Magnetic and electric birefringence in the isotropic phase of nematic liquid crystals

N V MADHUSUDANA and S CHANDRASEKHAR

Raman Research Institute, Bangalore 560006

Abstract. A theory is developed of the anomalous magnetic and electric birefringence in the isotropic phase of nematic liquid crystals taking into account orientational correlations between neighbouring molecules. Use is made of a modification of Bethe's method due to Krieger and James, and the properties of the system are derived in terms of a single parameter, viz., the two-particle interaction constant. The expressions for the magnetic and electric birefringence are similar in form to those given by the phenomenological model of de Gennes. Theoretical curves for p-azoxyanisole reproduce the trends in the observed data. A calculation of the nematic-isotropic transition point confirms that this treatment is an improvement over the mean field approximation in describing pre-transition phenomena in the isotropic phase.

1. Introduction

It is well established that short range order effects in the isotropic phase of nematic liquid crystals can be described in terms of the phenomenological model of de Gennes (1971) according to which certain properties like the magnetic birefringence, intensity of light scattering and flow birefringence may be expected to vary approximately as $(T-T^*)^{-1}$, where T^* is a temperature slightly below the nematic-isotropic transition point T_c. These predictions are in agreement with observations (Stinson and Litster 1970; Martinoty *et al* 1971). It is natural to suppose that the electric birefringence should also conform to this simple description, but measurements on a number of compounds have proved that this is not the case (Tsvetkov and Ryumtsev 1968; Filippini 1972; Schadt and Helfrich 1972). The most striking example is that of p-azoxyanisole (hereafter referred to as PAA) which exhibits an actual reversal of sign of the Kerr constant at about $T_c+5\,\mathrm{K}$ (Tsvetkov and Ryumtsev 1968). However, recent calculations have shown (Madhusudana and Chandrasekhar 1973a) that the behaviour of PAA is in fact consistent with the phenomenological model when proper allowance is made for the contributions of the polarizability and the permanent dipole moment to the free energy.

A molecular interpretation of these pre-transition effects is evidently of much interest. The influence of short range orientational order on the thermodynamic properties of the nematic and isotropic phases has been discussed on the basis of a very

simple model (Chandrasekhar and Shashidhar 1972), but the conclusions drawn are only of qualitative significance. The molecular mean field method (Maier and Saupe 1960; Chandrasekhar and Madhusudana 1971, 1972a; Chandrasekhar, *et al* 1971) does provide a quantitative description of long range orientational order and the related properties of the nematic phase, but fails to explain short range order effects. (Stinson 1971; Madhusudana and Chandrasekhar 1973b).

In this paper, we present a theory of the anomalous magnetic and electric bire-fringence in the isotropic phase of nematic liquid crystals which takes into account near neighbour correlations by a method similar to that developed by Chang (1937) and by Krieger and James (1954) in discussing orientational transitions in crystals. Application of the theory to PAA shows that it is an improvement over the molecular mean field treatment. A brief account of the theory for the magnetic case has been reported previously (Chandrasekhar and Madhusudana 1972b; Madhusudana and Chandrasekhar 1973b).

2. The Consistency Relation

We consider the isotropic phase of a nematic liquid crystal in which a weak long range orientational order has been induced by an external field (magnetic or electric) acting along the Z axis of the space-fixed cartesian coordinate system XYZ. It is assumed that every molecule is surrounded by z nearest neigbours, and that no two of the z nearest neighbours are nearest neighbours of each other. Let $E(\theta_{ij})$ be the orientational energy of interaction between the central molecule i and one of its nearest neighbours, and $V(\theta_j)$ that between j and the remaining molecules of the uniaxial medium. Let $W(\theta_i)$ be the orientational contribution of the potential energy of the molecule due to the external field.

