

**THEORETICAL STUDIES ON ORDER
AND PHASE TRANSITIONS IN
LIQUID CRYSTALS**

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for the Degree of

Doctor of Philosophy

By

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DECLARATION

I hereby declare that the thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

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CERTIFICATE

I certify that this thesis has been composed by Smt. K.L.Savithramma based on investigations carried out by her at the Liquid Crystals Laboratory, Raman Research Institute, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateahip, Fellowship or other similar title.



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CHAPTER I

INTRODUCTION

Liquid crystals represent states of matter that are intermediate between the crystalline solid and the amorphous liquid. Molecular shape anisotropy is an essential requirement for the existence of such phases. Mesomorphic phases were discovered at the end of the last century by Reinitzer (1888). Several thousands of such compounds have been found since then. The common feature of all such molecules is that they are narrow and relatively long. Recently Chandrasekhar et al (1977) discovered that pure compounds made up of relatively simple molecules of disc-like shape also form mesophases (discotic mesophases).

1.1 Liquid crystals of rod-like molecules

Liquid crystals of rod-like molecules can be formed by the influence of solvents (lyotropic liquid crystals) or by purely thermal processes (thermotropic liquid crystals). In this thesis, we deal with the latter type only. Following the nomenclature proposed originally by Friedel (1922), thermotropic liquid crystals composed of rod-like molecules

are classified broadly into three types: nematic, cholesteric and smectic.

Nematic liquid crystals are the simplest type of liquid crystals having a degree of long range orientational order (denoted by S) of the molecules, but no long range translational order. The molecules tend to be parallel to some common axis referred to as the director (see fig.1).

If the molecules forming the nematic phase are optically active, then they exhibit a twisted nematic or cholesteric phase in which the director follows a helical arrangement (fig. 2). The degree of twist is characterized by the pitch of the helix. At the gross level, the thermodynamics of cholesteric and nematic phases are almost similar as the energy associated with the twist is $\sim 10^5$ times smaller than the total energy associated with the parallel alignment of molecules (Saupe, 1968). However, in the molecular statistical theories of cholesteric phases, the nature of the molecules must be specifically taken into account. Keating (1969), Goossens (1971), Priest and Lubensky (1974), van der Meer et al (1976a,b), Lin Lei et al (1977) among others have developed detailed molecular statistical theories of the cholesteric phase.

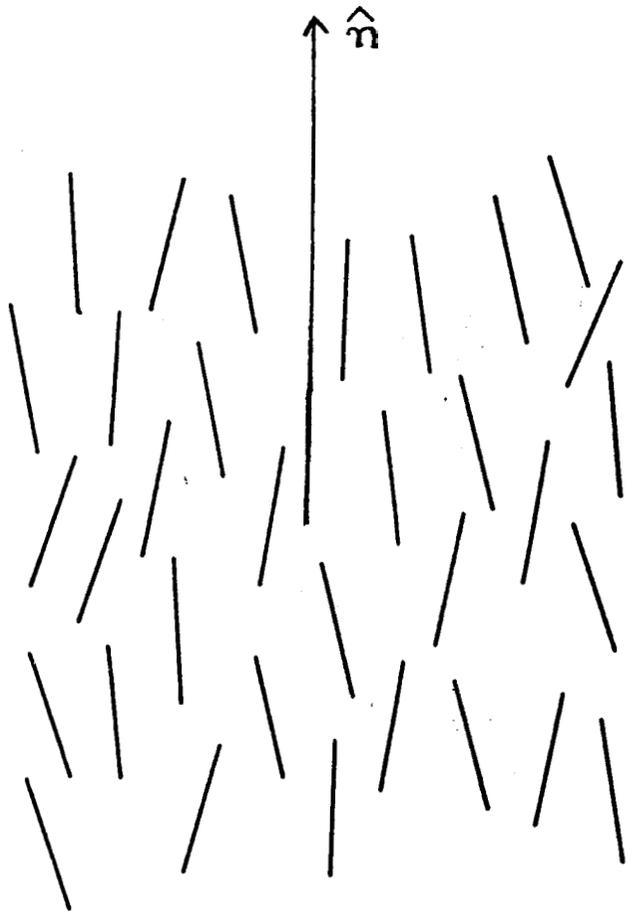
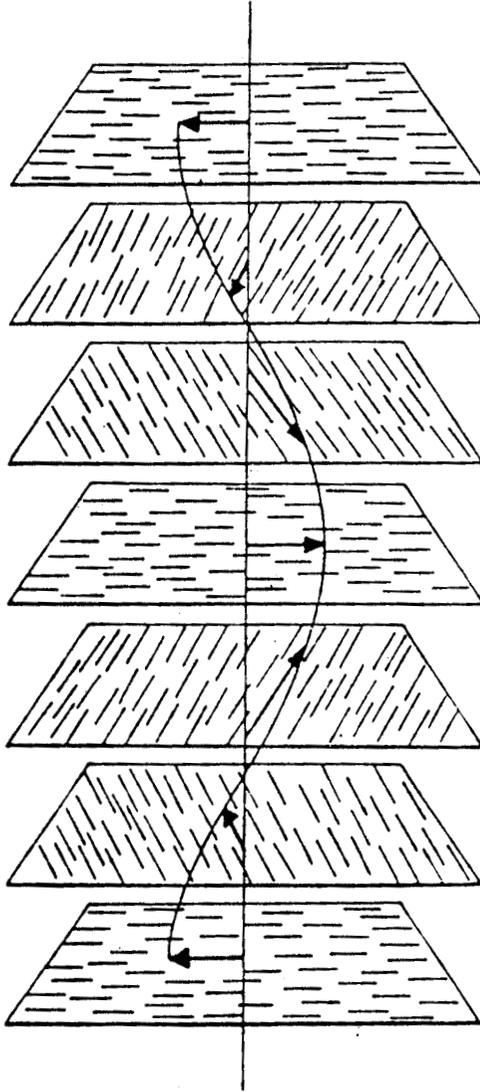


FIGURE 1: Schematic representation of molecular order in the nematic phase.

