CHAPTER 3

BETHE CLUSTER MODEL CALCULATIONS ON NEMATIC LIGUID CRYSTALS: II. POLAR MOLECULES

3.1 Introduction

The part played by permanent dipoles in determining nematic crystalling properties has been the subject of considerable discussion. Indeed the first theory of nematic liquid crystals by Max Born (1916) was developed by treating the medium as an oriented assembly of permanent electric dipolos, or in other words, as a ferroelectric medium. It: predicts a second order transition from nematic to isotropic phase. The experiments (Szivesay 1926) to detect free charges on the surface of the liquid crystal carried out with a view to testing Born's theory yielded negative results. Further it is now well established that permanent dipole moments are not necessary for the occurrence the Moreover/nematic-isotropic of the liquid crystalline phase. (NI) transition is always of first order mature even when the molecules are polar. Indeed as we discussed in the previous chapter, the first successful molecular theory of NI transition by Maier and Saupe was developed without taking into account the polar character of the molecules.

However a wast majority of newatogens are polar molecules. In particular there are a larger number of nematogenic compounds with a nitrile (-OM) group fixed to one end of the molecule. In such a case, the nitrile group with a dipole moment of ~ 4 debye points nearly parallel to the major molecular axis (see Chandrasekhar, 1977). The mesophase itself is non-ferroelectric, i.e., the negatic director is apolar and hence there is an equal probability for the dipoles to point in either direction. Because of this it is generally assumed that the permanent dipolar contribution to the orientational order is negligibly small. However, a simple calculation shows that this is certainly not a valid assumption, particularly for strongly polar materials. For such molecules the interaction energy between neighbouring dipoles is comparable with the dispersion energy. This suggests an entiparallel ordering of neighbouring molecules as was first pointed out by Madhusudana and Chandrasekhar (1973a).

For simplicity, the molecules are assumed to be cylindrically symmetric rods and the dipole moment is taken to be along the major molecular axis. Now if a dipole is fixed at 0 as shown in figure 1, I and II represent situations of minimum free energy for a neighbouring dipole in the side-on and end-on positions respectively. Evidently

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PIG.1: Preferred orientation of neighbouring dipoles in the end-on and broadaide-on positions. Maxexex, Because of the anisotropic shape of the molecules, situation I is much more important than II in the nematic structure and there results a net antiparallel correlation betwaen neighbouring dipoles. by virtue of the anisotropic shape of the molecule, situation I will be much more important than situation II in the nematic structure and hence there will be a greater tendency for the nearest neighbours to assume an antiparallel orientation. However, the absence of long range translational order in the nematic phase precludes the possibility of 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 orientation with this antiferroelectric cluster will clearly be apolar in nature. In other words, it will be fully equivalent whether the molecule is pointing 'up' or 'down'.

Direct X-ray evidence for antiparallel local ordering in the nematic and isotropic phases of 4'-npentyl and 4'-n-heptyl-4-cyanobiphenyls (5CB and 7CB) both of which are strongly polar compounds have been given by Leadbetter et al (1975). They found that the meridional reflections corresponding to a repeat distance along the preferred axis is about 1.4 times the molecular length. This has been interpreted as due to an overlapping headto-tail arrangement of the neighbouring molecules (see figure 2). Similar conclusion was drawn for octyl compound 8CB (Lydon and Coakley, 1975). Indeed using

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FIG.2: Schematic diagram of antiparallel local structure in 5CB (and 7CB) resulting in a repeat distance along the texture axis of 1.4 times the molecular length (proposed by Leadbetter et al, 1975).

neutron diffraction measurements on 808, Leadbetter et al (1979) positively confirmed and quantified the bilayer structure having overlapping molecular cores at the layer centre.