The relative weight for a given configuration of the cluster of $(z+1)$ molecules is given by

$$\prod_{j=1}^{z} f(\theta_{ij})g(\theta_j)h(\theta_i)h(\theta_j) \tag{1}$$

where
$$f(\theta_{ij}) = \exp[-E(\theta_{ij})/kT]$$
$$g(\theta_j) = \exp[-V(\theta_j)/kT]$$
$$h(\theta_i) = \exp[-W(\theta_i)/kT], \text{ etc.},$$

and θ_{ij} is a function of the usual spherical coordinates $\theta_i, \phi_i, \theta_j$ and ϕ_j. The relative probability that the central molecule and one of its nearest neighbours, say 1, are oriented along (θ_i, ϕ_i) and (θ_1, ϕ_1) is then

$$\psi(\theta_i, \phi_i; \theta_1, \phi_1) = f(\theta_{i1})h(\theta_i)g(\theta_1)h(\theta_1)$$
$$\times \prod_{j=2}^{z} \int \cdot \cdot \int f(\theta_{ij})g(\theta_j)h(\theta_j)\mathrm{d}(\cos\theta_j)\mathrm{d}\phi_j; \tag{2}$$

Since this probability should be the same irrespective of which molecule is regarded as the central one,

$$\psi(\theta_i, \phi_i; \theta_1, \phi_1) = \psi(\theta_1, \phi_1; \theta_i, \phi_i), \tag{3}$$

which represents the consistency relation.

It is assumed that $V(\theta_j)$ is given by a function of the form
$$V(\theta_j) = (-B/V^4)P_2(\cos\theta_j) \tag{4}$$

where $P_2(\cos\theta_j)$ is the Legendre polynomial of the second order, V the molar volume†
and B an interaction parameter which is a function of the long range order.   Similarly
the near neighbour interaction is taken to be

$$E(\theta_{ij}) = (-B^*/V^4)P_2(\cos\theta_{ij}).\tag{5}$$

We now expand $f(\theta_{ij})$ as

$$f(\theta_{ij}) = \tfrac{1}{2}D\sum_{k=0}^{\infty}(2k+1)c_k P_k(\cos\theta_{ij})\tag{6}$$

where

$$c_n = \frac{\int P_n(\cos\theta_{ij})f(\theta_{ij})\mathrm{d}(\cos\theta_{ij})}{\int f(\theta_{ij})\mathrm{d}(\cos\theta_{ij})}\tag{7}$$

is a measure of the short range order in the absence of an external field, and D the
denominator of Eq. (7).   In view of the form of the interaction given by Eq. (5), k
takes only even values in Eq. (6).   Similarly we write

$$g(\theta_j)h(\theta_j) = \sum_{k=0}^{\infty}a_k P_k(\cos\theta_j).\tag{8}$$

From Eq. (6), (8) and (2), it can be shown that

$$\frac{\displaystyle\sum_{k=0}^{\infty}a_k P_k(\cos\theta_i)}{h(\theta_i)[\displaystyle\sum_{l=0}^{\infty}a_l c_l P_l(\cos\theta_i)]^{z-1}} = \frac{\displaystyle\sum_{k=0}^{\infty}a_k P_k(\cos\theta_1)}{h(\theta_1)[\displaystyle\sum_{l=0}^{\infty}a_l c_l P_l(\cos\theta_1)]^{z-1}} = \rho\ (\text{say})\tag{9}$$

where ρ is a constant, and l takes only even values.   The consistency relation can
then be reduced to the form

$$\sum_{k=0}^{\infty}a_k P_k(\cos\theta) = \rho h(\theta)[\sum_{m=0}^{\infty}A'_m P_m(\cos\theta)]\tag{10}$$

where $$A'_m = (m+\tfrac{1}{2})\int P_m(\cos\theta)\ [\sum_{l=0}^{\infty}a_l c_l P_l(\cos\theta)]^{z-1}\mathrm{d}(\cos\theta).$$

From Eqs. (8) and (10), it follows that for the weakly ordered isotropic phase

$$1 + (B/kTV^4)\,P_2(\cos\theta) = \rho\,[A'_0 P_0(\cos\theta) + A'_2 P_2(\cos\theta)]\tag{11}$$

Remembering that $P_0(\cos\theta)=1$, we may equate the coefficients of $P_0(\cos\theta)$ and
$P_2(\cos\theta)$, so that

$$B/kTV^4 = A'_2/A'_0 = (z-1)a_2 c_2\tag{12}$$

which is the solution of the consistency relation in the limit $a_2 \ll 1$.
The long range order parameter Q is given by

$$Q = \frac{\int..\int P_2(\cos\theta_i)\psi(\theta_i,\phi_i;\theta_1,\phi_1)\mathrm{d}(\cos\theta_i)\mathrm{d}\phi_i\mathrm{d}(\cos\theta_1)\mathrm{d}\phi_1}{\int..\int \psi(\theta_i,\phi_i;\theta_1,\phi_1)\mathrm{d}(\cos\theta_i)\mathrm{d}\phi_i\mathrm{d}(\cos\theta_1)\mathrm{d}\phi_1}$$

