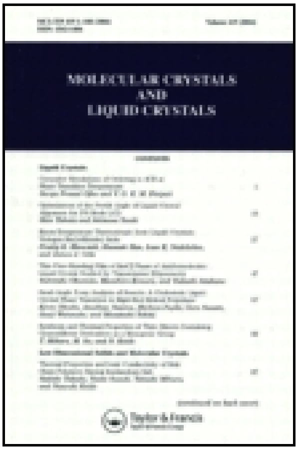

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A Study of the Effects of Short-range Correlation on the Permittivity of Nematic Liquid Crystals

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By accounting for two-particle interactions using director fluctuation theory, short-range correlations are shown to have a negligible effect on the permittivity of a nematic liquid crystal. An expression for the permittivity is obtained neglecting all correlations, and is shown to predict the refractive index of PAA at least as well as earlier theories in which special assumptions were made.

Keywords: liquid crystal fluctuations, permittivity, refractive index, theory

I. INTRODUCTION

In order to determine the dielectric properties of a liquid crystal from its molecular characteristics it is necessary to use a model for the internal field and several such models have been proposed.[1] However, of the recent models which include the anisotropy of the internal field,[2,3,4] only that of Bordewijk and de Jeu,[5,6] accurately predicts the observed temperature dependence of the refractive index. From the statistical mechanical expression for ϵ,[7] it is clear that this latter empirical formula corresponds closely to the assumption that the molecules are totally correlated, i.e. that they are all oriented at the same (variable) angle to the director.

In this paper we investigate the degree to which the dielectric permittivity ϵ of a nematic liquid crystal is affected by short-range (non-electrostatic) orientational correlation of its molecules (a feature which is ignored in mean field theories). This is done by evaluating the term in ϵ which accounts for two-particle interactions using Faber's continuum theory,[8,9] (this theory describes both director fluctuations and short-range correlations) and inferring from this the effect of local ordering in general.

We find that, for a reasonable spatial pair-correlation function, the effect of short-range orientational correlation is rather small and may be neglected. Therefore it is possible to obtain an expression for ϵ from the statistical mechanical series expansion by assuming the molecular orientations to be uncorrelated. Surprisingly perhaps, the resulting formula yields refractive index values for the liquid crystal PAA which agree closely with those predicted by the totally correlated expression. Since the former formula was derived in a semi-rigorous fashion, this may be seen as a justification for the completely empirical formula of de Jeu and Bordewijk.[6]

The paper is organised as follows. First the form of the pair-correlated terms is determined in section II, from an expression for ϵ. This expression relates ϵ to averages of molecular quantities and is a generalisation of a method derived by Bordewijk and de Jeu.[5] In sections III, IV and V we evaluate the two-particle term and consider the approximations involved in this. In section VI we calculate the averages appearing in the expression for ϵ, assuming no short-range correlations, and in the final section the numerical results for the refractive index of PAA are shown to be close to those obtained in Reference 6.

II. THE PERMITTIVITY EXPRESSION

An expression for the dielectric constant, ϵ, of an isotropic liquid in terms of averages of the polarisabilities and permanent dipole moments of its molecules (a generalisation of the Kirkwood-Fröhlich equation) has been derived by Bordewijk.[10] Bordewijk and de Jeu have shown how these averages may be evaluated if a particular internal field factor is assumed.[5,6] Without making special assumptions about the internal field we will use their method to obtain an equation for ϵ.

From Reference 5, the dielectric constant is given by

$$\frac{\epsilon_0(\epsilon_\lambda - \epsilon_{\infty\lambda})[\epsilon_\lambda + (1 - \epsilon_\lambda)\Omega_\lambda^\epsilon]^2 V}{\epsilon_\lambda[\epsilon_\lambda + (\epsilon_{\infty\lambda} - \epsilon_\lambda)\Omega_\lambda^\epsilon]}$$

$$= \frac{1}{k_b T}\left\langle \left(\sum_i \boldsymbol{\mu}^i \sum_j \mathbf{A}^{ji}\right)_\lambda \left(\sum_{i'} \boldsymbol{\mu}^{i'} \sum_{j'} \mathbf{A}^{j'i'}\right)_\lambda \right\rangle_0 \qquad (\lambda = \parallel, \perp) \qquad (1)$$

and the induced moment of the i^{th} dipole due to the external field (i.e. for fixed positions and orientations of the molecules) is

$$
\begin{aligned}
\mathbf{p}^i &= \boldsymbol{\alpha}^i \sum_j \mathbf{A}^{ji}\boldsymbol{\epsilon}[\boldsymbol{\epsilon} + (\mathbf{I} - \boldsymbol{\epsilon})\boldsymbol{\Omega}^{\epsilon}]^{-1}\mathbf{E} \\
&= \boldsymbol{\alpha}^i \sum_j \mathbf{A}^{ji}[\boldsymbol{\epsilon} + (\mathbf{I} - \boldsymbol{\epsilon})\boldsymbol{\Omega}^{\epsilon}]^{-1}[\boldsymbol{\epsilon} + (\boldsymbol{\epsilon}_{\infty} - \boldsymbol{\epsilon})\boldsymbol{\Omega}^{\epsilon}]\,\mathbf{E}_s
\end{aligned}
\tag{2}
$$

The sample is taken to be a sphere of volume V embedded in a dielectric of the same permittivity, the surroundings being treated as a continuous medium. The subscripts $\|$ and $\perp$ refer to directions parallel and perpendicular to the macroscopic director respectively, $\boldsymbol{\Omega}^{\epsilon}_{\lambda}$ is a geometrical factor depending on $\epsilon_{\|}/\epsilon_{\perp}$ and the subscript 0 indicates that the average is taken for zero external field. $\boldsymbol{\mu}^i$ is the permanent dipole and $\boldsymbol{\alpha}^i$ is the polarisability of the i^{th} molecule. $\mathbf{A}$ is a 3n-dimensional tensor $\mathbf{A} = (\mathbf{I} + \boldsymbol{\alpha}\ \mathbf{T}')^{-1}$ which accounts for the increase of each dipole due to the effects of the rest of the medium (see Reference 5) and $\mathbf{A}^{ij}$ is its projection on the product of the i and j subspaces. $\mathbf{E}$ and $\mathbf{E}_s$ are the Maxwell fields in the surrounding dielectric and inside the sample respectively. $\Sigma_j\mathbf{A}^{ji}$ is obtained by equating the right-hand side of (2) to an expression for the polarisation of a dipole in the same sample, but with the permanent moments set to zero, for the same Maxwell field. This is done in Reference 5 by using an independently obtained internal field factor. More generally, for given positions and orientations of the molecules, the induced polarisation can be obtained from that of the sphere in vacuo. In this case the external field $\mathbf{E}_o$ for a Maxwell field inside the sample $\mathbf{E}_s$ is given by $\mathbf{E}_o = (2\mathbf{I} + \boldsymbol{\epsilon}_{\infty})/3\ \mathbf{E}_s$ and therefore