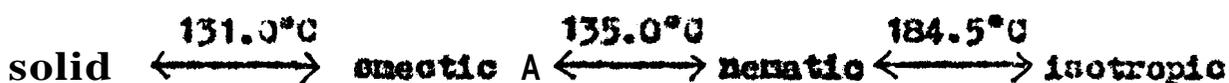


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FIGURE 2: The cholesteric liquid cry6 Schematic representation of the helical structure.

The smectic phase has both orientational and some translational order. From a structural point of view, all smectics have layered arrangement, with a well defined interlayer spacing. The smectics are sub-classified as smectic A, smectic B, etc. depending upon the molecular arrangement in the layer. For smectic A, the average direction of orientation of molecules is normal to the plane of the layer. The centres of gravity of molecules show no long range translational order within the layer and each layer is a two dimensional liquid (see fig. 3). The optic axis is thus normal to the plane of the layers and the system is optically uniaxial. We shall not be discussing other types of smectics here.

Many compounds exhibit both the smectic A and nematic phases and in such cases the nematic phase usually occurs at temperatures above those corresponding to the smectic phase. For example 4-(4-n-butyloxybenzylidene-phenyl)azoaniline (Arora and Ferguson, 1971) shows the following transitions:



However Gladis (1975) discovered that there may be a different sequence of transitions in some cases. She found that binary mixtures of certain mesogenic cyano

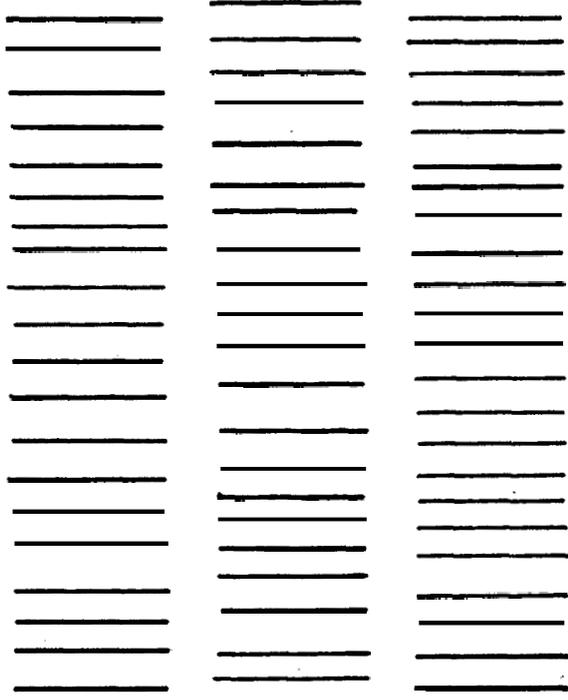


FIGURE 3: Schematic representation of smectic A structure.

FIGURE 4

- (a) Schematic representation of a 'liquid-like' stack of disc-shaped molecules (from Levelut, 1980).
- (b) Hexagonal modification D_h of an upright columnar structure. The filled circle depicts the molecular core which is normal to the columnar axis.
- (c) Rectangular modification D_r of an upright columnar structure. The circular cores are normal to the columnar axes and form a face-centered rectangular lattice, but the asymmetric disposition of the chains results in a herringbone pattern of ellipses, whose ellipticity is highly exaggerated here for the sake of clarity (Tinh et al, 1981; Destrade et al, 1981 and Levelut, 1980).
- (d) Tilted columnar structure D_t (Tinh et al, 1981 and Destrade et al, 1981).
- (e) Face-centered rectangular lattice of D_t . The cores are tilted with respect to the columnar axes (Tinh et al, 1981 and Destrade et al, 1981).
- (f) Nematic phase N_D of disc-shaped molecules (Tinh et al, 1981 and Destrade et al, 1981).