Applying the consistency relation (3) and using Eqs. (7) and (8),

$$Q = \tfrac{1}{5}\,a_2(1+c_2)\tag{13}$$

Therefore, $$B = 5kTQV^4(z-1)c_2/(1+c_2)\tag{14}$$

† Recent studies (McColl and Shih 1972, Chandrasekhar and Madhusudana 1973) on the effect of
pressure on the orientational order in *p*-azoxyanisole indicate a V^{-4} dependence of the potential.   We
shall therefore assume such a volume dependence throughout this discussion.

Since c_2 depends only on B^* all the properties of the system can be deduced in terms of a single parameter.

3. Magnetic birefringence

If the externally applied field is magnetic,
$$W(\theta) = -\tfrac{1}{3}\Delta\eta H^2 P_2 (\cos\theta) \tag{15}$$
where $\Delta\eta$ is the anisotropy of diamagnetic susceptibility of the molecule.

Hence, from Eq. (8),
$$a_2 = B/kTV^4 + \Delta\eta H^2/3kT, \tag{16}$$
Using Eqs. (12) and (14),
$$Q = \frac{\Delta\eta H^2}{15kT}\frac{1+c_2}{1-(z-1)c_2}. \tag{17}$$

Further, $Q=(X_e - X_0)/\Delta X$ where X_e, X_0 are the principal optical polarizabilities of the medium given by $X_e = 3(n_e^2 - 1)/4\pi\nu(n_e^2 + 2)$, etc., and ν is the number of molecules per cm³. Since the magnetic birefringence $\Delta n = n_e - n_0 \sim 10^{-7}$,
$$\Delta n = K\frac{(n^2+2)^2}{TVn}\frac{1+c_2}{1-(z-1)c_2} \tag{18}$$
where
$$K = (2\pi\mathcal{N}/135k)\,\Delta\chi\Delta\eta H^2 \tag{19}$$
and $\mathcal{N}$ is the Avogadro number.

Expressing c_2 given by Eq. (7) as a series, and substituting in the denominator of Eq. (18), we get
$$\Delta n = K\frac{(n^2+2)^2}{V_n}\frac{(1+c_2)}{T-T^*} \tag{20}$$
where
$$T^* = \frac{(z-1)B^*}{5kV^4}\left[1 + \frac{1}{7}\frac{B^*}{kTV^4} - \frac{1}{35}\frac{(B^*)^2}{k^2T^2V^8} + \cdots\right].$$
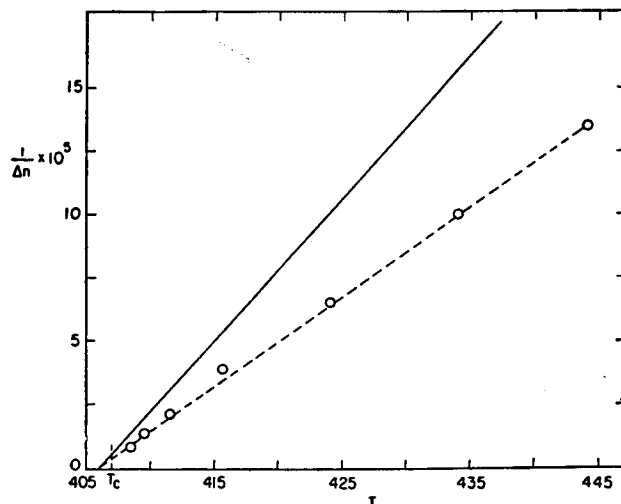

Figure 1. Reciprocal of magnetic birefringence of *p*-azoxyanisole versus temperature. Full line represents theoretical variation and circles the experimental data of Zadoc- Kahn (1936). The theoretical $(\Delta n)^{-1}$ is throughout higher by a nearly constant factor as can be seen from the dashed curve which is obtained by multiplying the theoretical values by 0·65.

