

## The role of permanent dipoles in nematic order

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**Abstract.** We propose a new model for the statistical description of short range order in nematic liquid crystals of positive dielectric anisotropy. We consider the molecules to be cylindrically symmetric and assume the pair potential to be of the form  $A^*P_1(\cos \theta_{ij}) - B^*P_2(\cos \theta_{ij})$  which favours an antiparallel arrangement of the permanent dipoles. From physical considerations, antiferroelectric long range ordering is not expected to be present in nematics. Applying the Krieger-James approximation, solutions are obtained with an *apolar* or  $\overline{P_2(\cos \theta)}$  type of *long range order*, but allowing for *antiferroelectric short range order*. Two important consequences of the theory are (i) the mean dielectric constant should *increase* slightly on passing from the nematic to the isotropic phase, (ii) the magnetic and electric birefringence in the isotropic phase should both vary approximately as  $(T-T^*)^{-1}$ , where  $T^*$  is the hypothetical second order transition point, except when the dipolar interactions are very strong, in which case the electric birefringence should exhibit a *slower* variation at temperatures well above  $T^*$ . Choosing values of  $A^*/B^*$ , illustrative calculations are given of the long range and short range order parameters, dielectric properties, electric and magnetic birefringence. The results are in general agreement with the experimental data for such compounds.

### Introduction

The part played by permanent dipoles in determining nematic liquid crystalline properties has been the subject of considerable discussion. Indeed the first theory of the nematic phase, proposed by Max Born<sup>1</sup> in 1916, was based on purely dipolar interactions. Early experiments<sup>2</sup> to detect free charges on the surface of the liquid crystal, carried out with a view to testing Born's theory yielded negative results; more significantly compounds were found, *e.g.*, quinquephenyl<sup>3</sup> and the alkylazobenzenes<sup>4</sup>, that do not possess permanent dipole moments but do nevertheless exhibit the nematic phase. The dipole theory was therefore abandoned. However, the vast majority of nematogens are in fact polar molecules, yet it is generally assumed that the dipolar contribution to nematic stability is negligible. In this paper, we put forward a new point of view regarding the influence of permanent dipoles on orientational order in nematics. We shall confine our attention for the present to materials of positive dielectric anisotropy in which the dipole moment is assumed to be along the major molecular axis.

It has been shown recently<sup>5</sup> that the Krieger-James approximation is an improvement over the mean field treatment in describing pretransition phenomena in the isotropic phase of a nematic liquid crystal. The theory was developed assuming a  $\overline{P_2(\cos \theta_{ij})}$  type of interaction between neighbouring molecules  $i$  and  $j$ , where  $P_2(\cos \theta)$  is the Legendre polynomial of the second order. The temperature dependence of the magnetic and electric birefringence in the isotropic phase of  $p$ -azoxyanisole calculated on the basis of this model was similar to that expected from the phenomenological theory<sup>6,7</sup> and was in qualitative agreement with the observed behaviour. We now extend this treatment to include permanent dipole interactions also.

### The Model

Let us suppose for simplicity that the molecules are cylindrically symmetric rods so that the dipole moment is along the major molecular axis. Evidently, nearest neighbours will tend to be antiparallel. However, the absence of long range translational order in the nematic liquid precludes the possibility of antiferroelectric long range order. We postulate, therefore, that the system has an antiferroelectric type of short range order, but no antiferroelectric long range order. The near neighbour correlations giving rise to antiparallel short range order will extend over a certain correlation length. But as far as a distant molecule is concerned, its interaction with this antiferroelectric cluster will clearly be *apolar* in nature, *i.e.*, it will be fully equivalent whether the molecule is pointing 'up' or 'down'. To express this in a mathematically tractable form we shall resort to the Krieger-James approximation<sup>8</sup>.

We choose a space-fixed cartesian coordinate system XYZ, with the Z axis parallel to the uniaxial direction of the nematic medium. Let us assume that every molecule is surrounded by  $z$  nearest neighbours, no two of the  $z$  neighbours being nearest neighbours of each other. The pair potential between the central molecule  $i$  and one of its neighbours  $j$  is taken to be

$$E(\theta_{ij}) = A^*P_1(\cos \theta_{ij}) - B^*P_2(\cos \theta_{ij}) \quad (1)$$

and the interaction between  $j$  and the *rest of the medium* to be

$$V(\theta_j) = -BP_2(\cos \theta_j) \quad (2)$$

Here  $P_1$  and  $P_2$  are the Legendre polynomials of the first and second order,  $\theta_{ij}$  is a function of the usual spherical coordinates  $\theta_i$ ,  $\varphi_i$ ,  $\theta_j$  and  $\varphi_j$ ,  $A^*$ ,  $B^*$  and  $B$  are interaction parameters. (We ignore the volume dependence of the potential functions as it does not play an important part except in certain calculations, *e.g.*, the determination of the absolute value of  $T_c$  for a specific compound).