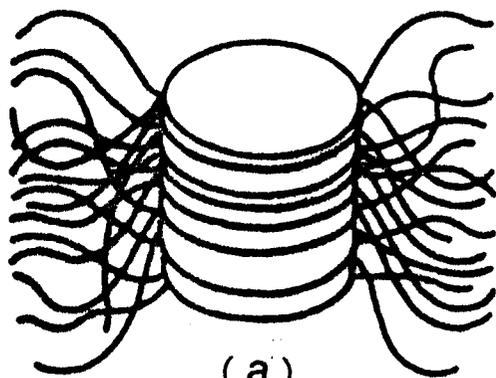
compounds exhibit the following sequence of phase transition on cooling:

isotropic \longrightarrow nematic \longrightarrow smectic A \longrightarrow nematic

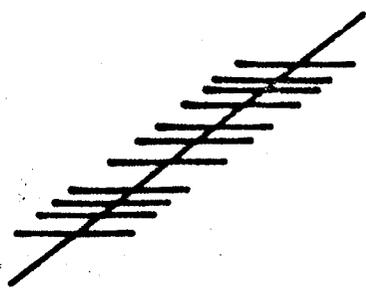
The second nematic phase, which occurs at temperatures lower than those of the smectic phase is called the 're-entrant nematic' phase in analogy with similar 're-entrant' phases observed in superconductors, He-3, etc. Madhusudana et al (1979), Hardouin et al (1979a) and Tinh and Gasparoux (1979) have subsequently observed re-entrant phenomena in some pure components. For some of the compounds a re-entrant smectic phase which exists at temperatures lower than those of the re-entrant nematic phase has also been found (see Hardouin et al, 1979b).

1.2 Liquid crystals of disc-like molecules

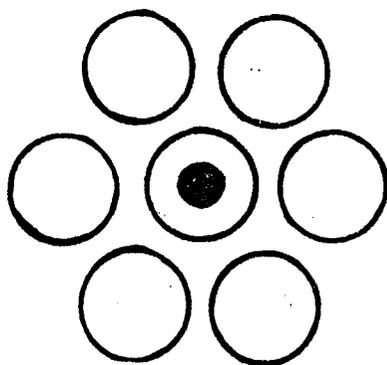
Disc-shaped molecules have been recently shown (Chandrasekhar et al, 1977) to exhibit a new class of liquid crystalline phases (the discotic phases). A number of disc-shaped molecules are now known to exhibit thermotropic mesomorphism (see Chandrasekhar, 1982). The mesophases so far discovered fall into two distinct categories, the columnar and the nematic. In columnar (D) type, the discs are stacked one on top of the other, the different



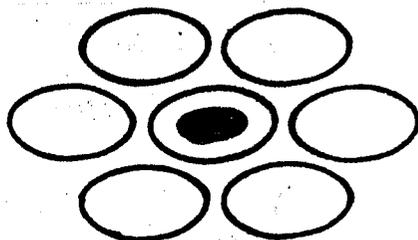
(a)



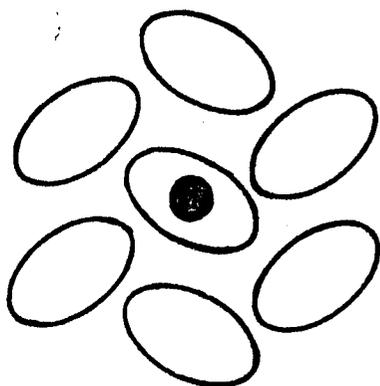
(d)



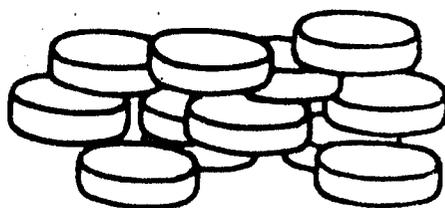
(b)



(e)



(c)



(f)

columnar stacks forming a two-dimensionally periodic array. Several variants of this structure have been identified: hexagonal, rectangular, tilted, etc. (see fig. 4a-4e). The nematic (N_D) is an orientationally ordered arrangement of the discs with no long range translational order (see fig. 4f). The twisted nematic (cholesteric) phase was observed in a family of disc-like molecules (see Destrade *et al.*, 1980a). It has also been found that some disc-like molecules show a re-entrant nematic phase (Destrade *et al.*, 1980b).

1.3 Properties of nematic liquid crystals

In several chapters of this thesis, we shall be discussing the statistical thermodynamics of the nematic phase of rod-like molecules. Hence, we shall first summarize briefly the properties of nematic liquid crystals of such molecules.

The nematic phase exhibited by molecules of arbitrary shape can be characterised by the orientational order parameters

$$S_{ij}^{\alpha\beta} = \frac{1}{2} \langle 3i_{\alpha}j_{\beta} - \delta_{\alpha\beta}\delta_{ij} \rangle \quad \begin{cases} \alpha, \beta = X, Y, Z \\ i, j = \xi, \eta, \zeta \end{cases} \quad (1)$$

where , Y, Z) refer to the (orthogonal) laboratory frame

and (ξ, η, ζ) to the frame linked to the molecule.

δ_{ij} and $\delta_{\alpha\beta}$ are Kronecker deltas. $S_{ij}^{\alpha\beta}$ is a symmetric tensor in ij and $\alpha\beta$, and has zero trace. By taking the director \hat{n} along the Z-axis, we get

$$S_{ij} = \frac{1}{2} \langle 3i_j j_i - \delta_{ij} \rangle \quad (2)$$

where

$$\begin{aligned} S_{\xi\xi} &= \langle \frac{1}{2}(3\sin^2 \theta \cos^2 \gamma - 1) \rangle \\ S_{\xi\eta} &= \langle -\frac{3}{2}\sin^2 \theta \cos \gamma \sin \gamma \rangle \\ S_{\xi\zeta} &= \langle -\frac{3}{2}\sin \theta \cos \theta \cos \gamma \rangle \\ S_{\eta\eta} &= \langle \frac{1}{2}(3\sin^2 \theta \sin^2 \gamma - 1) \rangle \\ S_{\eta\zeta} &= \langle \frac{3}{2}\sin \theta \cos \theta \sin \gamma \rangle \\ S_{\zeta\zeta} &= \langle \frac{1}{2}(3\cos^2 \theta - 1) \rangle \end{aligned} \quad (3)$$