$$
\begin{aligned}
\mathbf{p}^i = \boldsymbol{\alpha}^i &\left[\mathbf{I} - \sum_j \mathbf{T}^{ij}\boldsymbol{\alpha}^j + \sum_j \mathbf{T}^{ij}\boldsymbol{\alpha}^j \sum_K \mathbf{T}^{jk}\boldsymbol{\alpha}^k - \dots\right] \\
&\left[\frac{2\mathbf{I} + \boldsymbol{\epsilon}_{\infty}}{3}\right]\mathbf{E}_s
\end{aligned}
\tag{3}
$$

where $\mathbf{T}^{ij}$ is the vacuum dipole propagation tensor. Clearly, for the case of total correlation of orientation of the molecules, the average value of $\mathbf{p}^i$ is equal to that derived in Reference 6. However the expression before averaging is different because equation (3) assumes the external field $\mathbf{E}_0$ and not the Maxwell field $\mathbf{E}_s$ to be uncorrelated with the molecular orientations.

Since (3) holds generally for fixed molecules and a given Maxwell field $\mathbf{E}_s$, as in Reference 5 we can equate it to equation (2) and so

$$\sum_j \mathbf{A}^{ji} = \left[\mathbf{I} - \sum_j \mathbf{T}^{ij}\boldsymbol{\alpha}^j + \sum_j \mathbf{T}^{ij}\boldsymbol{\alpha}^j \sum_K \mathbf{T}^{jk}\boldsymbol{\alpha}^k - \dots\right]$$

$$\frac{(2\mathbf{I} + \boldsymbol{\epsilon}_\infty)}{3}\left[\boldsymbol{\epsilon} + (\mathbf{I} - \boldsymbol{\epsilon})\boldsymbol{\Omega}^\epsilon\right]\left[\boldsymbol{\epsilon} + (\boldsymbol{\epsilon}_\infty - \boldsymbol{\epsilon})\boldsymbol{\Omega}^\epsilon\right]^{-1}$$

Therefore from (1)

$$\frac{\epsilon_0(\epsilon_\lambda - \epsilon_{\infty\lambda})[\epsilon_\lambda + (\epsilon_{\infty\lambda} - \epsilon_\lambda)\Omega^\epsilon_\lambda]V}{\epsilon_\lambda}$$

$$= \frac{1}{k_B T}\left\langle \sum_{ii'}\left[\boldsymbol{\mu}^i\left(\mathbf{I} - \sum_j \mathbf{T}^{ij}\boldsymbol{\alpha}^j + \sum_j \mathbf{T}^{ij}\boldsymbol{\alpha}^j \sum_k \mathbf{T}^{jk}\boldsymbol{\alpha}^k \dots\right)\right]_\lambda \right.$$

$$\left.\left[\boldsymbol{\mu}^{i'}\left(\mathbf{I} - \sum_{j'} \mathbf{T}^{i'j'}\boldsymbol{\alpha}^{j'} + \dots\right)\right]_\lambda\right\rangle_0 \frac{(2 + \epsilon_{\infty\lambda})^2}{9} \quad (4)$$

This reduces to the Kirkwood-Fröhlich equation[7] in the isotropic case.

The averages in equation (4) may be calculated straightforwardly in the limiting cases of total orientational correlation and no orientational correlation (see section VI below), but an exact general evaluation would involve second, third and higher order particle correlations and is prohibitively difficult. In order to estimate the effect of short-range correlations we consider in the following sections how we may evaluate approximately the two-particle orientational averages.

III. THE PAIR CORRELATION TERM IN THE PERMITTIVITY

In this section we will consider the terms on the right-hand side of equation (4) which contain only orientational correlation of two particles. By making certain assumptions these can be expressed in a simple form and may then be evaluated using Faber's continuum theory.

Since there is no long-range translational ordering in the nematic phase, we will ignore third and higher order positional correlation and express all positional averages in terms of the spatial pair correlation function g_2 $(\mathbf{R},\mathbf{n}^i, \mathbf{n}^j)$. (Here $\mathbf{R}$ is the intermolecular separation and $\mathbf{n}^i$ is the director at the position of the i^{th} molecule). In this approximation we may consider the contribution to the polarisation from the i^{th} molecule. For each position of the j^{th} molecule we take for its orientation the average value given the position and orientation of the i^{th} molecule. Thus, for example, we assume $g_2 = g_2(\mathbf{R},\mathbf{n}^i,\mathbf{n}^j(\mathbf{R},\mathbf{n}^i)) = g(\mathbf{R},\mathbf{n}^i)$. Using this we replace the moment of the j^{th} molecule by its average value over all positions. Finally, we average over the positions and orientations of the i^{th} molecule. We will assume also that, with respect to axes fixed in the i^{th} molecule, g is independent of the orientation of i.[11] The first orientationally correlated term is:

$$\overline{\langle(\boldsymbol{\mu}^i.\mathbf{e})\boldsymbol{\mu}^i\mathbf{T}^{ij}\boldsymbol{\alpha}^j\mathbf{e}\rangle} = -\mathbf{e}\,\frac{1}{4\pi\epsilon_0 V}$$

$$\left\langle\int_{V_1+V_2} g\,\frac{(\mathbf{R},\mathbf{n}^i)}{R^3}\,\boldsymbol{\mu}^i\boldsymbol{\mu}^i\,(\mathbf{I} - 3\hat{\mathbf{R}}\hat{\mathbf{R}})\boldsymbol{\alpha}^j d^3\mathbf{R}\right\rangle\cdot\mathbf{e} \quad (5)$$

(since $\boldsymbol{\mu}^i$ is independent of $\mathbf{R}$ for given $\mathbf{n}^i$) where $R = |\mathbf{R}|$, $\hat{\mathbf{R}} = \mathbf{R}/R$, $^-$ and $\langle\ \rangle$ denote a positional and orientational average respectively and $\mathbf{e}$ is the unit vector in the direction of the applied field ($\|$ or $\perp$). The integration is performed over volumes V_1 and V_2 as shown in Figure 1, where R_2 is large enough for short-range correlation to be neglected in V_2. For a spherical sample the integral over V_2 vanishes.