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

$$\prod_{j=1}^z f(\theta_{ij}) g(\theta_j) \quad (3)$$

where

$$f(\theta_{ij}) = \exp[-E(\theta_{ij})/kT]$$

$$g(\theta_j) = \exp[-V(\theta_j)/kT]$$

The relative probability that the central molecule  $i$  and one of its nearest neighbours, say one, are oriented along  $\theta_i, \varphi_i$  and  $\theta_1, \varphi_1$  is then

$$\psi(\theta_i, \varphi_i; \theta_1, \varphi_1) = f(\theta_{i1}) g(\theta_1) \prod_{j=2}^z \int \int f(\theta_{ij}) g(\theta_j) d(\cos \theta_j) d\varphi_j$$

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

$$\psi(\theta_i, \varphi_i; \theta_1, \varphi_1) = \psi(\theta_1, \varphi_1; \theta_i, \varphi_i) \quad (4)$$

which represents the *consistency* relation.

In view of the assumed form of the potential, (4) can be re-expressed in the form<sup>5</sup>

$$\frac{\exp[BP_2(\cos \theta_i)/kT]}{[\int \int \exp\{-A^*/kT P_1(\cos \theta_{ij}) + (B^*/kT) P_2(\cos \theta_{ij}) + (B/kT) P_2(\cos \theta_j)\} d(\cos \theta_j) d\varphi_j]^{z-1}} = \text{constant}$$

This relation has to be satisfied for all values of  $P_2(\cos \theta_i)$ . Thus, if  $A^*/B^*$  is known, the parameter  $B$  influencing long range order can be deduced in terms of  $B^*$  at every temperature. In principle  $B^*$  can be determined for a specific compound from the transition temperature, provided, of course, proper allowance is made for the volume dependence of the potential function.

The short range order parameters are given by

$$\overline{P_1(\cos \theta_{ij})} = \frac{\int \dots \int P_1(\cos \theta_{ij}) \psi(\theta_i, \varphi_i; \theta_j, \varphi_j) d(\cos \theta_i) d\varphi_i d(\cos \theta_j) d\varphi_j}{\int \dots \int \psi(\theta_i, \varphi_i; \theta_j, \varphi_j) d(\cos \theta_i) d\varphi_i d(\cos \theta_j) d\varphi_j}$$

$$\overline{P_2(\cos \theta_{ij})} = \frac{\int \dots \int P_2(\cos \theta_{ij}) \psi(\theta_i, \varphi_i; \theta_j, \varphi_j) d(\cos \theta_i) d\varphi_i d(\cos \theta_j) d\varphi_j}{\int \dots \int \psi(\theta_i, \varphi_i; \theta_j, \varphi_j) d(\cos \theta_i) d\varphi_i d(\cos \theta_j) d\varphi_j}$$

and the long range order parameter

$$Q = \frac{\int \dots \int P_2(\cos \theta_i) \psi(\theta_i, \varphi_i; \theta_j, \varphi_j) d(\cos \theta_i) d\varphi_i d(\cos \theta_j) d\varphi_j}{\int \dots \int \psi(\theta_i, \varphi_i; \theta_j, \varphi_j) d(\cos \theta_i) d\varphi_i d(\cos \theta_j) d\varphi_j}$$

The internal energy of the system

$$U = \frac{1}{2} Nz [A^* \overline{P_1(\cos \theta_{ij})} - B^* \overline{P_2(\cos \theta_{ij})}].$$

Using the above equations we have calculated the internal energy and the order parameters for three representative values of  $A^*/B^*$ , viz., 0.2, 0.5 and 3.2. The integrals were evaluated numerically using Simpson's rules on an IBM 360 computer. Illustrative curves are shown in figures 1 and 2.