Here θ is the angle made by the molecular axis (ζ -axis) with the Z-axis and γ is the Eulerian angle made by the line of interaction of XY and $\xi\eta$ planes with the η -axis (see fig. 5). Since the medium is apolar, all odd terms in θ and γ should vanish, i.e.,

$$S_{\xi\eta} = S_{\eta\xi} = S_{\xi\zeta} = S_{\zeta\xi} = S_{\eta\zeta} = S_{\zeta\eta} = 0 .$$

S_{ij} is now a diagonal matrix with zero trace. Hence for a uniaxial nematic medium made of biaxial particles, there

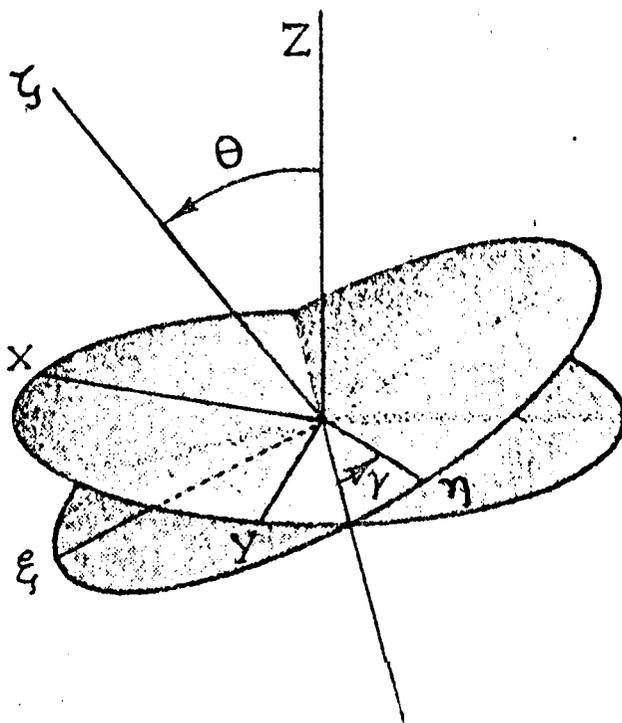


FIG. 5: The Eulerian angles defining the orientations of (ξ, η, ζ) with reference to (X, Y, Z) .

are two independent order parameters (see Freiser, 1970; Alben et al, 1972; Alben, 1973; Straley, 1974; Luckhurst et al, 1974; and Gelbart and Barbov, 1979). These are defined as

$$\begin{aligned}
 S &= S_{\zeta\zeta} = \iint \frac{1}{2}(3\cos^2 \theta - 1)f(\theta, \gamma)d(\cos \theta)d\gamma \\
 D &= S_{\xi\xi} - S_{\eta\eta} = \iint \frac{3}{2}\sin^2 \theta \cos 2\gamma f(\theta, \gamma)d(\cos \theta)d\gamma \quad (4)
 \end{aligned}$$

where $f(\theta, \gamma)$ is the single particle distribution function. S gives the degree of orientational order of the long axes of the molecules with respect to the nematic director. The order parameter D describes the difference between the tendencies of the two transverse molecular axes to align along the nematic director, i.e., D arises due to the deviation from axial symmetry around the long molecular axis .

If the molecules are cylindrically symmetric, the distribution function will be independent of γ . This simplifies $S_{\xi\xi}$ and $S_{\eta\eta}$ to

$$\begin{aligned}
 S_{\xi\xi} &= S_{\eta\eta} = \frac{1}{2} \left\langle \frac{3}{2} \sin^2 \theta - \frac{1}{2} \right\rangle \\
 &= -\frac{S}{2} \\
 1 \quad 0 \quad . \quad &= 0 .
 \end{aligned}$$

The matrix S_{ij} will then be

$$S_{ij} = \begin{bmatrix} -S/2 & 0 & 0 \\ 0 & -S/2 & 0 \\ 0 & 0 & S \end{bmatrix}$$

The only independent order parameter S is given by

$$S = \int \frac{1}{2}(3\cos^2 \theta - 1) f(\theta) d(\cos \theta) \quad (5)$$

The distribution function $f(\theta)$ is symmetric about $\theta = \pi/2$, i.e., $f(\theta) = f(\pi - \theta)$. The general appearance of $f(\theta)$ is given in fig. 6. The order parameter S takes a maximum value equal to 1 when all the molecules are packed parallel to the director. And it takes a value equal to zero, when the molecules can take all possible orientations with equal probability.