We will use axes fixed in the i^{th} molecule, with one axis parallel to the molecular long axis (i-axes). Then $g = g(\mathbf{R})$ and we assume further that g is independent of the azimuthal angle φ_R. As in continuum theory we take the correlations to be isotropic, therefore in equation (5) only $\hat{\mathbf{R}}\hat{\mathbf{R}}$ has any φ_R dependence and when this tensor is expressed in i-axes the contributions from its off-diagonal elements vanish because of the φ_R integration. Therefore by rotation of uniaxial tensors the average on the right-hand side of (5) is

$$\mathbf{H} = -\int_{V_1}\frac{g(\mathbf{R})}{R^3}\,\langle[\mu_\perp^2(1 - 3\mathcal{R}_\perp^2)\mathbf{I}$$

$$+ \Delta(\boldsymbol{\mu}^2(\mathbf{I} - 3\mathbf{R}^2))\mathbf{n}^i\mathbf{n}^i]\,[\alpha_\perp\mathbf{I} + \Delta\alpha\mathbf{n}^j\mathbf{n}^j]\rangle d^3\mathbf{R} \quad (6)$$

where $\boldsymbol{\alpha}$, $\boldsymbol{\mu}\boldsymbol{\mu} = \boldsymbol{\mu}^2$ and $\hat{\mathbf{R}}\hat{\mathbf{R}} = \mathbf{R}^2$ are referred to axes fixed in the molecule. (The molecule is assumed to be rotating about its long axis

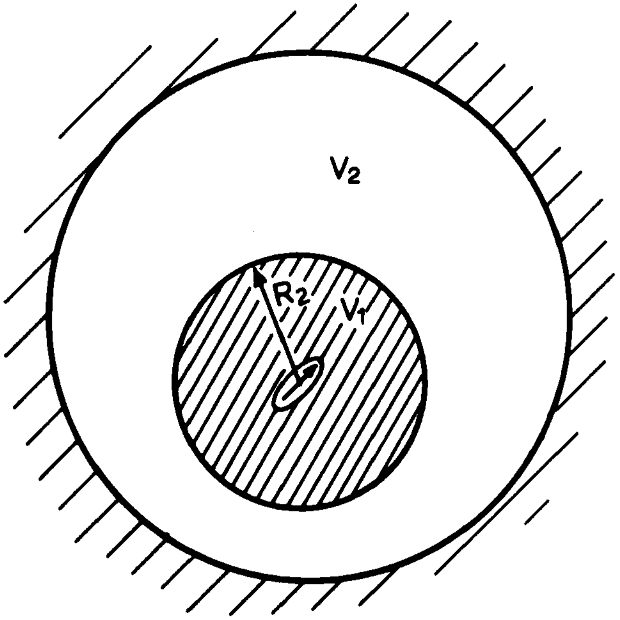

FIGURE 1 Integration volumes V_1 and V_2.

so we treat $\boldsymbol{\mu}\boldsymbol{\mu}$ as a uniaxial tensor) $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ and similarly for $\Delta(\mu^2 \cdot (I - 3\,\mathfrak{R}^2)$.) From (6) the only term in **H** which depends on short-range correlation is

$$\mathbf{J} = \Delta\alpha\left(\mu_{\parallel}^2 + \frac{\mu_{\perp}^2}{2}\right) \int_{V_1} d^3\mathbf{R}\, g\, \frac{(\mathbf{R})}{R^3}\,(1 - 3\mathfrak{R}_{\parallel}^2)\langle \mathbf{n}^i\mathbf{n}^i \cdot \mathbf{n}^j\mathbf{n}^j\rangle \qquad (7)$$

In the next section we will use continuum theory to evaluate this integral.

IV. EVALUATION USING FLUCTUATION THEORY

In Faber's continuum theory[8] orientation dependent averages may be expressed (in the Random Phase Approximation R.P.A.)) in terms of the sum of the director fluctuations X defined in Reference 8 and, if the orientations of two molecules are involved, a factor $\alpha(R)$ indicating the lack of correlation at separation R:

$$\alpha(R) = \frac{2}{q_c}\int_0^{q_c}\left(1 - \frac{\sin qR}{qR}\right)dq$$

for minimum fluctuation wavelength $\frac{2\pi}{q_c}$

The parallel and perpendicular components of **J** may be evaluated using:[8]

$$\langle\cos\theta^i \cos\theta^{ij} \cos\theta^j\rangle = U = \frac{4S}{9} + \frac{1}{9} - \frac{2Q}{9} - \frac{4}{9\alpha}\frac{dQ}{dX}$$

and

$$\langle\sin\theta^i \cos\phi^i \cos\theta^{ij} \sin\theta^j \cos\phi^j\rangle = \frac{U}{2} - \frac{V}{4} + \frac{1}{12} - \frac{S}{3} + \frac{2}{3}\,\mathrm{Re}\,C$$

respectively, where the polar angles of $\mathbf{n}^l$ are θ^l,φ^l with respect to the fixed frame and θ^{ij} is the angle between $\mathbf{n}^i$ and $\mathbf{n}^j$, $Q = \frac{1}{2}\langle 3\cos^2\theta^{ij} - 1\rangle$, $V = \langle\cos^2\theta^i \cos^2\theta^j\rangle$, $C = 4\pi/5\,\langle Y_{22}(\theta^i,\varphi^i)\, Y^*_{22}(\theta^j,\varphi^j)\rangle$, ($Y_{22}(\theta,\varphi)$ is a normalised spherical harmonic) and U, Q, V and C can all be obtained from differential equations in X.

In Figure 2 we show $J_\parallel = \int_{V_1} (g(\mathbf{R})/R^3)\,(1 - 3\mathcal{R}_\parallel^2)\, U(R)\, d^3\mathbf{R}$ as a function of the order parameter S, limiting our consideration to high values of S for which the R.P.A. should be valid. We have taken

$$g(R) = \begin{cases} 0 & \text{if } \mathbf{R} \in E \\ 1 & \text{if } \mathbf{R} \notin E \end{cases} \tag{8}$$

where E is the set of points in a spheroid with the long molecular axis as its major axis. The ratio of the major to minor axis b_l/b_t is 2.4, and we have assumed this to be independent of temperature. The error introduced by this approximation is likely to be small as we are considering a small temperature range and additionally there is short-range correlation of anisotropic molecules even in the isotropic phase.[11] Changing b_l/b_t to e.g. 1.8 appears to make no qualitative difference to $J_\parallel$, which is not surprising in view of the isotropy of α.