The internal energy plotted as a function of  $1/T$  (figure 1) shows the characteristic sigmoid shape. The curves for the ordered and disordered phases meet at the second order transition point  $T^*$ . [As we shall see later,  $T^*$  is also the temperature at which the short range order parameter  $\bar{P}_2(\cos \theta_{ij})$  in the *isotropic* phase =  $1/(z-1)$ ]. The first order transition point  $T_c$  is the temperature at which the shaded areas are equal, i.e., when the Helmholtz free energies of anisotropic and isotropic phases are equal. The present calculation gives  $T^*/T_c = 0.951, 0.953$  and  $0.967$ , for  $A^*/B^* = 0.2, 0.5$  and  $3.2$  respectively as compared with  $0.95$  obtained when the permanent dipolar interaction is neglected<sup>5</sup>. The mean field theory gives  $T^*/T_c \simeq 0.90$ .

The curves for the short range and long range order parameters as functions of temperature are shown in figure 2.  $\bar{P}_1(\cos \theta_{ij})$  is negative signifying antiparallel ordering. All these curves show discontinuous changes at  $T_c$ ; the long range order drops to zero at the transition, but the short range order persists even in the isotropic phase.

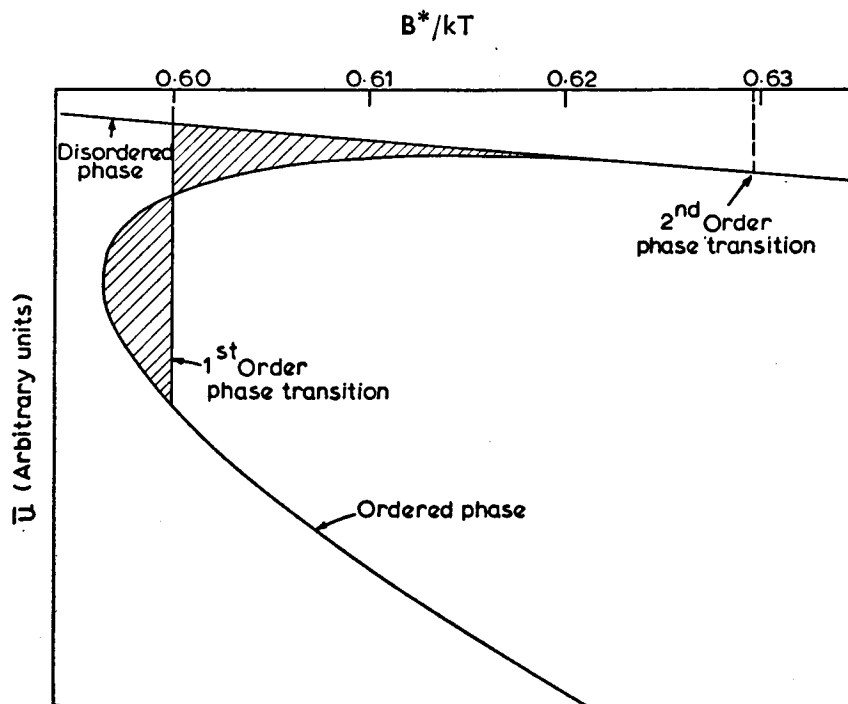


Figure 1 Plot of the internal energy vs. reciprocal of temperature for  $A^*/B^* = 0.5$ . At the first order transition point the shaded areas are equal and at the second order transition point  $c_2 = 1/7$ .

For comparison, we present in figure 3 the universal curves for the order parameters when the permanent dipole interaction is neglected<sup>5</sup>. As is to be expected putting  $A^* = 0$  reduces the value of  $Q$  considerably. It is also of interest to note that this curve lies much below the universal curve of the mean field theory according to which  $Q \simeq 0.44$  at  $T_c$ .

### Dielectric constants of the ordered phase

We shall now investigate the dielectric properties of the ordered phase to test whether the model leads to the correct magnitude of the anisotropy. The compounds with nitrile end groups studied by Schadt<sup>9</sup> show a very strong static dielectric anisotropy. Before developing a theory of the dielectric properties, it must be noted that a low voltage ( $\sim 2$  V) was used in these measurements to avoid any disturbing influence on the alignment of the sample, so that the orientational energy due to the external field is small compared to the intermolecular interactions. The field dependent orientational energy arises from two factors (i) the anisotropy of the low frequency molecular polarizability,  $\Delta\alpha$ , and (ii) the net permanent dipole moment of the molecule. We shall follow closely the treatment of Maier and Meier<sup>10</sup> who have applied the Onsager theory to take into account the effect of the cavity field produced in the medium.