The order parameter S is a function of temperature. It decreases as the temperature increases (see fig. 7) and drops abruptly to zero at the nematic-isotropic transition temperature (T_{NI}). The NI transition is of first order, associated with a heat of transition (ΔH) which is typically only a few per cent of that of the crystal-nematic transition. Since the transition is weak, it is associated with strong pre- and post-transition effects. For instance

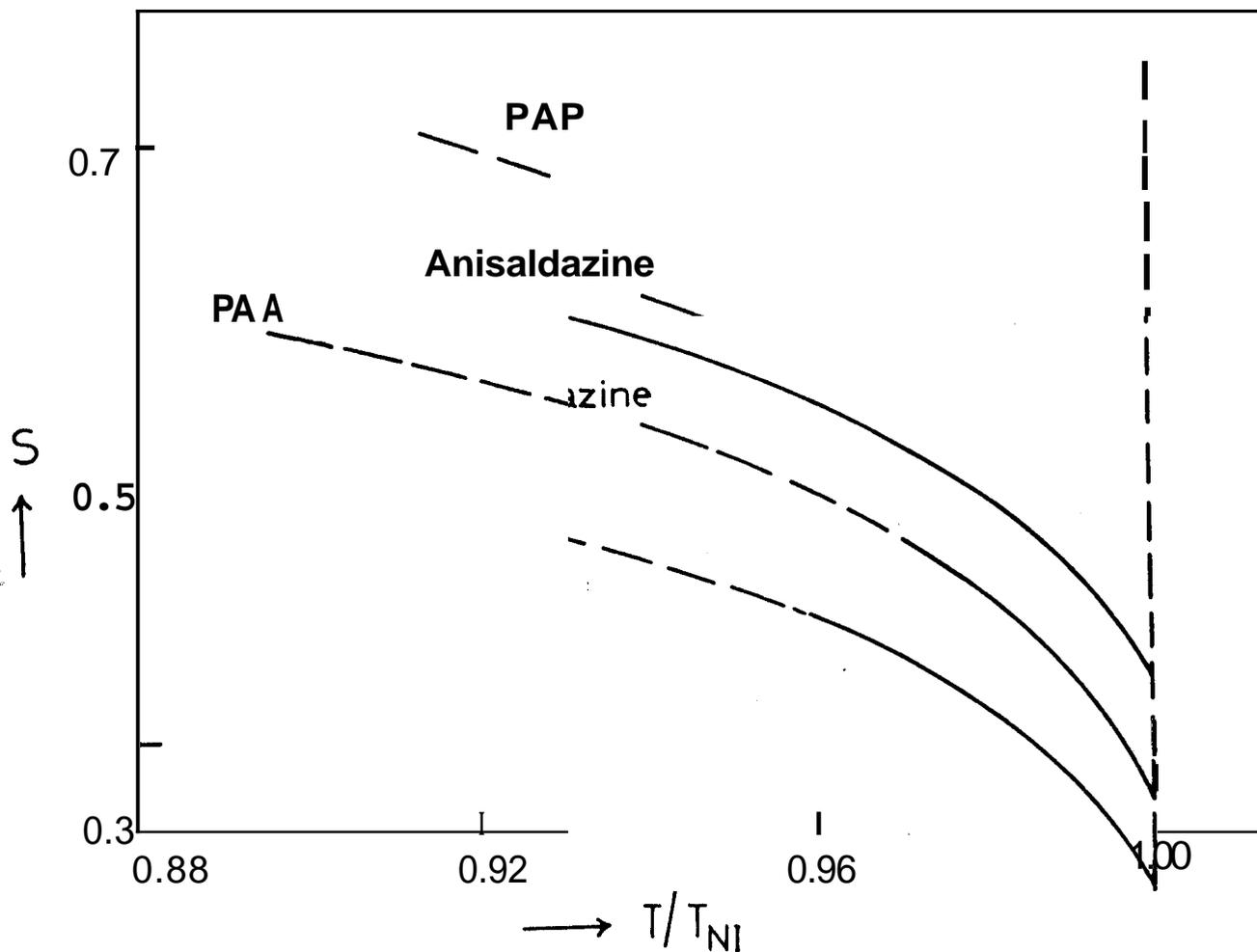


FIGURE 7: Experimental curves of S for *p*-azoxyanisole (PAA), anisaldazine and *p*-azoxyphenetole (PAP) (Reproduced from Chandrasekhar et al, 1970 and Madhusudana et al, 1971).

magnetic (Δn_M) and electric birefringence (Δn_E) of the isotropic phase exhibit strong anomalies as the temperature is lowered to T_{NI} (Tsvetkov and Ryustsev, 1968). Similar anomalies are seen in the flow birefringence (Tolstoi and Fedotov, 1947) and nuclear spin lattice relaxation (Cabane and Clark, 1970).

Associated with the variation of the order parameter, the specific heats C_p and C_v , the isothermal compressibility β and the coefficient of thermal expansion α increase sharply as the temperature approaches T_{NI} in the nematic phase (see figs. 8, 9, 10).

High pressure studies on nematic liquid crystals show that the order parameter S at T_{NI} is very nearly independent of the pressure. Further the curves of constant order parameter in $\ln V - \ln T$ diagram are almost parallel (see fig. 11). The slope of these lines is given by

$$\gamma = - \left[\frac{\partial \ln T}{\partial \ln V} \right]_S \quad (6)$$

γ is a measure of the relative importance of volume V compared to that of temperature T in determining the variation of order parameter S of the medium. For nematic

