{\left(\frac{n_x}{n_z} N\right)}. \tag{26}$$

Such measurements have been made [37]. The absorption dichroism of $(\mathrm{P\ Mo_{12}O_{40}})^{3-}$ ions dissolved in a liquid-crystalline mixture have been measured. The solute molecules have a spherical shape (for the case of absorption this means a symmetry not lower than tetrahedral) and correspondingly S is zero. The local field has been shown to be almost isotropic ($\tau = -0{\cdot}067$, $\Delta n = 0{\cdot}35$) for frequencies at the long wavelength edge of the absorption band of the probe. Based on these observations it was concluded that the isotropic local field model is the most preferable for the interpretation of optical experiments for the majority of liquid crystals.

More precise measurements have been made for $\mathrm{W(CO)_6}$, $\mathrm{Cr(CO)_6}$ and $\mathrm{Mo(CO)_6}$ dissolved in a compensated cholesteric mixture [38]. This matrix, which is transparent to short wavelengths down to 250 nm, permits detailed studies of the frequency dependence of the solute dichroism to be performed. It has been found that the dispersion of the dichroism is not monotonic and is qualitatively different for the various spherical probes studied. This lead to the conclusion that for these probes the main contribution to the absorption dichroism is not from the local field anisotropy, but from the lowering of the molecular symmetry caused by molecular interactions with the liquid crystal host. It should be added that because of the nature of the hexacarbonyl probes, not only their geometry but to a greater extent also the electro-optical molecular parameters may be changed drastically by charge-transfer complexation with the host. The significance of these specific interactions is also confirmed by absorption dichroism studies of halogenated methanes in an MBBA host [22]. It is impossible to explain the observed dichroic ratio values for $\mathrm{CBr_4}$ and their temperature dependence for $\mathrm{CCl_4}$ within a reasonable range of values for the structural anisotropy factors. In order to determine the local field anisotropy, it was decided to perform optical probing in the I.R. spectral range [39]. Tetramethylsilane and tetramethylsilane-d_{12} were used as probes for they are characterized by rather intense vibrational absorption bands. These compounds do not form quasi-chemical bonds with the host molecules and it can be expected that their absorption dichroism is caused only by the local field anisotropy. The results are given in figure 5. The question which remains is what is the relationship between the local field acting on a probe molecule and that on a liquid crystal host molecule? Of course, the local field is only a method for the description of the molecular interactions, primarily the dipole–dipole interactions induced by the external field. These interactions are long range in nature and therefore the anisotropy of the local field acting on a probe molecule is determined by the structure of the liquid-crystalline sample as a whole. It seems reasonable therefore to take the same local field for different molecules in the same host, but we should stress that at this stage we do not yet have any real evidence for this. In other words, we do not know the relative contributions from higher multipoles, non-dispersive interactions and the contributions caused by the peculiarities of the shape of the solute molecules.

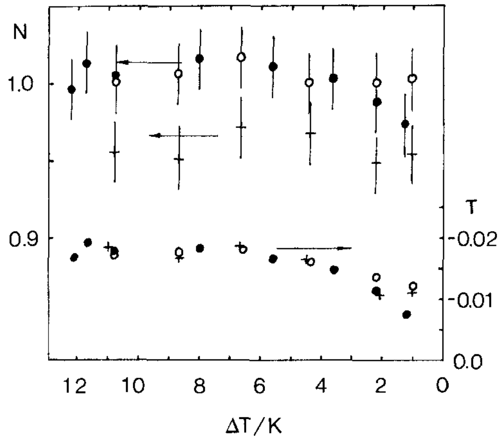

Figure 5. The dichroic ratios for some I.R. bands of tetramethylsilane (TMS) and tetramethylsilane-d_{12} (DTMS) in a 5CB host and τ values obtained from these data via equation (26) (τ_4 in table 1). Vibrational frequencies of the solutes: +, 861 cm^{-1} TMS; (●), 742 cm^{-1} DTMS; (o), 694 cm^{-1} TMS.