The effective induced dipole moments per molecule along and perpendicular to the unique axis of the medium are respectively

$$\begin{aligned} \bar{m}_1 &= [\alpha + \frac{2}{3} \Delta\alpha Q] FhE_1 \\ \bar{m}_2 &= [\alpha - \frac{1}{3} \Delta\alpha Q] FhE_2 \end{aligned}$$

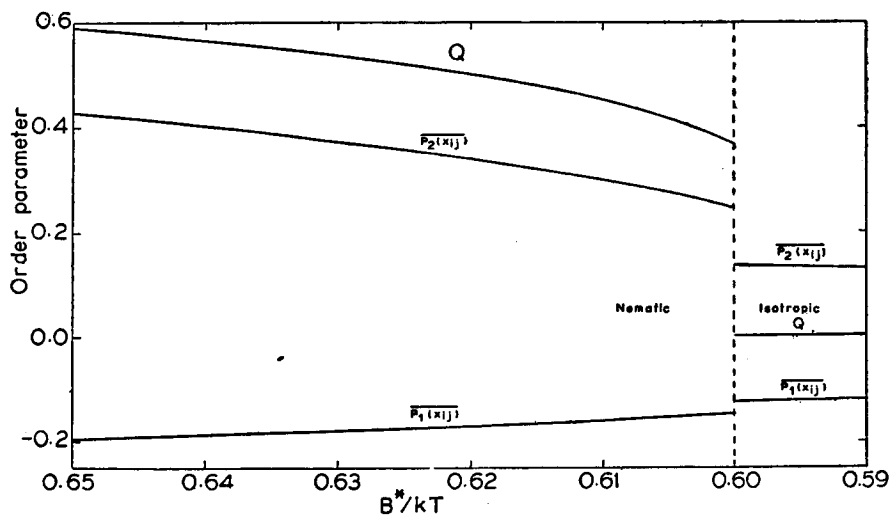


Figure 2 Plot of the short-range order parameter  $\overline{P_1(x_{1j})}$  and  $\overline{P_2(x_{1j})}$  and the long-range order parameter  $Q$  vs.  $B^*/kT$ ;  $A^*/B^* = 0.5$ .

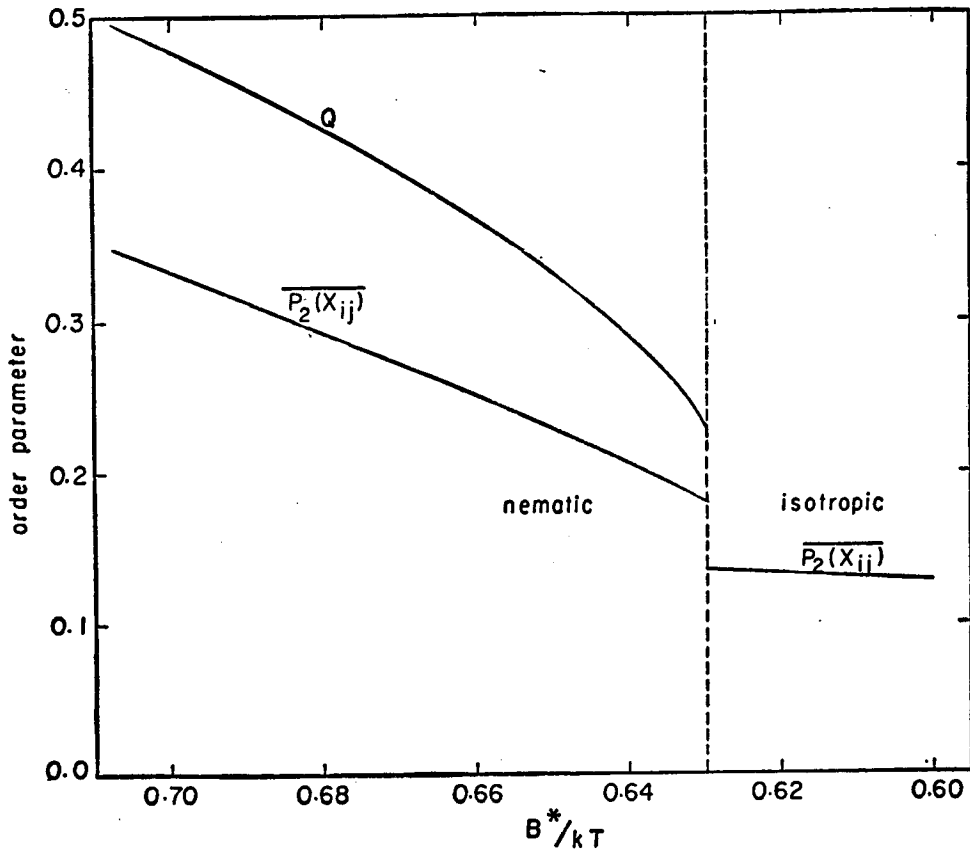


Figure 3 Plot of the short-range order parameter  $\overline{P_2(X_{ij})}$  and the long-range order parameter  $Q$  vs.  $B^*/kT$ ;  $A^* = 0$ .