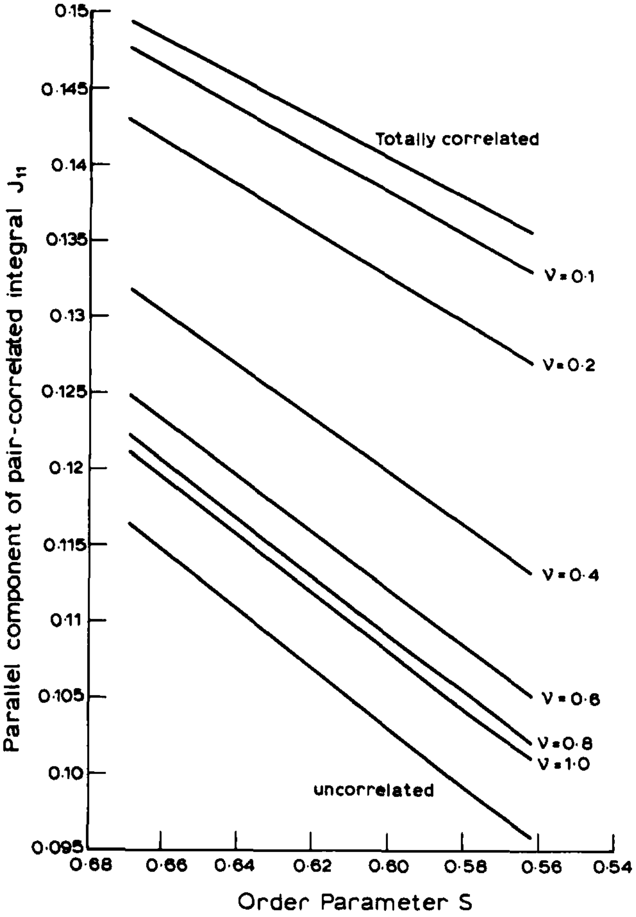

FIGURE 2 Variation with S of pair correlated integral assuming isotropic correlations, $J_\parallel \cdot b_l/b_t = 2.4$. Curves are shown for $b_t = \nu\, 2\pi/q_c$ for various ν and for the totally correlated and uncorrelated cases.

Clearly the shortest wavelength fluctuation must be at least as long as b_t and so $b_t = \nu \cdot 2\pi/q_c$ for some $\nu \leqslant 1$. Faber has suggested that for a nematic composed of hard spheres with packing fraction 0.4, $\nu \sim 0.64$.[8] By the same reasoning, for hard spheroids with packing fraction p,

$$q_c b_t \approx 1.1 \times \left[\frac{36\,\pi p}{b_l/b_t}\right]^{1/3}$$

Since there is long-range orientational order we would expect $p >$ 0.4, but $b_l/b_t > 1$ also and so $q_c b_t$ is likely to be only weakly shape dependent for small values of b_l/b_t. Therefore we would expect $\nu \simeq$ 0.55 – 0.6.

For the purpose of comparison we have shown in Figure 2 $J_{\|}$ for several values of ν and also for no correlation and total correlation. The totally correlated case appears to be a good approximation only when the shortest fluctuation wavelength is significantly longer than (~5 – 10 times) b_t, i.e. when there is very little disorder at lengths of 2–3 molecular widths. Clearly for $\nu \sim 0.6$ the S dependence of $J_{\|}$ is closer to that for no short-range correlation.

The obvious limitation of the above considerations is the neglect of the anisotropy of the correlations. We discuss this briefly in the next section.

V. ANISOTROPY OF THE CORRELATIONS

In reality, because the bend elastic constant K_3 is larger than the splay elastic constant K_1, the orientational correlation between two molecules is likely to be larger when $\mathbf{R}$ is parallel to the director than when it is perpendicular to it. We can include this anisotropy in the R.P.A. averages of correlated terms if the degree of uncorrelation α depends on the direction as well as the magnitude of $\mathbf{R}$.

In the appendix an approximate analytical expression is derived for $\alpha(\mathbf{R})$. For PAA at $S = 0.669, 0.562$, using data from References 1 and 2, we find that the anisotropy of α is less than ±20% and is only weakly temperature dependent. (This may help to justify the assumed temperature independence of b_l/b_t.) We can try to quantify the effect of this small anisotropy by calculating the pair-correlation dependent term in equation (5) with an isotropic excluded volume (for isotropic correlations this integral vanishes). Now $\hat{\mathbf{R}}\hat{\mathbf{R}}$ cannot be replaced by a diagonal molecular tensor since the correlations are not independent of the azimuthal angle in molecular axes, e.g. the parallel component is given by

$$L = \int_{R > \frac{\nu 2\pi}{q_c}} d^3\mathbf{R}\, \frac{(3\cos^2\theta - 1)}{R^3}\, \frac{(3V - U)}{2}$$

In Table I we give some values of L for PAA, for various S. Clearly the integral is nearly two orders of magnitude smaller than $J_{\|}$. We

TABLE I

Values of integral L for PAA for $b_t = b_l = \nu \times 2\pi/q_c$

T/K	s \ ν	0.6	0.8
378	0.669	0.237×10^{-2}	0.203×10^{-2}
383	0.646	0.221×10^{-2}	0.193×10^{-2}
388	0.620	0.210×10^{-2}	0.187×10^{-2}
393	0.597	0.190×10^{-2}	0.173×10^{-2}
398	0.562	0.170×10^{-2}	0.160×10^{-2}

conclude that the anisotropy of the hard core is much more important than that of the correlations.

In order to express the anisotropy of the correlations relative to molecular axes it is necessary to consider the change locally of the elastic constants resulting from the disorder. Thus the correlations between fluctuations must be described and so the random phase approximation should be abandoned. This can be avoided by simply using the anisotropic $\alpha(\mathbf{R})$ in the expressions for $\langle \mathbf{n}^i\mathbf{n}^i \cdot \mathbf{n}^j\mathbf{n}^j \rangle$ in equation (7). The resulting integral $L_\parallel$ is shown in Figure 3. However the physical interpretation of the integral is now not clear. Since we have found that the anisotropy of the correlations is small, we shall assume that the isotropic case is a good approximation to the correct value.

VI. EXPRESSION FOR ϵ NEGLECTING CORRELATIONS

We now consider how we may obtain an expression for ϵ. Using the approximations described in section III, the average in (4) can be evaluated in the limiting cases of no short-range correlation and total orientational correlation. The latter leads to a formula similar to that derived by Bordewijk and de Jeu[5] (see section II). However, from Figure 2, the uncorrelated value of $J_\parallel$ is ~9% less than its value when $b_t = 0.6 \times 2\pi/q_c$ while the totally correlated value is ~19% larger than this value. Therefore if we assume that these results hold qualitatively for higher order correlations too, we would expect the uncorrelated case to lead to a better approximation to ϵ. The term containing $\mathbf{J}$ is likely to contribute ~25% of the value of $\mathbf{H}$, which suggests ~3% error from the neglect of local ordering.