3.2 Theory

To express the ideas in a mathematically tractable form, Bethe's cluster model is employed (see chapter II). The pair potential between the central molecule i and one of its neighbours j is now written as

 $E(\cos \theta_{ij}) = A^{H}P_{i}(\cos \theta_{ij}) - B^{H}P_{2}(\cos \theta_{ij}),$ (1) where $P_{i}(\cos \theta_{ij})$ and $P_{2}(\cos \theta_{ij})$ are the first and second order Legendre polynomials. The positive sign of A^{H} favours an antiparallel arrangement of the permanent dipoles. Madhusudana and Chandrasekhar (1973a,b) made calculations by assuming the long range potential to be of the form

$$\Psi(\theta_j) = -B_2 P_2(\cos \theta_j). \qquad (2)$$

As we have discussed in the previous chapter retaining only $P_2(\cos \theta_j)$ term in the long range potential does not yield satisfactory results. Hence we refine their calculations by using the following potential:

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$$\Psi(\theta_j) = -B_2 P_2(\cos \theta_j) - B_4 P_4(\cos \theta_j) \qquad (3)$$

To determine the coefficients B_2/kT and B_4/kT the Krieger-James (KJ) approximation was used, i.e.,

$$g(\theta)/P^{n-1}(\theta) = constant.$$
 (4)

where

$$g(\theta_1) = \exp \left\{ [B_2 P_2(\cos \theta_1) + B_4 P_4(\cos \theta_1)] / kT \right\}$$

and

$$\mathbb{P}(\Theta_{j}) = \iint (\cos \Theta_{j}) g(\Theta_{j}) d(\cos \Theta_{j}) d\phi$$

where $f(\cos \theta_{ij}) = \exp\{[B^{MP}_{2}(\cos \theta_{ij}) - A^{MP}_{2}(\cos \theta_{ij})]/kT,\},\$ s is the number of nearest neighbours and $\varphi = \varphi_{i} - \varphi_{j}$. To locate T_{MI} , we have used the two-site cluster free energy:

$$[Y/NkT]_{nem} = (s-1) \ln Z_1 - g/2 \ln Z_{12},$$

$$[Y/NkT]_{iso} = -g/2 \ln Z_{12}^{0},$$
 (5)

where

and

$$Z_{1} = \int [g(\theta)]^{g/(g-1)} d(\cos \theta),$$

$$Z_{12} = \int \int \int f(\cos \theta_{1j})g(\theta_{1})g(\theta_{1})g(\theta_{2})d(\cos \theta_{1})d(\cos \theta_{2})d\phi$$

$$Z_{12}^{0} = \int \exp[\{B^{H}P_{2}(\cos \theta_{1j}) - A^{H}P_{1}(\cos \theta_{1j})\}/kT]d(\cos \theta_{1j})$$
.... (6)

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The heat of transition is given by

$$\Delta \mathbf{U} = \mathbf{U}_{nem} - \mathbf{U}_{1so} \tag{7}$$

whore

$$\begin{split} U_{\text{nem}} &= -\frac{M_{2}}{2} \left[B^{\text{M}} \left\langle P_{2}(\cos \theta_{1j}) \right\rangle - A^{\text{M}} \left\langle P_{1}(\cos \theta_{1j}) \right\rangle \right], \\ U_{160} &= -\frac{M_{2}}{2} \left[B^{\text{M}} \left\langle P_{2}(\cos \theta_{1j}) \right\rangle_{0} - A^{\text{M}} \left\langle P_{1}(\cos \theta_{1j}) \right\rangle_{0} \right], \\ \left\langle x(\theta_{1j}) \right\rangle &= -\frac{1}{2} \left\{ \int \int \int x(\theta_{1j}) f(\cos \theta_{1j}) g(\theta_{1}) g(\theta_{1}) g(\theta_{1}) d(\cos \theta_{1}) d($$

$$\langle \mathbf{x}(\theta_{ij}) \rangle_{0} = \frac{1}{20} \left\{ \mathbf{x}(\theta_{ij}) \exp[\{B^{H}P_{2}(\cos\theta_{ij}) - A^{H}P_{1}(\cos\theta_{ij})\}/kT] \right\}$$

d(cos θ_{ij})