Eq. (20) is formally similar to de Gennes's expression; T^* is now governed by short range correlations and exhibits a slight temperature dependence.

From Eqs. (18) and (20) it is clear that when $T = T^*$, $c_2 = 1/(z-1)$, which at once determines the value of B^*. The temperature at which $c_2 = 1/(z-1)$ has been called the 'branching' temperature by Krieger and James (1954) and in analogy with the phenomenological model it may be identified as the hypothetical second order transition point T^*.

Taking $z = 8$ for an imbricated nematic arrangement (Bernal and Crowfoot 1933) we get $c_2 = 1/7$ at $T_c - 1$ (which is the value of T^* indicated by experiment). For PAA this gives $B^* = 0.9621 \times 10^{-4}$ erg cm^{12}. Evaluating c_2 at different temperatures from Eq. (7) and substituting $\Delta\chi = 25.9 \times 10^{-24}$ cm^3 (Saupe and Maier 1961), $\Delta\eta = 104.2 \times 10^{-30}$ cm^3 (Gasparoux *et al* 1971) and $H = 33,900$ G (Zadoc-Kahn 1936) in Eq. (19), Δn^{-1} has been calculated from Eq. (18). The full line in figure 1 shows the theoretical variation of Δn^{-1}, and the circles the experimental data of Zadoc-Kahn (1936). It is found that the calculated Δn^{-1} is throughout higher by a nearly constant factor. This discrepancy may be partly due to the uncertainties in the experimental values of $\Delta\chi$, $\Delta\eta$ and H^2 which have been substituted in Eq. (19). Taking a different value of z, say 6 or 12, alters the value of B^* but has little influence on the temperature variation of Δn.

4. Electric birefringence

Under the action of an applied electric field, the orientational potential energy of the molecule arises from (i) the anisotropy of low frequency polarizability $\Delta\alpha$ and (ii) the net permanent dipole moment μ. Moreover, the effect of the cavity field and the reaction field produced in the medium cannot be ignored as in the diamagnetic case (see, e.g., Böttcher 1952). Applying the Onsager theory, Maier and Meier (1961a) have worked out these various contributions to the dielectric properties of the nematic phase. The orientational potential energy due to the induced dipole moment is given by

$$W_1(\theta) = -\tfrac{1}{3} F h^2 \, \Delta\alpha \, E^2 P_2(\cos\theta)$$

where $h = 3\epsilon/(2\epsilon+1)$ is the cavity field factor, ϵ is the average dielectric constant, $F = 1/(1-\alpha f)$ is the reaction field factor, α is the average polarizability, $f = 4\pi N\rho (2\epsilon-2)/3M(2\epsilon+1)$, ρ is the density and M the molecular weight. (The effect of the anisotropy of the dielectric constant may be neglected since we are concerned with the very weakly ordered isotropic phase.) θ is the angle which the long molecular axis, assumed to be the direction of maximum molecular polarizability, makes with the applied field E.

To evaluate the potential energy due to the permanent dipole moment, we choose XYZ as the space-fixed coordinate system and $\xi\,\eta\,\zeta$ as the molecule-fixed coordinate system, ζ coinciding with the long axis of the molecule and ξ being in the plane containing ζ and μ. If the electric field E acts along the Z axis and γ is the Eulerian angle between the ξ-axis and the line of intersection of the XY and $\xi\eta$ planes, the orientational potential energy

$$W_2(\theta) = -F h \mu \, (\cos\beta \cos\theta + \sin\beta \sin\gamma \sin\theta) E$$

where β is the angle between μ and the ζ-axis.

Putting $W(\theta) = W_1(\theta) + W_2(\theta)$, we obtain from Eq. (8)

$$a_2 = \frac{BQ}{kTV^4} + \frac{F h^2 E^2}{3kT} \left[\Delta\alpha - \frac{F\mu^2}{2kT} (1 - 3\cos^2\beta) \right]$$

where we have averaged over all values of γ since the medium has uniaxial symmetry. Proceeding as before