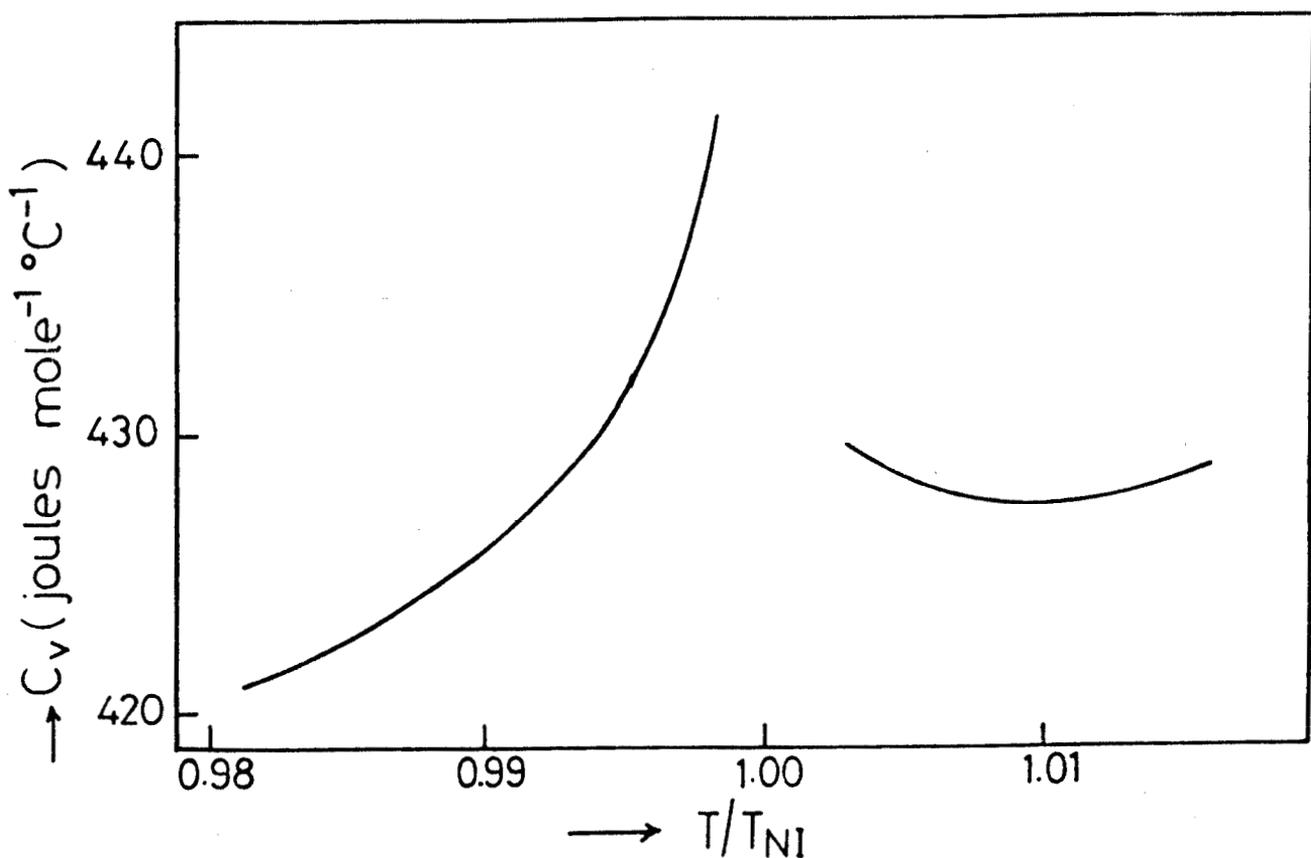


FIGURE 8: Experimental curve of specific heat at constant volume C_v in the nematic and isotropic phases for PAA derived from the observed values of C_p (Arnold, 1964) and β (Kapustin and Bykova, 1966).