4.3. *Absorption dichroism measurements for nematics*

It is possible to determine the local field anisotropy by studying the dichroism not only for spherical probes but also for the nematogenic molecules themselves. In fact, the presence of the anisotropic local field results in a difference between the orientational order parameters determined from light absorption by uniform planar and homeotropically oriented nematic films [24]. In other words, measuring the ratios

$$\left.\begin{aligned} N_z &= \frac{\varrho}{\varrho_{is}}\frac{n_{is}}{n_z}\left[\frac{1 + L_{zz}(n_z^2 - 1)}{\frac{1}{3}(n_{is}^2 - 2)}\right]^2 (1 + 2S), \\ N_x &= \frac{\varrho}{\varrho_{is}}\frac{n_{is}}{n_x}\left[\frac{1 + L_{xx}(n_x^2 - 1)}{\frac{1}{3}(n_{is}^2 + 2)}\right]^2 (1 - S), \end{aligned}\right\} \qquad (27)$$

where $N_k = D_k/D_{is}$, D_k and D_{is} are the absorption densities for the parallelly polarized band of the mesomorphic substance in the nematic and isotropic phases, it is possible to determine both the orientational order parameter and the structural anisotropy. Moreover, for the determination of τ in contrast to the determination of S, it is not necessary to know the orientation of the transition dipole moment under consideration (S in equation (27) is simply replaced by SS_β for cylindrically symmetric molecules). This method has been extended to biaxial molecules [40], i.e. when none of the components in the tensor $\hat{S}$ characterizing molecular orientational ordering in a uniaxial mesophase are equal. It should be noted that even mean field or cavity models will give a biaxial local field tensor in this case. Unfortunately, this fact is neglected in [40] which accounts for the limited applicability of their expressions. It may be that similar local field problems are responsible for the discrepancies in the dependencies of the magnetic and the dielectric susceptibility anisotropies on the uniaxial and biaxial order parameters which have been found [41]: their treatment of the dielectric phenomena based on Faber's model of a continuous nematic is by no means the way to overcome the local field correction problem.

The absorption dichroism method has been used to determine the local field in various liquid crystals (see [42] and references therein). The values of τ calculated in

Table 2. The structural anisotropy factor of some nematic liquid crystals with different optical anisotropy at $(T_{NI} - T) = 10\,K$.

Liquid crystal	Δn [41]	L_{xx} [41]	τ	$\frac{1}{3}(m_{zz} - m_{xx})$	S	$\frac{1}{3}S(m_{zz} - m_{xx})$
5CB	0·185	0·40	−0·07	−0·107	0·58 [24]	−0·062
8OCB	0·166	0·39	−0·06	−0·12	0·60 [24]	−0·072
CPHOB†	0·150	0·38	−0·05	−0·12	0·55 [40]	−0·066
5BCO‡	0·102	0·36	−0·03	−0·107	0·54 [41]	−0·058

† CPHOB: 4-cyanophenyl ester 4′-*n*-hexyloxybenzoic acid.
‡ 5BCO: 1-(4′-cyanophenyl)-4-*n*-pentyl-(2,2,2)-bicyclooctane.

this way from the polarized component intensities of the C⋮N stretching vibration band for 5CB and 7CB, for example, are in good agreement with those obtained from equations (23) and (24) [24] (see also table 1). It is interesting to compare the results of these systematic studies with the predictions of the models mentioned previously. As we can see from table 2, the agreement of the data obtained from I.R. measurements and from the Segre model (i.e. from the relation $\tau = \frac{1}{3}(m_{zz} - m_{xx})S$) is not very encouraging. There are many reasons for such a discrepancy and one of them is the neglect of the short range correlations in the model calculations.