where  $h = 3\varepsilon/(2\varepsilon + 1)$  is the cavity field factor.  $\varepsilon$  is the average dielectric constant,  $F = 1/(1 - \alpha f)$  is the reaction field factor,  $\alpha$  the average polarizability,  $f = 4\pi N\rho(2\varepsilon - 2)/3M(2\varepsilon + 1)$ ,  $\rho$  the density,  $M$  the molecular weight and  $E$  the applied electric field. (Strictly speaking, these factors require some corrections to allow for the anisotropic dielectric constant, but as we are interested in the order of magnitude of the dielectric anisotropy we shall neglect these corrections.)  $Q = \frac{1}{2}(3\cos^2\theta - 1)$  where  $\theta$  is the angle which the long molecular axis, assumed to be the direction of maximum polarizability, makes with the uniaxial direction.

To calculate the effective permanent dipole moment, we choose XYZ as the space fixed coordinate system, Z being parallel to the unique axis of the medium, and  $\xi\eta\zeta$  as the molecule fixed coordinate system,  $\zeta$  coinciding with the long axis of the molecule. Let  $\nu$  be the Eulerian angle between the  $\xi$ -axis and the line of intersection of the XY and  $\xi\eta$  planes, and  $\nu'$  the angle between this line and the X-axis. We assume as

before that the molecules are cylindrically symmetric so that the permanent dipole moment  $\mu$  is parallel to the long molecular axis. Since the potential energy of the dipoles due to the external field is small, we can write the effective dipole moment along the field direction as

$$\bar{\mu}_2 = \frac{\int \dots \int [1 + (\mu_{x1} + \mu_{xj}) hE_2/kT] \mu_{x1} \phi(\theta_1, \varphi_1; \theta_j, \varphi_j) \sin\theta_1 d\theta_1 d\varphi_1 \sin\theta_j d\theta_j d\varphi_j}{\int \dots \int [1 + (\mu_{x1} + \mu_{xj}) hE_2/kT] \phi(\theta_1, \varphi_1; \theta_j, \varphi_j) \sin\theta_1 d\theta_1 d\varphi_1 \sin\theta_j d\theta_j d\varphi_j}$$

$$\bar{\mu}_1 = \frac{\int \dots \int [1 + (\mu_{z1} + \mu_{zj}) hE_1/kT] \mu_{z1} \phi(\theta_1, \varphi_1; \theta_j, \varphi_j) \sin\theta_1 d\theta_1 d\varphi_1 \sin\theta_j d\theta_j d\varphi_j}{\int \dots \int [1 + (\mu_{z1} + \mu_{zj}) hE_1/kT] \phi(\theta_1, \varphi_1; \theta_j, \varphi_j) \sin\theta_1 d\theta_1 d\varphi_1 \sin\theta_j d\theta_j d\varphi_j}$$

where  $\mu_{z1} = \mu F \cos \theta_1$

and  $\mu_{x1} = \mu F \sin \nu'_1 \sin \theta_1$ .

(The integration over  $\nu'$  is essentially the same as integration over  $\varphi$  and hence need not be shown separately). The above integrals then reduce to the form :

$$\bar{\mu}_1 = \frac{hF^2\mu^2}{kT} [\overline{\cos^2\theta_1} + \overline{\cos\theta_1 \cos\theta_j}] E_1$$

$$\text{and } \bar{\mu}_2 = \frac{hF^2\mu^2}{kT} [\frac{1}{2} \overline{\sin^2\theta_1} + \overline{\sin\nu'_1 \sin\nu'_j \sin\theta_1 \sin\theta_j}] E_2$$

$$\text{Since } \frac{\epsilon_{||} - 1}{4\pi} E_1 = N \frac{\rho}{M} [\bar{m}_1 + \bar{\mu}_1],$$

$$\epsilon_{||} = 1 + 4\pi \frac{N\rho hF}{M} [\alpha + \frac{2}{3} \Delta\alpha Q + \frac{F\mu^2}{3kT} (2Q+1) + \frac{F\mu^2}{kT} \overline{\cos\theta_1 \cos\theta_j}]$$

and similarly

$$\epsilon_{\perp} = 1 + 4\pi \frac{N\rho hF}{M} [\alpha - \frac{1}{3} \Delta\alpha Q + \frac{F\mu^2}{3kT} (1-Q) + \frac{F\mu^2}{kT} \overline{\sin\nu'_1 \sin\nu'_j \sin\theta_1 \sin\theta_j}]$$