$$Q = \frac{Fh^2 E^2}{15k} \left[\Delta\alpha - \frac{F\mu^2}{2kT} (1-3\cos^2\beta) \right] \frac{1+c_2}{T[1-(z-1)c_2]}$$
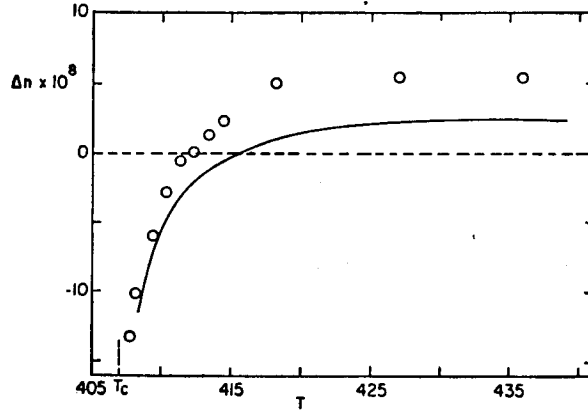

Figure 2. Electric birefringence of *p*-azoxyanisole versus temperature. Full line represents theoretical variation and circles the experimental data of Tsvetkov and Ryumtsev (1968).

and the electric birefringence

$$\Delta n = \frac{2\pi \mathcal{N} \Delta\chi E^2}{135k} Fh^2 \left[\Delta\alpha - \frac{F\mu^2}{2kT}(1-3\cos^2\beta) \right] \frac{(n^2+2)^2}{TnV} \frac{1+c_2}{[1-(z-1)c_2]} \quad (21)$$

The form of this expression is similar to that given by the phenomenological model (Madhusudana and Chandrasekhar 1973a). Clearly, the birefringence can be positive or negative depending on the sign of $[\Delta\alpha-(F\mu^2/2kT)\ (1-3\cos^2\beta)]$. For the elongated molecules of nematogenic compounds $\Delta\alpha$ is always positive, but the sign of the permanent dipole contribution depends on the angle β. If β is small, the two terms add to give rise to a strong positive Δn, whereas if β is sufficiently large Δn may be negative. Further, since the second term is proportional to T^{-1}, there can occur, in principle, a reversal of sign of Δn with temperature, as has indeed been observed in PAA.

We shall now calculate Δn for PAA according to Eq. (21) by substituting the known values of the molecular parameters. The relevant data reported by Maier and Meier (1961b) are: $\mu=2.22$D; $\beta \approx 64°$ from dielectric anisotropy measurements in the nematic phase and 61° from the Kerr constant in dilute solutions (we shall use the mean value of $\beta=62.5°$ in the present calculations); $\Delta\alpha$, the anisotropy of low frequency polarizability extrapolated from the value in the optical region, $=23.0 \times 10^{-24}$ cm^3, $\epsilon=5.65$ at T_c+5 K. Putting $E=1.2 \times 10^4$ volt cm^{-1} and using the same value of B^* as in the magnetic birefringence calculation, Δn derived from Eq. (21) has been plotted in figure 2 as a function of temperature along with the experimental points of Tsvetkov and Ryumtsev (1968). It may be emphasized that since there is a competition between the polarizability and the permanent dipole contributions, even a small error in β will cause an appreciable shift in the temperature at which $\Delta n=0$. Nevertheless, it is clear that the theoretical curve agrees fairly well with the trend in the observed data.

5. Evaluation of T_c—T^*

In order to determine the first order nematic-isotropic transition point T_c we have to solve the consistency relation in the *ordered* phase. As described earlier, Krieger and James (1954) expanded the relevant distribution function as a series in Legendre polynomials to obtain solutions in the infinitesimal approximation. This procedure is not suitable for the ordered phase in which Q takes large values. We therefore rewrite the consistency relation in the form

$$\frac{\exp\left[(B/kTV^4)\,P_2\,(\cos\theta_i)\right]}{\left[\int\int \exp\left\{(B^*/kTV^4)\,P_2\,(\cos\theta_{ij})+(B/kTV^4)\,P_2\,(\cos\theta_j)\right\}\mathrm{d}(\cos\theta_j)\mathrm{d}\phi_j\right]^{z-1}}=\text{constant}\quad(22)$$