The advantage of this method over optical probing is that it deals with the local field acting on the mesogenic molecules themselves. However it is worth noting that the large absorption dichroism for liquid crystals results in large experimental errors in the determination of N_{ii}, while the band intensity change due to the local field anisotropy at the phase transition is very small. In this way the orientational ordering can mask the local field anisotropy which results in large uncertainties in the values obtained [24].

Furthermore, we can compare this method with that proposed for dealing with refractive index data (see equation (22)). Equations (27) imply a constancy of the oscillator strength. Keeping in mind the Kramers–Kronig relation it is clear that almost all criticism concerning equation (22) for the refractive indices is applicable here. Thus changes in the molecular conformation and local packing and as a result changes in the non-central molecular interactions during the phase transition lead to variations in the molecular oscillator strength which are of the same order as those caused by the local field anisotropy. Only for I.R. spectra or, more precisely, for the absorption bands originating from vibrations of a separate bond in a large molecule, do our assumptions seem to be less arbitrary, because here we are dealing with interactions of almost point dipoles in comparison with intermolecular distances. This can help us to calculate more reliably the contribution of the dipoles induced by an external field, i.e. the local field effects. However we still know nothing about how the permanent dipole interactions can affect the absorption spectra.

4.4. *Theoretical basis for dichroism measurements in polar liquid crystals*

To deal properly with polar fluids we have to base our discussion on another model, for the interaction of the whole liquid-crystalline sample with the light wave must be considered and not just the process of light absorption by only one molecule placed in the local field of the light wave. Here we shall develop this approach for the case of vibrational spectra.

The absorption coefficient for an infrared active band of an isolated molecule is given by

$$k = \frac{4\pi^2}{\hbar c}\,\omega_{mn}|\mathscr{M}_{mn}\cdot\mathbf{l}|^2, \tag{28}$$

where $\mathscr{M}_{mn} = \langle m|\mathscr{M}|n\rangle$ and ω_{mn} are the dipole moment and frequency for the transition between the mth and the nth vibrational states, respectively; $\mathbf{l}$ and c denote the polarizations and velocity of the radiation. In condensed matter all molecules interact with each other and the process of the absorption of light is a collective one. To obtain a relationship between the total absorption coefficient and the properties of the constituent molecules we consider an infinitesimal *macroscopic* volume element of the sample as an absorbing system in the macroscopic Maxwell field of the light wave in the medium. Thus, similarly to equation (28), the expression for the intensity becomes

$$k = \frac{4\pi^2}{\hbar v V}\,\omega_{mn}|\mathbf{M}_{mn}\cdot\mathbf{l}|^2, \tag{29}$$

where $\mathbf{M}_{mn}$ is now the transition dipole moment of the volume V and v denotes the velocity of light in the sample. Using perturbation theory, $\mathbf{M}_{mn}$ for the fundamental bands of a harmonic oscillator can be shown to be proportional to the derivative of the dipole moment of the sample with respect to the vibrational normal coordinate.

The instantaneous dipole moment of the sample depends upon the molecular arrangement. It can be written as the sum of the permanent and induced terms (see, for example, [2])

$$\mathbf{M} = \sum_i \mathscr{M}_i - \sum_i \alpha_i \left[\sum_{l\neq i} D_{il}\mathscr{M}_l + \sum_{m\neq i} T_{im}\alpha_m D_{mi}\mathscr{M}_i\right], \tag{30}$$

where

$$D_{ij} = T_{ij} + \sum_{l\neq i,j} T_{il}\alpha_l T_{lj} + \dots,$$

$T_{ij} = T(\mathbf{r}_i - \mathbf{r}_j)$ is the dipole–dipole interaction tensor. Here we have omitted terms resulting from higher electric moments. In the same way we can write the dipole moment of a sample consisting of non-polar molecules placed in an electric field $\mathbf{E}$ as

$$\begin{aligned}\mathbf{M} &= \sum_i \alpha_i \left[I + \sideset{}{'}\sum_{j\neq i} D_{ij}\alpha_j + \sum_{m\neq i} D_{im}\alpha_m T_{mi}\alpha_i\right]\mathbf{E} \\ &\equiv \sum_i \alpha_i f_i \mathbf{E}.\end{aligned} \tag{31}$$