In the case of the nitrile compounds we assume  $\rho \simeq 1.2$ , the average polarizability  $\alpha = 28 \times 10^{-24} \text{ cm}^3$ ,  $\Delta\alpha = 15 \times 10^{-24} \text{ cm}^3$  (evaluated by assuming additivity of the bond polarizabilities extrapolated to low frequency and a reasonable structure of the molecule),  $\mu = 5 \text{ D}$  along the long axis of molecule. Substituting the theoretically derived  $Q$  (figure 2), the calculated variation of  $\epsilon_{||}$ ,  $\epsilon_{\perp}$  as well as  $\epsilon = \frac{1}{2} (\epsilon_{||} + 2\epsilon_{\perp})$  are shown in figure 4. It should be emphasized that if the volume variation is also taken into account, we should get a much more rapid temperature variation of the dielectric constants especially near  $T_c$ , but it does not affect the orders of magnitude that we are interested in at present. A comparison with the experimental data of Schadt shows that the theory does indeed lead to the right magnitude of the dielectric anisotropy of these strongly

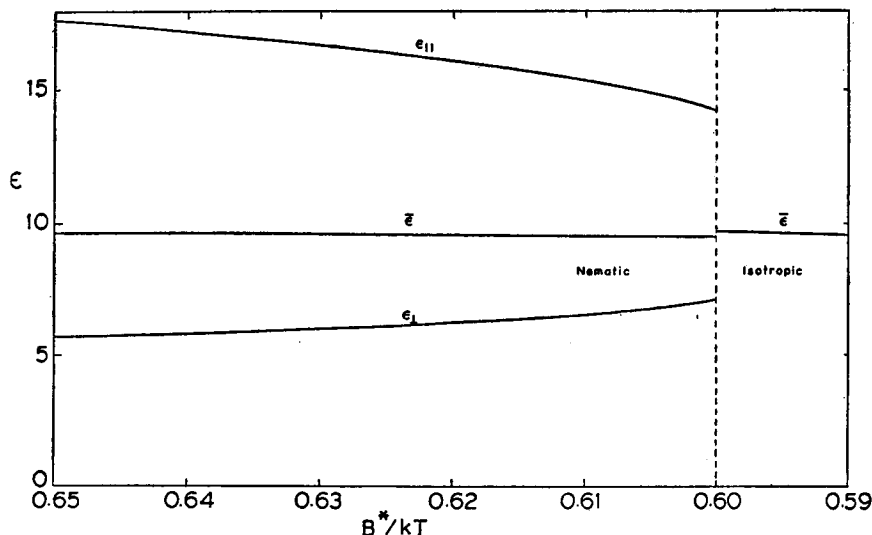


Figure 4 Variation of the dielectric constants  $\epsilon_{||}$ ,  $\epsilon_{\perp}$  and  $\bar{\epsilon} = \frac{1}{3}(\epsilon_{||} + 2\epsilon_{\perp})$  in the nematic and isotropic phases  $A^*/B^* = 0.5$ .

positive materials. It may be pointed out that if there was antiparallel long range order the dielectric anisotropy would be negative (in analogy with antiferromagnetism).

An interesting result that emerges from Schadt's measurements<sup>9</sup> on the nitrile compounds is that the mean dielectric constant increases by a few per cent at the nematic-isotropic transition, the value being *higher* in the isotropic phase. The suggestion has been made that this may possibly be attributed to a second order flexoelectric effect<sup>11</sup>, but in fact a more straightforward explanation can be given in terms of the present model: the increase in the average polarizability (or dielectric constant) of the isotropic phase arises from the decrease in the antiferroelectric short range order  $\overline{P_1(\cos \theta_{ij})}$  at  $T_c$  (figure 2). The theoretical variation of the mean dielectric constant in the nematic and isotropic phases is shown in figure 4.