The specific heat at constant volume is given by

$$\mathbf{G}_{\mathbf{v}} = (\mathbf{\sigma}_{\mathbf{v}})_{\mathbf{v}} \cdot \mathbf{G}_{\mathbf{v}} \cdot \mathbf{G}_$$

The detailed expression of C_y is given in appendix II. As in the previous chapter, the hypothetical second order transition point T^{H} is obtained by using the condition

$$\frac{\int P_2(\cos\theta) \exp[\{B^{HP}P_2(\cos\theta) - A^{HP}P_1(\cos\theta)\}/kT]d(\cos\theta)}{\int \exp[\{B^{HP}P_2(\cos\theta) - A^{HP}P_1(\cos\theta)\}/kT]d(\cos\theta)} = \frac{1}{z-1}$$

Schadt (1972) measured the dielectric constants (ε_{\parallel} and ε_{\perp}) of some cyano compounds and found that the mean dielectric constant $\overline{\varepsilon}(=(\varepsilon_{\parallel}+2\varepsilon_{\perp})/3)$ goes up at $T_{\rm HI}$. Madhusudana and Chandrasekhar (1977) pointed out that their model can account for this observation. We now derive the expressions for the dielectric constants of such compounds.

We follow closely the treatment of Maier and Meier (1961) who have applied the Onsager theory to take into account the effect of cavity field produced in the medium. The effective <u>induced</u> dipole moments per molecule along and perpendicular to the unique axis of the medium are respectively

$$\langle \mathbf{m}_{\mathrm{l}} \rangle = \left[\alpha + \frac{2}{3} \Delta \alpha \langle \mathbf{P}_{2} \rangle \right] \mathbf{P} \mathbf{h} \mathbf{E}_{\mathrm{l}} ,$$

 $\langle \mathbf{m}_{\mathrm{l}} \rangle = \left[\alpha - \frac{1}{3} \Delta \alpha \langle \mathbf{P}_{2} \rangle \right] \mathbf{P} \mathbf{h} \mathbf{E}_{\mathrm{l}} ,$ (10)

where $h = 3\overline{\epsilon}/(2\overline{\epsilon} + 1)$ is the cavity factor. $\overline{r} = 1/(1-\alpha f)$ is the reaction field factor, α the average polarizability, $f = 4\pi i \beta' (2\overline{\epsilon} - 2)/3M(2\overline{\epsilon} + 1)$, β the density, H the molecular weight and $\overline{\epsilon}$ the applied electric field. $\Delta \alpha$ is the anisotropy of the polarizability of a perfectly ordered system. In principle we should apply some correch

18 .78 dielectric constant, but as we are interested only in the order of magnitude of the dielectric anisotropy, we shall neglect these corrections.

To calculate the effective permanent dipole moments, we choose a space fixed coordinate system XYZ, Z being parallel to the unique axis of the medium, and $\xi \eta \zeta$ as the molecular fixed coordinate system, G coinciding with the long axis of the molecule. Let \forall be the Eulerian angle between the ξ ---axis and the line of intersection of the XY and $\xi \eta$ -planes, and \forall^{\dagger} the angle between this line and the X-axis. We assume as before that the molecules are cylindrically symmetric and that the permanent dipole moment μ is parallel to the long molecular axis. The potential energy of the dipoles due to the external field is small. Hence the Boltzman factor is expanded and the retained only up to second term.