Comparing equations (30) and (31) and taking the symmetry of the tensors $\mathbf{T}$ and $\boldsymbol{\alpha}$ into account, equation (30) can be rewritten as

$$\mathbf{M} = \sum_i \mathscr{M}_i f_i. \tag{32}$$

Now we expand $\mathbf{M}$, $\mathscr{M}$ and α in powers of the normal coordinate of the vibration being considered. For example,

$$\mathscr{M} = \mathscr{M}^{\mathrm{e}} + \mathscr{M}'Q + \tfrac{1}{2}\mathscr{M}''Q^2 + \dots, \tag{33}$$

(the subscript e refers to the equilibrium configuration, and the derivatives, denoted by primes, are also taken at the equilibrium position). Equations (32) and (33) lead to

$$\begin{aligned}\mathbf{M}' = {} & \sum_i \mathscr{M}_i' f_i + \sum_i \mathscr{M}_i^{\mathrm{e}} \Bigg[\sum_{j \neq i} D_{ij}' \alpha_j + \sum_{k \neq i} D_{ik} \alpha_k' \\ & + \sum_{l \neq i} D_{il}' \alpha_l T_{li} \alpha_i + \sum_{m \neq i} D_{im} \alpha_m' T_{mi} \alpha_i + \sum_{n \neq i} D_{in} \alpha_n T_{ni} \alpha_i' \Bigg]. \qquad (34)\end{aligned}$$

The first term contains the well-known local field correction factor but the second is less familiar. These terms have been analysed within the scope of the Segre model [43], i.e. for a spheroid not perfectly oriented in an anisotropic medium. It has been shown that the second term depends on the shape of the cavity, the value of the permanent dipole moment and relative orientation of $\mathscr{M}^{\mathrm{e}}$ and $\mathscr{M}'$, the form of Raman tensor and the dielectric permittivity tensor. The expression for the contribution from the electrostatic interactions to the absorption dichroism contains not only the second rank orientational order parameter S but also those of fourth rank. For non-polar compounds or for those vibrations where $\alpha' = 0$, only the first term in equation (34) remains: this is the only case when equations (25)–(27) are valid.

The effect of the polarity on the absorption dichroism has been studied [39, 43]. Some experimental results concerning the electrostatic interactions have been given in [39] and have been used to determine the local field anisotropy for 5CB (τ_3 in table 1). But they are based only on the measurements of the spherical probe absorption dichroism and there is a lack of direct measurements of the local field anisotropy and the permanent dipole contributions to the absorption dichroism of mesogenic molecules themselves. Hence, the answer to the question concerning the relative importance of electrostatic interactions remains incomplete.

4.5. *Some additional remarks*

It should be emphasized that not only are the absorption coefficients and refractive indices dependent on the local field, but all other optical properties are also. In the same way as we have discussed for absorption spectra, the results of other optical experiments, namely Rayleigh and Raman (especially resonance) scattering, luminescence can be treated in the same way. In addition, we can consider the use of optically active probes [44]. This modification permits us, in principle, to obtain information from methods involving the dispersion of the optical rotation and circular dichroism. Of course, there are additional difficulties for not only does the anisotropy but also the fluctuations of the local field can contribute to the depolarization ratios [45]; orientational relaxation often modifies luminescence spectra.