In the absence of short range correlation, we have

$$\langle \overline{\boldsymbol{\mu}^i\boldsymbol{\mu}^i\,\mathbf{T}^{ij}\boldsymbol{\alpha}^j\mathbf{T}^{jk}\boldsymbol{\alpha}^k \,.\,.\,.\,.\, \boldsymbol{\alpha}^\gamma} \rangle_0 = \langle \overline{\boldsymbol{\mu}^i\boldsymbol{\mu}^i\mathbf{T}^{ij}} \rangle_0 \langle \overline{\boldsymbol{\alpha}^j\mathbf{T}^{jk}} \rangle_0 \langle \overline{\boldsymbol{\alpha}^k\mathbf{T}^{kl}} \rangle_0 \,.\,.\,.\,.\, \langle \overline{\boldsymbol{\alpha}^\gamma} \rangle$$

and for a large number of molecules N, such that $N^l + 0(N^{l-1}) \sim$

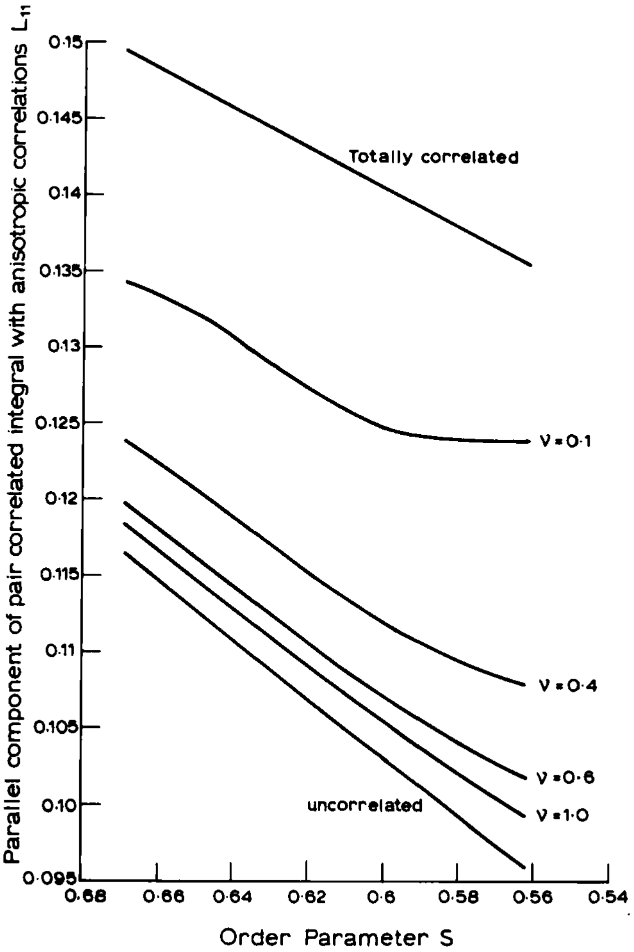

FIGURE 3 Variation with S of pair correlated integral assuming anisotropic correlations, $L_{\parallel}$ for the liquid crystal PAA. Curves are shown for $b_t = \nu\, 2\pi/q_c$ for various ν and for the totally correlated and uncorrelated cases.

N^l, since $\langle\overline{\alpha^j\,\mathbf{T}^{jk}}\rangle$, $\langle\alpha^j\rangle$ are independent of j,k, writing $\mathbf{A}^i = (\mathbf{I} - \Sigma_j\mathbf{T}^{ij}\alpha^j + \Sigma_j\mathbf{T}^{ij}\alpha^j\Sigma_k\mathbf{T}^{jk}\alpha^k - \ldots)$

$$\sum_i\sum_{i'}\langle\overline{(\mu^i\mathbf{A}^i.\mathbf{e})(\mu^{i'}\mathbf{A}^{i'}.\mathbf{e})}\rangle_0$$

$$\approx \sum_i\sum_{i'}\langle\overline{(\mu^i - N\mu^i\mathbf{T}^{ij}(\mathbf{I} + \langle\alpha^j\mathbf{T}^{jk}\rangle)^{-1}\langle\alpha^k\rangle).\mathbf{e}}$$

$$\overline{(\mu^{i'} - N\mu^{i'}\mathbf{T}^{i'j'}(\mathbf{I} + \langle\alpha^{j'}\mathbf{T}^{j'k'}\rangle)^{-1}\,\langle\alpha^{k'}\rangle).\mathbf{e}}\rangle_0 \tag{9}$$

Writing $\mathbf{D}^i = N\boldsymbol{\mu}^i\,(\mathbf{T}^{ij}\langle\boldsymbol{\alpha}^j\rangle - \langle\boldsymbol{\alpha}^j\mathbf{T}^{jk}\rangle)$, since $\langle\overline{\boldsymbol{\alpha}^j\mathbf{T}^{jk}}\rangle$ is diagonal, (9) becomes

$$\sum_i \sum_{i'} \langle\overline{(\boldsymbol{\mu}^i\mathbf{A}^i.\mathbf{e})(\boldsymbol{\mu}^{i'}\mathbf{A}^{i'}.\mathbf{e})}\rangle_0$$

$$= \sum_i \sum_{i'} \langle\overline{(\boldsymbol{\mu}^i - \mathbf{D}^i).\mathbf{e}(\boldsymbol{\mu}^{i'} - \mathbf{D}^{i'})}.\mathbf{e}\rangle_0\,\mathbf{e}(\mathbf{I} + \langle\overline{\boldsymbol{\alpha}^j\,\mathbf{T}^{jk}}\rangle)^{-2}.\mathbf{e}$$

$\langle\overline{\boldsymbol{\alpha}^j\mathbf{T}^{jk}}\rangle$ can be evaluated as in section III, but more simply, to give

$$\langle\boldsymbol{\alpha}^j\mathbf{T}^{jk}\rangle = \frac{1}{V\epsilon_0}\,[\alpha_\perp U_\perp\mathbf{I} + (\alpha_\parallel U_\parallel - \alpha_\perp U_\perp)\langle\mathbf{n}^j\mathbf{n}^j\rangle] \tag{10}$$

where

$$\mathbf{U} = -\frac{1}{4\pi}\int_{V_1} d^3\mathbf{R}\,g\,\frac{(\mathbf{R})}{R^3}\,(\mathbf{I} - 3\mathbf{R}^2)$$