### Electric and magnetic birefringence in the isotropic phase

We shall first consider the effect of an electric field on the isotropic phase. Unlike the dielectric measurements discussed in the previous section which employ low fields, electric birefringence measurements in the isotropic phase usually require strong fields,  $\sim 4$  kV/cm. When the field is very strong, there is actually a slight shift in the transition temperature in materials of strong positive anisotropy<sup>12</sup>, as is to be expected. However, in the present discussion, we shall ignore this small change in



$T_c$  (about  $5 \times 10^{-3}$  K for 4 kV/cm). The theoretical treatment in this case is somewhat more complex because the electric field induces a long range order parameter  $\overline{P_1(\cos \theta)}$  in addition to the usual long range parameter  $Q$ .

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

$$\prod_{j=1}^z f(\theta_{1j}) g(\theta_j) \chi(\theta_1) \chi(\theta_j)$$

where  $f(\theta_{1j})$  is the same as defined in (3),

$$g(\theta_j) = \exp [ \{ AP_1(\cos \theta_j) + BP_2(\cos \theta_j) \} / kT ]$$

$$\chi(\theta_1) = \exp [ \{ Fh_{\mu}EP_1(\cos \theta_1) + \frac{1}{2} \Delta \alpha Fh^2E^2P_2(\cos \theta_1) \} / kT ]$$

$$\chi(\theta_j) = \exp [ \{ Fh_{\mu}EP_1(\cos \theta_j) + \frac{1}{2} \Delta \alpha Fh^2E^2P_2(\cos \theta_j) \} / kT ],$$

and  $A$  is another interaction parameter to be determined.

Therefore

$$\begin{aligned} \phi(\theta_1, \varphi_1; \theta_1, \varphi_1) &= f(\theta_{11}) g(\theta_1) \chi(\theta_1) \chi(\theta_1) \\ &\times \prod_{j=2}^z \int \dots \int f(\theta_{1j}) g(\theta_j) \chi(\theta_j) d(\cos \theta_j) d\varphi_j \end{aligned} \quad (5)$$

Since the induced long range order is very small ( $10^{-4}$  or less) we may use the infinitesimal approximation. We expand  $f(\theta_{1j})$  as

$$f(\theta_{1j}) = \frac{1}{2} D \sum_{k=0}^{\infty} (2k+1) c_k P_k(\cos \theta_{1j})$$

where

$$c_k = \frac{\int P_k(\cos \theta_{1j}) f(\theta_{1j}) d(\cos \theta_{1j})}{\int f(\theta_{1j}) d(\cos \theta_{1j})} \quad (6)$$

is a measure of the short range order in the absence of an external field, and  $D$  is the denominator of (6).

Similarly,

$$g(\theta_j) \chi(\theta_j) = \sum_{k=0}^{\infty} a_k P_k(\cos \theta_j) \quad (7)$$

As before, the consistency relation reads

$$\phi(\theta_1, \varphi_1; \theta_1, \varphi_1) = \phi(\theta_1, \varphi_1; \theta_1, \varphi_1).$$

Using (5), (6) and (7), the consistency relation takes the form

$$\frac{1 + a_1 P_1(\cos \theta) + a_2 P_2(\cos \theta)}{\chi(\theta) [1 + a_1 c_1 P_1(\cos \theta) + a_2 c_2 P_2(\cos \theta)]^{z-1}} = \rho \text{ (constant)}$$

We rewrite this as

$$1 + a_1 P_1(\cos \theta) + a_2 P_2(\cos \theta) = \rho [C_0 + C_1 P_1(\cos \theta) + C_2 P_2(\cos \theta)]$$

where

$$C_m = (m + \frac{1}{2}) \int P_m(\cos \theta) \chi(\theta) \left[ \sum_{l=0}^{\infty} a_l c_l P_l(\cos \theta) \right]^{z-1} d(\cos \theta).$$

Therefore, for the weakly ordered system.

$$a_1 = C_1/C_0 = (z-1) c_1 a_1 + Fh \mu E / kT$$

$$a_2 = (z-1) c_2 a_2 + \frac{\Delta \alpha Fh^2 E^2}{3 kT} + \frac{(Fh \mu E)^2}{3 k^2 T^2} + \frac{2}{3} (z-1) a_1 c_1 \frac{Fh \mu E}{kT} + \frac{(z-1)(z-2)}{3} a_1^2 c_1^2$$