The effective dipole moments along and perpendicular to the field direction are then given by

 $\langle \mu_{ii} \rangle = \langle \mu_{Z} \rangle$ $= \frac{ \left\{ \iint \left[1 + (\mu_{Z1} + \mu_{Zj}) \hbar E_g / kT \right] \mu_{Z1} f(\cos \theta_{ij}) g(\theta_{i}) g(\theta_{j}) d(\cos \theta_{i}) d(\cos \theta_{j}) d\phi \right] \right\}$ $= \frac{ \left\{ \iint \left[1 + (\mu_{Z1} + \mu_{Zj}) \hbar E_g / kT \right] f(\cos \theta_{ij}) g(\theta_{i}) g(\theta_{j}) d(\cos \theta_{i}) d(\cos \theta_{j}) d\phi \right\} \right\}$

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$$\langle \mu_{\perp} \rangle = \langle \mu_{\chi} \rangle$$

$$= \frac{ \left(\int \left[1 + (\mu_{\chi \downarrow} + \mu_{\chi j}) h E_{\chi} / k \right] \mu_{\chi \downarrow} f(\cos \theta_{\downarrow j}) g(\theta_{\downarrow}) g(\theta_{\downarrow}) d(\cos \theta_{\downarrow}) d(\cos$$

where

$$\mu_{Zi} = \mu^{2} \cos \theta_{i}$$

$$\mu_{Xi} = \mu^{2} \sin \theta_{i} \cos \phi_{i}$$
(12)

From eqs. (11) and (12), we get

$$\langle \mu_{Z} \rangle = \frac{h F^{2} \mu^{2}}{kT} [\langle \cos^{2} \theta_{i} \rangle + \langle \cos \theta_{i} \cos \theta_{j} \rangle] E_{Z}$$

$$\langle \mu_{X} \rangle = \frac{h F^{2} \mu^{2}}{kT} [\langle \sin^{2} \theta_{i} \cos^{2} \phi_{j} \rangle + \langle \sin \theta_{i} \sin \theta_{j} \cos \phi_{i} \cos \phi_{j} \rangle] E_{X}$$

$$\dots \qquad (13)$$

But

$$\frac{\varepsilon_{11}-1}{4\pi}B_{Z} = \frac{N\beta}{K}(\langle m_{11}\rangle + \langle \mu_{Z}\rangle)$$

and

$$\frac{e_{\perp} - 1}{4\pi} \Sigma_{X} = \frac{\pi \gamma}{3} (\langle \Xi_{\perp} \rangle + \langle \mu_{X} \rangle)$$
(14)

Substituting for $\langle \mu_Z \rangle$ and $\langle \mu_X \rangle$ from equations (13) in the equations (14), we get ε_{11} and ε_{\perp} as

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$$\varepsilon_{||} = 1 + \frac{4\pi N PhF}{M} \left[\alpha + \frac{2}{3} \Delta \alpha \langle P_2 \rangle + \frac{R^2}{3kT} \left(2 \langle P_2 \rangle + 1 \right) + \frac{R^2}{kT} \left(\cos \theta_1 \cos \theta_1 \rangle \right]$$

$$\varepsilon_{\perp} = 1 + \frac{4\pi i \,({}^{\circ}hF}{M} \left[\alpha - \frac{1}{3} \Delta \alpha \left< P_2 \right> + \frac{R_1^2}{3kT} \left< \sin^2 \theta_1 \cos^2 \phi_1 \right> + \frac{R_1^2}{kT} \left< \sin^2 \theta_1 \cos^2 \phi_1 \right> \right] + \frac{R_1^2}{kT} \left< \sin^2 \theta_1 \sin^2 \theta_1 \cos^2 \theta_1 \cos^2 \theta_1 \right> \right]$$

3.3 Results and Discussion

To make numerical calculations on the properties of the menatic and isotropic phases, we assumed that $A^{H}/B^{H} = 0.5$. For a given value of z, we made the calculations as follows. Assuming a certain value of B^{H}/kT (and hence A^{T}/kT) we iterate on B_{2}/kT and B_{4}/kT to satisfy the KJ approximation (eq. 4) as accurately as possible at 32 values of Θ ranging from 0 to $\pi/2$. The integrals are ovaluated by 32-points Gaussian quadrature method. The iteration was done by adapting a least square fitting procedure. The calculations have been carried out in double precision on an IBH-360 computer. The free emergies of both menatic and isotropic phases are calculated by using the equation (5). The difference between them

×1 81 is made equal to zero by iterating on the assumed value of B^{H}/kT . The heat of transition ΔU (eq. 7), T^{H} (eq. 9) and the specific heat at constant volume C_{V} are calculated. This procedure has been repeated for z = 3,4 and 8 and the results are tabulated in table 1.