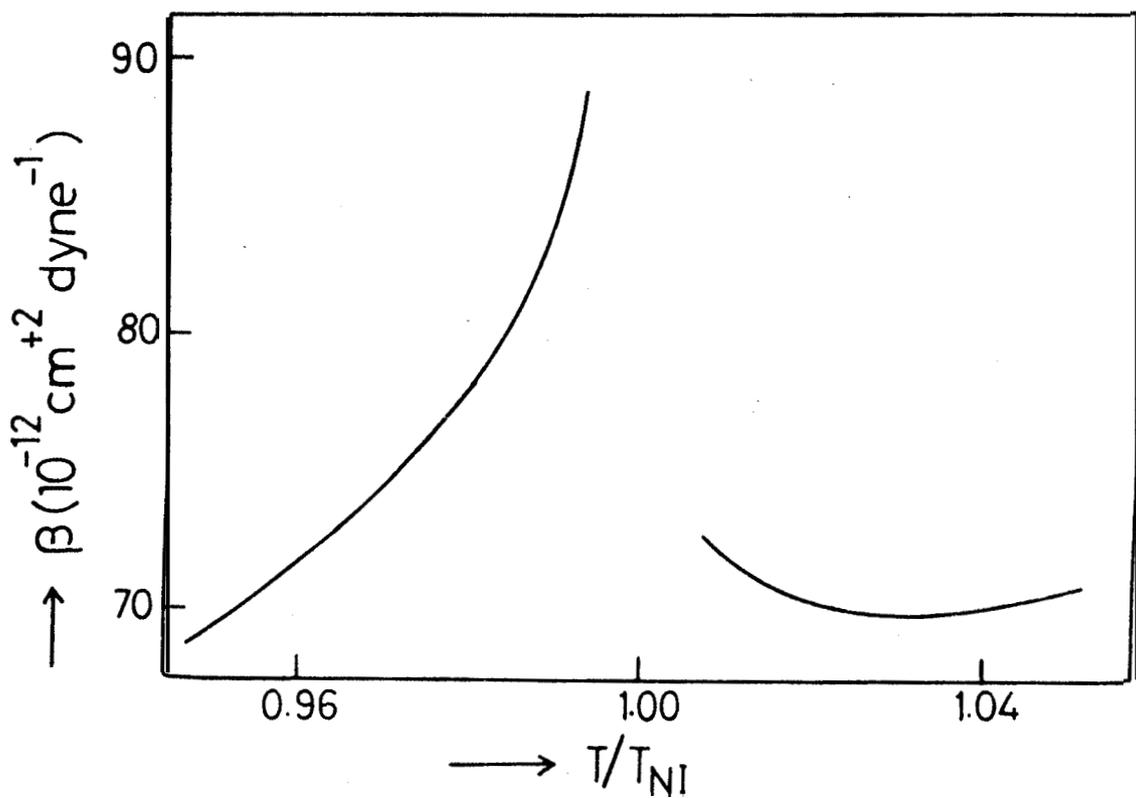


FIGURE 9: Experimental curve of isothermal compressibility β in the nematic and isotropic phases for PAA (from Kapustin and Bykova, 1956).

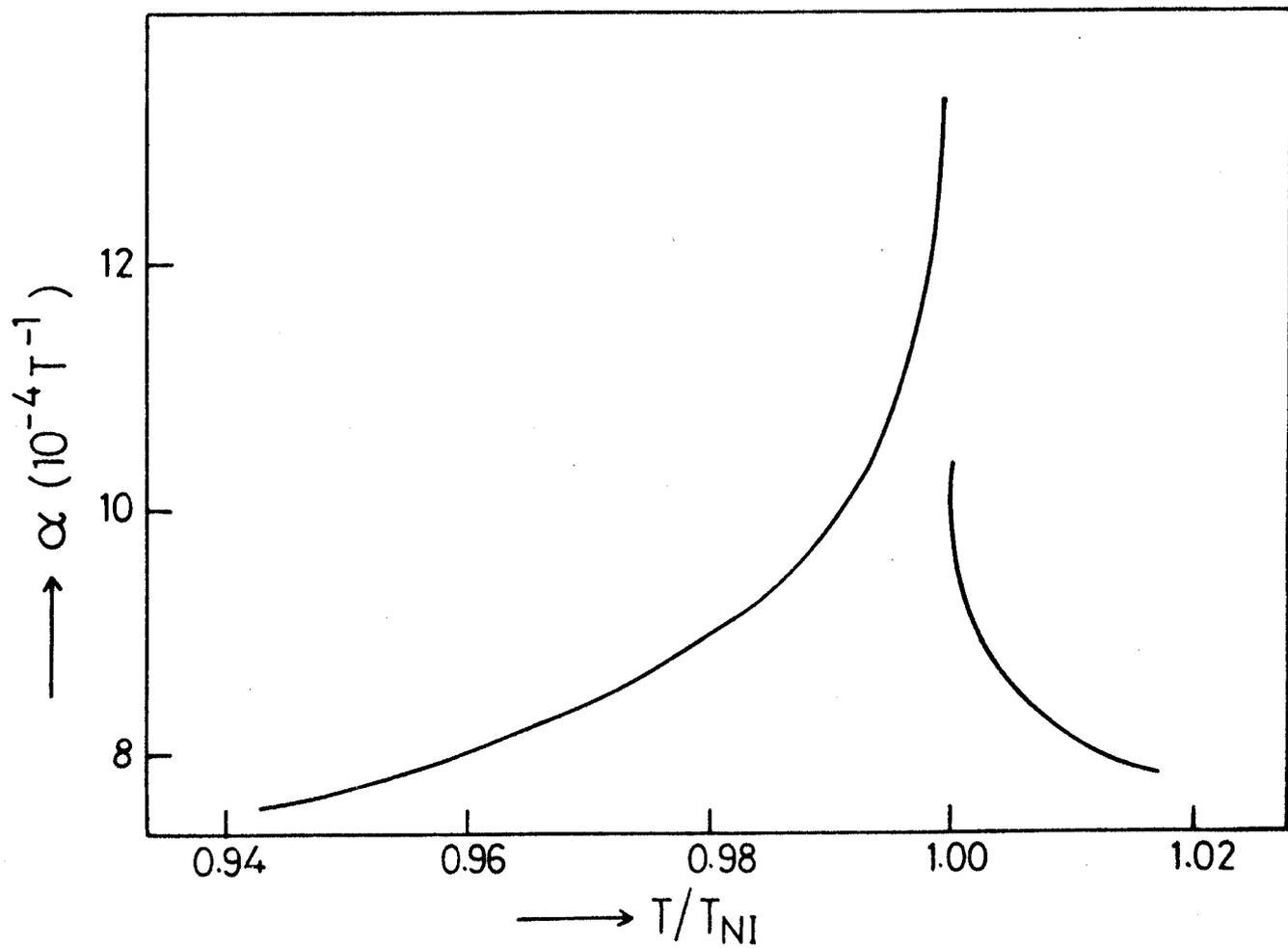


FIGURE 10: Experimental curve for the coefficient of thermal expansion α in the nematic and isotropic phases for PAA (from Maier and Saupe, 1960).