5. Conclusions

What should be done in the future? In a theoretical sense it is clear that there are several unresolved problems in overcoming such simplifications as the cavity/continuum model, the point polarizability approximation, etc., to obtain a more adequate Lorenz–Lorentz like relation. In view of the large size and complexity of mesogenic molecules, these problems may be never resolved in a simple manner. However we wish to stress that existing theories have already given us the main difference between the Lorenz–Lorentz equation for an anisotropic liquid and that for isotropic liquid: **L** is a tensor and its anisotropy is determined by the pair distribution function. As we can see from table 1, the uncertainties in predicting and determining τ are still of the order of 100 per cent. We believe that in the near future progress can be made in the evaluation of the structural anisotropy factor. We have mentioned that almost all optical experiments contain information about this factor; unfortunately we do not know how to extract it properly. Most of the work in this field deals with absorption dichroism. In the previous section we have discussed the shortcomings and some of the difficulties of this method: uncertainties in the evaluation of the electrostatic interaction contribution and all statistical averages do not characterize the molecule as a whole but only the behaviour of the chromophore. On the other hand this last feature gives us considerable advantages. Combining I.R. and N.M.R. data, we can determine the local field experienced by different bonds in the molecule. This is the way to improve the point-polarizability approximation and to introduce, for example, in the Lorenz–Lorentz equation for liquid crystals a more realistic electron density distribution over the molecule. In this sense, other optical methods (probably in combination with magnetic methods) seem to be even more informative.

The interest in such investigations lies not in the possibility of reproducing the order parameter for real liquid crystals (although it is encouraging to find quantitative agreement). The order parameter S is a coefficient in the single-particle orientational distribution function and, as we have shown, the structural anisotropy factor is a coefficient in the expansion of the pair distribution function in an infinite series in Wigner rotation functions. The pair distribution function is undoubtedly much less studied. Keeping in mind that such interesting phenomena as antiferroelectric packing, induced and re-entrant phases are characterized frequently not by peculiarities in the temperature dependence of the parameter S, but primarily by changes in the pair distribution, we can understand the significance of the local field studies in liquid crystals. However because of the complexity of liquid-crystalline systems, only by a combination of the results of theory, experiment and probably computer simulations can we hope to improve our understanding of these fascinating materials.

Appendix

An alternative local field correction can be found in the literature concerning the molecular statistical theory of the refractive indices of liquid crystals [4, 15]. A microscopic L tensor has been defined [4] in such a way that $L_{ii} = \frac{1}{3}$, and the local field factor is obtained as

$$f_{ii} = \tfrac{1}{3}(\varepsilon_{ii} + 2). \qquad \text{(A 1)}$$

In this approach all correlation terms are included in the right hand side of the Lorenz–Lorentz equation. We shall not discuss here the results of [4, 15] in a more detailed way because of some strange consequences. Thus the general equations for the L tensor obtained [4] in the limiting case of a solid crystal constituted of perfectly oriented molecules are according to [15] (in the notations of equations (12) and (13)):

$$\left.\begin{aligned} L_{zz} &= \frac{1}{3} + \frac{1}{4\pi}\int\int_0^\infty \frac{g(r\hat{r}) - 1}{r}\,dr(3z^2 - 1)d\Omega, \\ L_{xx} &= \frac{1}{3} + \frac{1}{4\pi}\int\int_0^\infty \frac{g(r\hat{r}) - 1}{r}\,dr(3x^2 - 1)d\Omega. \end{aligned}\right\} \qquad \text{(A 2)}$$

Because of the discontinuity of $1/r[g(r\hat{r}) - 1]$ in the limit $r \rightarrow 0$, it can be shown, that the results of [4, 15] do not satisfy the normalization condition $L_{zz} + 2L_{xx} = 1$ and so are unlikely to be reliable.

At the same time, another approach [5] which is valid in the absence of short range orientational correlations (this means valid both for perfect alignment and in the absence of any orientational correlation) gives (*cf.* equation (14))

$$\left.\begin{aligned} L_{zz} &= \frac{1}{3} + \frac{1}{4\pi}\int\int_0^\infty \frac{g(r\hat{r})}{r}\,dr(3z^2 - 1)d\Omega, \\ L_{xx} &= \frac{1}{3} + \frac{1}{4\pi}\int\int_0^\infty \frac{g(r\hat{r})}{r}\,dr(3x^2 - 1)d\Omega. \end{aligned}\right\} \quad (A\,3)$$

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