For g as in (8), $\mathbf{U} = 1/3\,\mathbf{I} - \boldsymbol{\Omega}$, where $\boldsymbol{\Omega}$ is the depolarising tensor of the ellipsoid E.
Similarly,

$$\langle\overline{(\boldsymbol{\mu}^i - \mathbf{D}^i).\mathbf{e}(\boldsymbol{\mu}^i - \mathbf{D}^i).\mathbf{e}}\rangle_0 = \mathbf{e}(M_\perp^2\mathbf{I} + (M_\parallel^2 - M_\perp^2)\langle\mathbf{n}\mathbf{n}\rangle)\cdot\mathbf{e}$$

where

$$M_\perp^2 = \mu_\perp^2\mathbf{e}\left(\mathbf{I} + \frac{N}{V}\,\Delta U\alpha_\parallel\langle\mathbf{n}\mathbf{n}\rangle\right)^2\cdot\mathbf{e}$$

and

$$M_\parallel^2 = \mu_\parallel^2\mathbf{e}\left(\mathbf{I} - \frac{N}{V}\,\Delta U\alpha_\perp(\mathbf{I} - \langle\mathbf{n}\mathbf{n}\rangle)\right)^2\cdot\mathbf{e}$$

Thus if as usual we write

$$g_{k_\lambda} = 1 + \sum_{i\neq i'}\frac{\langle\overline{(\boldsymbol{\mu}^i - \mathbf{D}^i).\mathbf{e}(\boldsymbol{\mu}^{i'} - \mathbf{D}^{i'}).\mathbf{e}}\rangle}{\langle\overline{(\boldsymbol{\mu}^i - \mathbf{D}^i).\mathbf{e}(\boldsymbol{\mu}^i - \mathbf{D}^i).\mathbf{e}}\rangle}$$

then from (4)

$$\frac{\epsilon_0(\epsilon_\lambda - \epsilon_{\infty\lambda})[\epsilon_\lambda + (\epsilon_{\infty\lambda} - \epsilon_\lambda)\Omega_\lambda^\epsilon]V}{\epsilon_\lambda(2 + \epsilon_{\infty\lambda})^2}$$

$$= \frac{N}{9KT} g_{k_\lambda} \frac{\mathbf{e} \cdot (M_\perp^2 \mathbf{I} + (M_\parallel^2 - M_\perp^2)\langle \mathbf{n}\mathbf{n}\rangle)\,\mathbf{e}}{\mathbf{e} \cdot (\mathbf{I} + N\langle \overline{\boldsymbol{\alpha}^i \mathbf{T}^{ij}}\rangle)^2\,\mathbf{e}} \qquad \gamma = \parallel, \perp$$

Hence in addition to the long-range orientational order effects, there is an effective contribution to the dipole moment as a result of the anisotropy of the molecules, ΔU, even when short-range order is neglected.

As usual we can derive $\boldsymbol{\alpha}$ from the extrapolated high frequency permittivity $\boldsymbol{\epsilon}_\infty$. From (3), summing terms as in (9),

$$\epsilon_0(\boldsymbol{\epsilon}_\infty - \mathbf{I}) = \frac{N}{V}\left(\mathbf{I} + \frac{N}{V}\langle\overline{\boldsymbol{\alpha}^i \cdot \mathbf{T}^{ij}}\rangle\right)^{-1} \langle\boldsymbol{\alpha}^j\rangle \tag{11}$$

and $\langle\overline{\boldsymbol{\alpha}^i \mathbf{T}^{ij}}\rangle$ is given by (10).

VII. COMPARISON WITH EXPERIMENTAL DATA

In general, verification of expressions for $\boldsymbol{\epsilon}$ is difficult because of the uncertainty in the values of the various molecular parameters, e.g. $\boldsymbol{\alpha}, \boldsymbol{\mu}$. For polar molecules it is further complicated by the lack of a model for the degree of permanent dipole anti-parallel ordering; an alternative expression for $\boldsymbol{\epsilon}$ just provides another possible value for g_k. For the refractive index (and the permittivity of non-polar molecules) this latter problem does not arise and so we will compare theory with the experimental data in this case.

From (11) and (10), for $g(\mathbf{R})$ as in (8),

$$\epsilon_{\infty\gamma} = 1 + \frac{\dfrac{N}{V\epsilon_0}\left[\bar{\alpha} + \Delta\alpha\left(\langle\mathbf{n}\mathbf{n}\rangle_\gamma - \dfrac{1}{3}\right)\right]}{1 - \dfrac{N}{V\epsilon_0}\left[\overline{\alpha\Omega} + \Delta(\alpha\Omega)\left(\langle\mathbf{n}\mathbf{n}\rangle_\gamma - \dfrac{1}{3}\right)\right]} \qquad \gamma = \parallel, \perp \tag{12}$$

where

$$\bar{\alpha} = \frac{1}{3}\alpha_{\parallel} + \frac{2}{3}\alpha_{\perp}, \qquad \overline{\alpha\Omega} = \frac{1}{3}\alpha_{\parallel}\Omega_{\parallel} + \frac{2}{3}\alpha_{\perp}\Omega_{\perp},$$

$$\Delta(\boldsymbol{\alpha\Omega}) = \alpha_{\parallel}\Omega_{\parallel} - \alpha_{\perp}\Omega_{\perp}$$

Equation (12) is rather similar to the expression derived by Palffy-Muhoray and Balzarini.[3,13] However they assumed that the polarisation $\mathbf{P}$ and the local field $\mathbf{F}$ satisfy $\langle \mathbf{P} \rangle = \langle \boldsymbol{\alpha} \cdot \mathbf{F} \rangle = \langle \boldsymbol{\alpha} \rangle \cdot \langle \mathbf{F} \rangle$, while we have found that the second equality does not hold for anisotropic molecules.