This relation has to be satisfied for all values of $P_2(\cos\theta_i)$. Here B^* is a constant already determined, but B has to be evaluated at each temperature. Those pairs of values of B^*/kTV^4 and B/kTV^4 which give a constant ratio (22) for every $P_2(\cos\theta_i)$ represent the solutions of the consistency relation at that temperature. The integrals were evaluated numerically for ranges of values of B^*/kTV^4 and B/kTV^4 and for various $P_2(\cos\theta_i)$. Pairs of values have been found that fulfil Eq. (22) to a very good approximation for $P_2(\cos\theta_i)$ lying between 1 and 0. Using these pairs, the internal energy

$$U=-\frac{Nz}{2}\frac{B^*}{V^4}\frac{\int\cdots\int \exp\left[\frac{B^*}{kTV^4}P_2\,(\cos\theta_{ij})+\frac{B}{kTV^4}\left\{P_2(\cos\theta_i)+P_2(\cos\theta_j)\right\}\right]\times P_2\,(\cos\theta_{ij})\mathrm{d}(\cos\theta_i)\mathrm{d}\phi_i\mathrm{d}(\cos\theta_j)\mathrm{d}\phi_j}{\int\cdots\int \exp\left[\frac{B^*}{kTV^4}P_2\,(\cos\theta_{ij})+\frac{B}{kTV^4}\left\{P_2(\cos\theta_i)+P_2(\cos\theta_j)\right\}\right]\times\mathrm{d}(\cos\theta_i)\mathrm{d}\phi_i\mathrm{d}(\cos\theta_j)\mathrm{d}\phi_j}\quad(23)$$
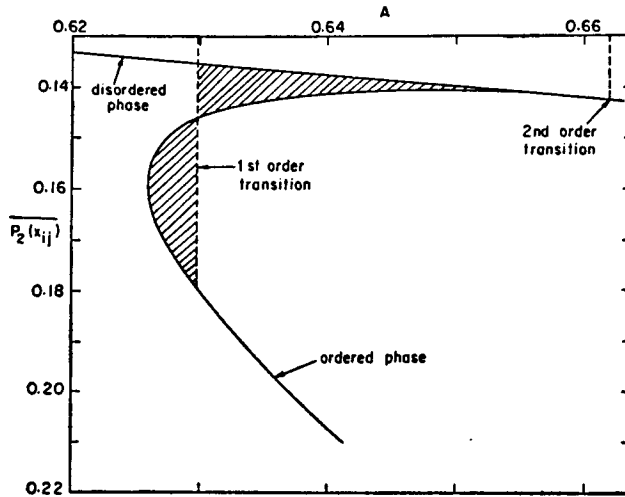

Figure 3. Plot of $\overline{P_2\,(x_i)}_j$ $[=-2(V^*)^4\,U/NzB^*]$ A versus $[=B^*/k(V^*)^4T]$, where V^* is the molar volume at the second order transition point T^*. At the first order transition point the shaded areas are equal so that the Helmholtz free energy of the ordered and disordered phases are the same. At the second order transition point $\overline{P_2(x_{ij})}=c_2=1/7$.

has been calculated as a function of temperature. The plot of U versus $1/T$ at constant volume at once yields both T_c and T^* (figure 3). It is found that $T^*/T_c = 0.95$ which is a significant improvement over the mean field value of 0.90, but still appreciably less than that derived from experiment. It may be emphasized that this procedure ignores the volume change at T_c. We have also evaluated some of the properties of the ordered phase, e.g., the long range order parameter as a function of temperature, which will be discussed elsewhere.

6. Specific heat of the isotropic liquid

In the absence of an external field, the internal energy of the isotropic liquid due to short range orientational order is

$$U = -\tfrac{1}{2}NzB^*c_2/V^4$$

and the specific heat

$$C_V = \frac{9Nz(B^*)^2}{8kT^2V^8}[\overline{\cos^4\theta} - \overline{(\cos^2\theta)^2}].$$

For PAA, C_V turns out to be 3.22 J mole^{-1} K^{-1} at $T_c+1.5$ K decreasing to 2.10 J mole^{-1} K^{-1} at T_c+40 K. Judging from the available measurements of the specific heat at constant pressure (Arnold 1964), the isothermal compressibility (Gabrielli and Verdini 1955; Hoyer and Nolle 1956, Kapustin and Bykova 1966) and the thermal expansion (Maier and Saupe 1960) the theoretical value of C_V appears to be of the right magnitude but varies rather too slowly with temperature.

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