Hence, the electrically induced long range order

$$\begin{aligned} Q_{e1} &= \frac{\int \cdot \int P_2(\cos \theta_1) \phi(\theta_1, \varphi_1; \theta_2, \varphi_2) d(\cos \theta_1) d\varphi_1 d(\cos \theta_2) d\varphi_2}{\int \cdot \int \phi(\theta_1, \varphi_1; \theta_2, \varphi_2) d(\cos \theta_1) d\varphi_1 d(\cos \theta_2) d\varphi_2} \\ &= \frac{1}{3} (a_2 + c_2 a_2 + \frac{2}{3} c_1 a_1^2) \\ &= \left[ \frac{\Delta \alpha Fh^2 E^2}{3 kT} + \frac{(Fh \mu E)^2}{3 k^2 T^2} \frac{1 - (z-1) c_1^2}{\{1 - (z-1) c_1\}^2} \right] \frac{1 + c_2}{5 \{1 - (z-1) c_2\}} \\ &\quad + \frac{1}{15} \frac{c_1 (Fh \mu E)^2}{k^2 T^2 \{1 - (z-1) c_1\}^2} \end{aligned} \quad (8)$$

The short range order parameters  $c_1$  and  $c_2$  depend only on the two particle interaction constants  $A^*$  and  $B^*$ . If the applied field is magnetic, we put  $F = h = 1$ ,  $\mu = 0$  and replace  $\Delta \alpha$  by  $\Delta \eta$  in (8) to obtain<sup>5</sup>

$$Q_{mag} = \frac{\Delta \eta H^2}{15 kT} \frac{1 + c_2}{1 - (z-1) c_2} \quad (9)$$

Since there is no spontaneous  $\overline{P_1(\cos \theta)}$  type of long range order in the nematic phase, the second order transition point is determined by the temperature  $T^*$  at which  $c_2 = 1/(z-1)$ . Thus as has been shown previously<sup>5</sup>,  $Q_{mag}$  given by (9) varies as  $(T-T^*)^{-1}$  to a very good approximation. On the other hand, if the dipolar interactions are very large,  $Q_{e1}$  given by (8) may exhibit a slower variation. For example, it is found that for  $A^*/B^* = 0.2$  and  $0.5$ , the exponent  $\nu \sim 1.0$  as in the case

of magnetic birefringence. However for  $A^*/B^* = 3.2$ ,  $\gamma \sim 0.7$ . The Kerr constant measurements of Schadt and Helfrich<sup>13</sup> on some strongly positive nematogenic materials indicate that the  $\gamma$  may indeed be less than 1 at temperatures well above  $T_c$ . Further studies on the magnetic and electric birefringence of such materials would be of much interest.

In principle the arguments put forward here should, with suitable modifications, be applicable to negatively anisotropic materials also. Further, this model has a bearing on the flexoelectric effect<sup>14</sup>. Qualitatively, it can be seen that the magnitude of the effect will be diminished because of the tendency of the neighbouring dipoles to be antiparallel.

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## DISCUSSION

**de Vries:** Your model has  $z$  nearest neighbours around the reference molecule. You stated that of these  $z$  molecules no two are nearest neighbours of each other. How do you physically picture this?

**Chandrasekhar:** It merely implies that in writing down the pairwise interaction of the central molecule with its  $z$  nearest neighbours, the interaction between any two of the  $z$  neighbours is neglected. It is an approximation that is often used in such problems.

**Blic:** You are in fact using the Bethe approximation.

**Chandrasekhar:** Yes, that is correct. It is Bethe's method as modified by Krieger and James for treating orientational transitions in crystals.

**Blic:** Why not also include the  $P_1$  type of long range order in the theory?

**Chandrasekhar:** We have made the physically realistic assumption that long range antiferroelectric order is not present in the nematic liquid. Indeed even ferromagnetism in the liquid state is considered to be improbable\*.

**Nityananha:** Was the exponent of the magnetic birefringence 0.7 from the analytical form of the expressions or from fitting the numerical results? As a question of principle I felt it should be one near  $T_c$  for a Bethe type of calculation.

**Chandrasekhar:** The exponent  $\gamma \sim 1$  for magnetic birefringence and  $< 1$  for electric birefringence when dipolar interactions are large result from the analytical form of the expressions at temperatures *not too close* to the second order transition point  $T^*$ . The particular value of 0.7 for the electric case was, of course, got for a specific ratio of the  $P_1$  to  $P_2$  types of interaction. Very close to  $T^*$ , the exponent does in fact tend to approach unity.

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\* see e.g., Honda K and Kato Y *Phys. Lett.* 44 497 (1973)