We have calculated values for the components of the refractive index $n_{\parallel}$, $n_{\perp}$, for PAA from (12) (with $n_{\gamma}^2 \equiv \epsilon_{x\gamma}$) and from the totally correlated case as in Reference 6, i.e. from

$$n_{\gamma}^2 = 1 + \frac{N}{V\epsilon_0}\left[\frac{1}{3}\frac{\alpha_{\parallel}}{\left(1 - \frac{N}{V\epsilon_0}\alpha_{\parallel}\Omega_{\parallel}\right)} + \frac{2\alpha_{\perp}}{3\left(1 - \frac{N}{V\epsilon_0}\alpha_{\perp}\Omega_{\perp}\right)}\right.$$
$$\left. + \left(\frac{\alpha_{\parallel}}{\left(1 - \frac{N}{V\epsilon_0}\alpha_{\parallel}\Omega_{\parallel}\right)} - \frac{\alpha_{\perp}}{\left(1 - \frac{N}{V\epsilon_0}\alpha_{\perp}\Omega_{\perp}\right)}\right)\left(\langle \mathbf{nn} \rangle_{\gamma} - \frac{1}{3}\right)\right]_{\gamma = \parallel, \perp} \tag{13}$$

We have used values from Reference 6 for $\boldsymbol{\alpha}$, b_l and b_t. Since (12) and (13) are identical for $S = 1$ we have used the value of $\boldsymbol{\alpha}$ calculated from the solid state refractive indices. The values of b_l and b_t are those generated from the crystallographic data. S and the density ρ are from References 1 and 14 respectively. Figure 4 shows the percentage deviation of the calculated $n_{\gamma}^2 - 1 (\gamma = \parallel, \perp)$ from the measured value[15] as a function of S. The two sets of curves correspond to equations (12) and (13).

From Figure 4 it is clear that both sets of curves deviate from the measured value in a very similar way, which suggests a common error. In fact, the deviation is consistent with errors in the values of $\bar{\alpha}$, $\Delta\alpha$ and indeed, e.g. $\bar{n}^2/\rho$ is different for the nematic phase and solid phase data. This effect appears to dominate any which might result from the neglect or otherwise of short-range correlation. There is no

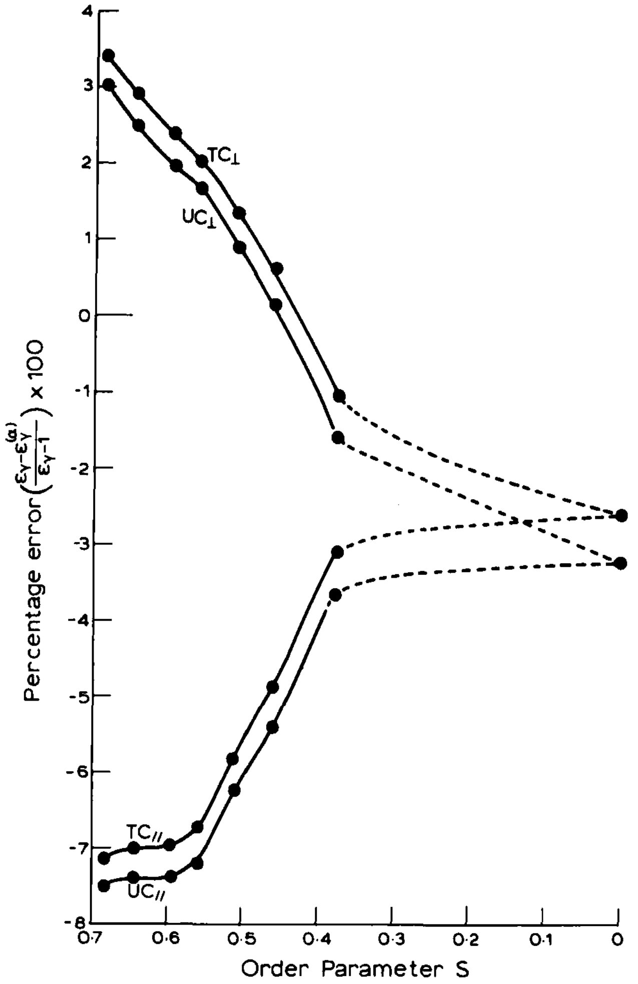

FIGURE 4 The percentage difference of calculated $\epsilon_\gamma^{(\alpha)} - 1(\gamma = \parallel,\perp)$ from the measured value $\epsilon_\gamma - 1$ as a function of S for PAA. The curves $TC_\parallel$, $TC_\perp$ show the results using the totally correlated formula and $UC_\parallel$, $UC_\perp$ show the results using the uncorrelated formula.

indication that (12) is a better approximation than (13). However, if the treatment of correlation were the only error, we would expect the measured value to lie between the two calculated ones. Since this is not the case it is difficult to determine the degree of correlation suggested by the data.

Equation (13) was derived in order to satisfy the conditions that $\Delta n^2/\rho \sim S$ and $(\bar{n}^2 - 1)/\rho \sim$ constant, obtained from the experimental data. Since the values of $n_{\|}$, $n_{\perp}$ calculated from (12) and (13) are very similar it follows that (12) too has these properties to a good approximation. Therefore it seems that the observed temperature dependence of the refractive indices may be obtained without any assumption about the degree of correlation as long as the dependence of $g(\mathbf{R})$ on the orientation of the molecules is properly accounted for. The close agreement between the totally correlated and uncorrelated cases may be seen as a justification for the empirical equation (13). However, the different S dependences may be significant to the calculation of the static permittivity.

VIII. CONCLUSION

We have investigated the effect of short-range orientational correlation on the term in the expression for $\boldsymbol{\epsilon}$ which describes two-particle interaction and found that it is likely to be small. Therefore we have averaged over molecular orientations neglecting the effects of local ordering and hence obtained a relationship between $\boldsymbol{\epsilon}$, the molecular parameters $\boldsymbol{\alpha}$, $\boldsymbol{\mu}$, $\boldsymbol{\Omega}$ and the order parameter S. This equation both describes an anisotropic internal field and predicts, to a good approximation, the temperature dependence of the refractive index data. Theoretical considerations suggest that it should be an improvement on previous expressions for $\boldsymbol{\epsilon}$. However, because of the difficulty in extracting molecular parameters from the experimental data, we have not yet been able to determine whether this is in fact the case.

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APPENDIX

A method for predicting the degree of short-range correlation using continuum theory has been given.[8] However, the calculation has been simplified by considering isotropically averaged correlations. In this appendix we will remove this simplification and determine approximately the anisotropy of the correlations. We use the notation of Reference 8.