The short range order parameters, viz., $\langle P_2(\cos \theta_{ij}) \rangle$ and $\langle P_1(\cos \theta_{ij}) \rangle$ of both menatic and isotropic phases are plotted as functions of T/T_{NI} in figure 3. The long range order parameters $\langle P_2(\cos \theta) \rangle$ and $\langle P_4(\cos \theta) \rangle$ are plotted in figures 4 and 5 respectively for z = 3, 4, 6and co (mean field limit). The specific heat at constant volume C_{ij} is also plotted for both the phases in fig. 6.

To calculate ε_{\parallel} and ε_{\perp} for a strongly polar (nitrile) compound of the type studied by Schadt, we assume that M = 300, $\overline{\varepsilon} = 10$, $\beta = 1$, $\alpha = 28 \times 10^{-24} \text{ cm}^3$, $\Delta \alpha = 15 \times 10^{-24} \text{ cm}^3$, $\mu = 50$. ε_{\parallel} , ε_{\perp} and $\overline{\varepsilon}$ are calculated in both nematic and isotropic phases for z = 4 and 8 and are shown in figure 7.

As seen from table I, the ratio $(T_{\rm HI} - T^{\rm H})/T_{\rm HI}$ decreases as z is decreased. This trend is similar to what we have noted in the previous chapter for non-polar molecules. TABLE I

0.156 0.078 0.191 52/5 0.038 0.059 0.028 -IN-0.068% Ó BRA 0.29× 0.39% jouies/ 91.53 71.75 84.97 joules/ 1137.02 522.0 810.4 Δu -0.06769 -0.02311 -0.04927 B_1/B2 B2/kT 1.2774 1.6016 1.0568 1.9750 1.3035 0.5924 B*/kr ø m

Results for various properties at the NI transition point

 $\delta \tilde{c}/\tilde{c}$ is the relative jump in the mean dielectric constant at $T_{\rm MI}$

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FIG.4: Long range order parameter (P2) as function of T/TNI for different values of 2.



FIG.5: Long range order parameter $\langle P_4 \rangle$ as function of T/T_{NI} for different values of Z.



FIG.6: Specific heat at constant volume C, as function of T/T, for different values of Z.

The long range order parameter $\langle P_2 \rangle$ of p-n-pentylp*-cyanobiphenyl (50B), which is a strongly polar material (Miyano, 1978) agrees well with the theoretical values for s = 3 and 4. (see:Mignocides Experimentally $\langle P_4 \rangle$ value of 50B changes sign close to $T_{\rm HI}$ and is negative at $T_{\rm HI}$. However our theory cannot account for such negative values of $\langle P_A \rangle$.

before the specific heat C_{ψ} (figure 6) at constant volume at all temperatures and $\triangle C_{\psi}$ - the jump in O_{ψ} at $T_{\rm NI}$ increase systematically as a decreases from co (mean field limit) to 4, but drop to lower values for z = 3. A similar trend was also found in the previous chapter for the system of non-polar molecules.

 $\epsilon_{\rm H}$, ϵ_{\perp} and $\overline{\epsilon}_{\rm iso}$ for n (4*-ethoxybenzylidene)-4aminobenzonitrile (Schadt 1972) are given in figure 8. Comparing these with theoretical results given in figure 7, we find that the variation of calculated dielectric constant near $T_{\rm HI}$ is not as rapid as the experimental values. 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 $T_{\rm HI}$. But apart from that it is clear from a comparison with figure 8 that the dielectric anisotropy is of the right order of magnitude.



TG.7: Theoretical values of dielectric constants as functions of I/T_{NI} .



FIG.8: Experimental values of dielectric constants for 4-&nobenoonitrile (Reproduced from Schadt, 1972). $\varepsilon_{\rm W}$ and $\varepsilon_{\rm L}$ refer to the values along and perpendicular to the optic axis of the nematic medium and $\varepsilon_{\rm iso}$ is the isotropic value.

An interesting consequence of the theory is that the mean dielectric constant $\overline{\epsilon}$ should increase by a few per cent on going from the mematic to the isotropic phase because of the diminution in $\langle P_1(\cos \theta_{ij}) \rangle$ (as shown in figure 3). This is found to be the case experimentally in a number of strongly positive materials (acts figure 8) (see also Batna et al. 1976, 1979). Recently very accurate measurements on the dielectric constants of 7GB were made by Bradshaw and Baynes (1981). The results are reproduced in figure 9. It can be seen that the value of $\overline{\epsilon}$ takes a jump at $T_{\rm HI}$. Further it is interesting to note that $\overline{\epsilon}$ takes a maximum in the isotropic phase.

The short range antiparallel correlations between near neighbouring molecules with a cyano end group give rise to another interesting phenomenon. Cladis (1975) discovered that bihary mixtures of certain nesogenic cyano compounds exhibit the phenomenon of re-entrant nematic phase. On cooling, the mematic phase goes usually over to the smectic phase which has one dimensional translational order. But Cladis observed the following sequence of phase transitions:

Isotropic ---> Nematio ---> Smectic ---> Nematic The second nematic phase which is obtained on cooling the

FIG.9: Variation of mean dielectric constant $\overline{\epsilon}$ of the nematic and the isotropic phases as function of $(T - T_{NI})$.

smectic phase is called the re-entrant nematic phase, in analogy with similar re-entrant phases observed in superconductors, He-3, etc. Later Cladis et al (1977, 1978) also observed the re-entrant nematic phase in some pure cyano compounds at elevated pressures. Recently, the re-entrant nematic phase has been observed in some pure compounds at atmospheric pressure (Madhusudana et al, 1979; Hardouin et al, 1979; Tinh and Gasparoux, 1979). For some of the compounds, a re-entrant smectic phase which exists at temperatures below those corresponding to the re-entrant nematic phase has also been found (see Hardouin et al, 1979).

As we mentioned earlier, cyano compounds have a bilayer structure. As the temperature or pressure is varied the molecular packing is altered slightly and the resultant subtle changes in the bilayer structure appear to be responcible for the occurrence of the re-entrant phases. Thus the antiparallel arrangement of polar molecules has an important consequence in the new phenomenon of the re-entrant phases.

Ipma and Vertogen (1976) have also studied the effect of introducing $P_1(\cos \theta_{ij})$ type of term in the near neighbour interaction. They assumed the potential to be of the form

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$$E(\cos \theta_{ij}) = -J_1 P_1(\cos \theta_{ij}) - J_2 P_2(\cos \theta_{ij})$$
$$V(\theta_j) = -h_1 P_1(\cos \theta_j) - h_2 P_2(\cos \theta_j) .$$

It is interesting to note that they have taken a $P_i(\cos \Theta_j)$ type of term in the long range potential $V(\Theta_j)$. Depending upon the sign of J_1 , the system can exhibit either ferroelectric (positive J1) or antiferroelectric (negative J_1) phases. They have found that for $(J_1/J_2) \leq 0.3$, the menatic phase $h_1 = 0'$ goes over to a system with nonsero value of $\langle P_1(\cos \theta_1) \rangle$, i.e., a (anti) ferroelectric phase. For $(J_1/J_2) > 0.3$, they find that the (anti)ferroelectric phase goes directly to the isotropic phase. However it can be noted that no such (anti) ferroelectric phase has been found up to now. Further in the case of the antiparallel short range order that we have discussed, it is difficult to imagine the (anti)ferroelectric long range order in the absence of long range translational order. Indeed even ferromagnetism in the liquid state is considered to be improbable (see Honda and Kato, 1973).

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