For a single fluctuation $\psi = \psi_0 \cos(\mathbf{q} \cdot \mathbf{R})$, the difference between the twists at $\mathbf{R}_i$ and $\mathbf{R}_j$ is

$$\begin{aligned} \Delta\psi &= \psi_j - \psi_i \\ &= -2\psi_0 \sin\left(\frac{1}{2}\mathbf{q} \cdot (\mathbf{R}_j + \mathbf{R}_i)\right) \sin\left(\frac{1}{2}\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_i)\right) \end{aligned} \tag{8}$$

Averaging over $\mathbf{R}_i + \mathbf{R}_j$ for fixed $\mathbf{R}_i - \mathbf{R}_j$ gives

$$(\overline{\Delta\psi})^2 = \frac{2}{3}\psi_0^2\big(1 - \cos\big(\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_i)\big)\big)$$

Taking a thermal average and so substituting for ψ_0^2 its average value,

$$\langle(\Delta\psi)_\gamma^2\rangle = 2\,\frac{k_BT}{Vq^2}\,\frac{\big(1 - \cos\big(\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_i)\big)\big)}{(K_\gamma \sin^2\theta + K_3 \cos^2\theta)}$$

where $\gamma = 1,2$ for a splay/bend, twist/bend mode respectively, and $\mathbf{q} = (q \sin\theta \cos\varphi,\, q \sin\theta \sin\varphi,\, q \cos\theta)$.

Summing all modes, retaining an isotropic cut-off for the fluctuation wavelengths, $2\pi/q_c$, and using the definitions of X and K

$$\begin{aligned} \sum \langle(\Delta\psi_\gamma)^2\rangle &= \frac{V}{(2\pi)^3}\sum_{\gamma=1}^{2}\int \frac{2\,k_BT}{Vq^2}\,\frac{K\big(1 - \cos(qR\cos\theta_{qR})\big)}{(K_\gamma \sin^2\theta + K_3\cos^2\theta)}\,d^3\mathbf{q} \\ &= X\left[2 - \frac{K}{4\pi q_c}\sum_{\gamma=1}^{2}\int \frac{\cos(qR\cos\theta_{qR})\sin\theta\,d\theta d\varphi dq}{(K_\gamma \sin^2\theta + K_3\cos^2\theta)}\right] \end{aligned}$$

where θ_{qR} is the angle between **q** and **R**.
Thus we define $\alpha(\mathbf{R})$ analogously to $\alpha(R)$ by

$$\alpha(\mathbf{R}) = 2 - \frac{K}{4\pi q_c} \sum_{\gamma=1}^{2} \int \frac{\cos(qR\cos\theta_{qR})\sin\theta\, d\theta d\varphi dq}{(K_\gamma \sin^2\theta + K_3\cos^2\theta)}$$

The integral M appearing in this expression cannot be evaluated straightforwardly. However the **R** dependence is contained in the term $\cos(qR\cos\theta_{qR})$ and the denominator is just a "weighting" factor indicating the fluctuation amplitude for each q. Therefore we substitute

$$D_2 = \frac{1}{K_\gamma} + \left(\frac{1}{K_3} - \frac{1}{K_\gamma}\right)[(1 + \bar{K}_\gamma)\cos^2\theta - \bar{K}_\gamma\cos^2\theta] \quad \text{for}$$

$$D_1 = \frac{1}{(K_\gamma \sin^2\theta + K_3\cos^2\theta)}$$

and assume that the anisotropy with respect to **R** will not be significantly altered. The two expressions are equal for $\cos\theta = 0$ and $\cos\theta = 1$. $\bar{K}_\gamma$ is obtained by a least squares estimate fit of D_1 to D_2 for $\theta = 0$ to π. This yields

$$\bar{K}_\gamma = \frac{128}{3}\left[\frac{1}{16} - \frac{3}{8L} - \frac{3}{2L^2} - \frac{1}{L^3} + \left(\frac{1}{L} + \frac{2}{L^2} + \frac{1}{L^3}\right)\frac{1}{\sqrt{L+1}}\right]$$

where

$$L = \left(\frac{K_3 - K_\gamma}{K_\gamma}\right)$$

With this substitution and by taking the polar axis parallel to **R** we can write for M,

$$M \approx \int \cos(qR\cos\theta_{qR})\sin\theta_{qR}\, D_2(\theta)\, d\theta_{qR}\, d\varphi_{qR} dq$$

Writing $\cos\theta = \cos\theta_{qR}\cos\theta_R + \sin\theta_{qR}\sin\theta_R\cos(\varphi_{qR} - \varphi_R)$ where $\mathbf{R} = (R, \theta_R, \varphi_R)$ w.r.t. the fixed z (extraordinary) axis, the expression can be integrated to yield

$$\alpha(\mathbf{R}) \approx 2 - K\sum_{\gamma=1}^{2}\left\{\frac{1}{K_\gamma}Q_1(q_cR) + \frac{1}{2}\left(\frac{1}{K_3} - \frac{1}{K_\gamma}\right) \times\right.$$

$$[P_{1\gamma}(\cos^2\theta_R)Q_1(q_cR) + P_{2\gamma}(\cos^2\theta_R)\, Q_2(q_cR)$$

$$\left. + P_{3\gamma}(\cos^2\theta_R)Q_3(q_cR) + P_{4\gamma}(\cos^2\theta_R)\, Q_4(q_cR)]\right\}$$

where

$$Q_1(q_cR) = \int_0^1 \frac{\sin(q_cRx)}{q_cRx}\, dx$$

$$Q_2(q_cR) = \frac{\cos(q_cR)}{q_c^2R^2}$$

$$Q_3(q_cR) = \frac{\sin(q_cR)}{q_c^3R^3}$$

$$Q_4(q_cR) = \frac{1}{q_c^4R^4}\left[\cos(q_cR) - \frac{\sin(q_cR)}{q_cR}\right]$$

$$P_{1\gamma}(\cos^2\theta_R) = 1 + \frac{\overline{K}_\gamma}{4} + \left(-1 + \frac{\overline{K}_\gamma}{2}\right)\cos^2\theta_R - 3\,\frac{\overline{K}_\gamma}{4}\cos^4\theta_R$$

$$P_{2\gamma}(\cos^2\theta_R) = 1 + \frac{\overline{K}_\gamma}{4} - 3\left(1 + \frac{\overline{K}_\gamma}{2}\right)\cos^2\theta_R + \frac{5}{4}\,\overline{K}_\gamma\cos^4\theta_R$$

$$P_{3\gamma}(\cos^2\theta_R) = -1 - \frac{7}{4}\,\overline{K}_\gamma + \left(3 + \frac{33}{2}\,\overline{K}_\gamma\right)\cos^2\theta_R - \frac{75}{4}\,\overline{K}_\gamma\cos^4\theta_R$$

$$P_{4\gamma}(\cos^2\theta_R) = -6\overline{K}_\gamma\left[\frac{3}{4} - \frac{15}{2}\cos^2\theta_R + \frac{35}{4}\cos^2\theta_R\right]$$