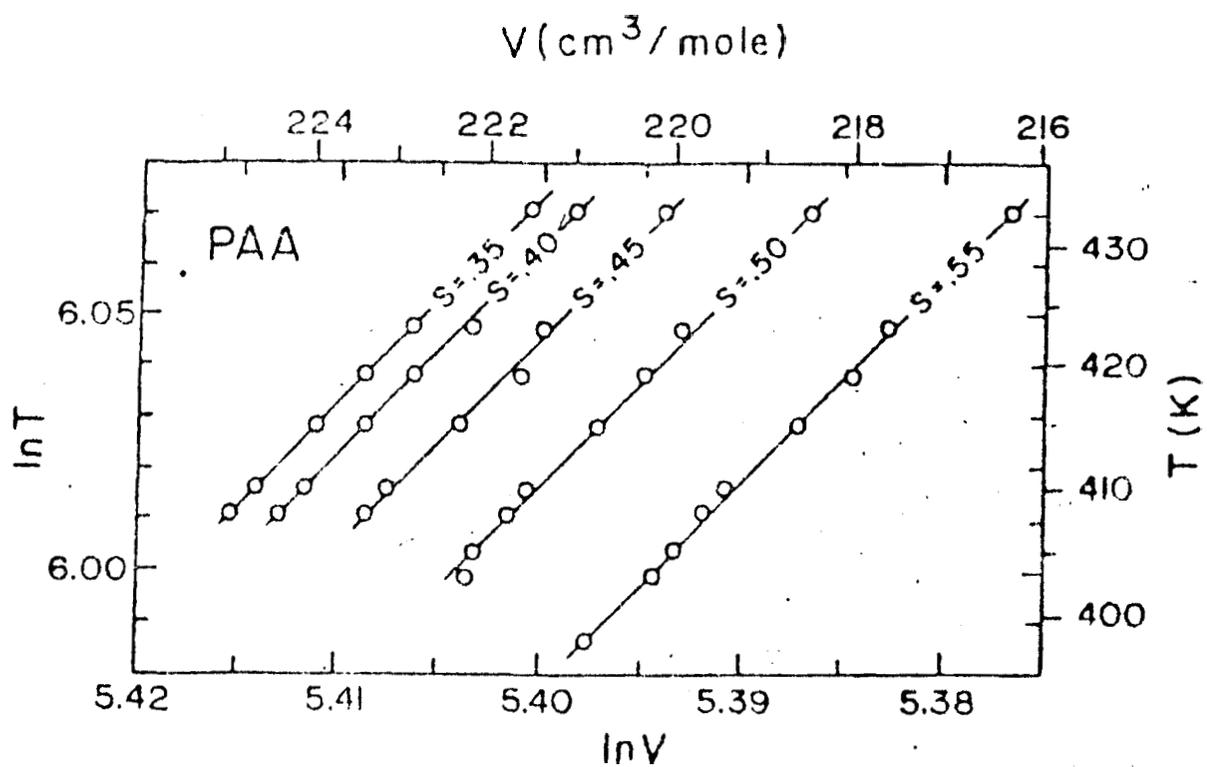


FIG. 11: Experimental curves of $\ln V$ vs. $\ln T$ for values of constant nematic order parameter S for FAA (from McColl and Shih, 1972).

liquid crystals of rod-like molecules, γ ranges from 4 to 6. (see McCall and Shih, 1973; Horn, 1978; Kuss, 1978; Keyes and Daniels, 1979).

The first theory of the nematic phase was proposed by Born in 1916 and since then several attempts have been made to develop a suitable statistical model. As is well known, there is no exact statistical theory of simple liquids made up of spherical molecules. For the nematic, which is an oriented liquid composed of highly anisotropic molecules, the theory becomes even more complicated.

1.4 Scope of the thesis

In this thesis, we present our contributions to the study of statistical thermodynamic properties of nematic phase exhibited by rod-like and disc-like molecules. Further, in the case of discotic liquid crystals we have also presented some calculations on the more ordered columnar and smectic A phases.

In chapter II, we have discussed the statistical theory of nematic phase based on attractive interactions alone. In particular the short range order effects in the nematic and isotropic phases are studied. The mean field theory developed by Maier and Saupe (1958-1960) and its

subsequent improvements (Chandrasekhar and Madhusudana, 1971; Humphries et al, 1972) are successful in predicting the qualitative behaviour of the thermodynamic properties of nematic liquid crystals. However, they predict too strong a NI transition. If T^M is ^{the} hypothetical second order transition point, the mean field theory predicts that $(T_{NI} - T^M) \simeq 40^\circ\text{K}$ whereas the experimental value is $\sim 1^\circ\text{K}$. Further the theory fails to explain the short range order effects in the nematic and isotropic phases. In an attempt to overcome some of these drawbacks, Madhusudana and Chandrasekhar (1973a) and Ypma and Vertogen (1976) developed a theory which includes short range correlations between neighbouring molecules, employing the Bethe cluster model. In Bethe's model, a molecule is assumed to have z nearest neighbours and its interaction with one of its nearest neighbours is taken as

$$E(\theta_{ij}) = -B^M P_2(\cos \theta_{ij})$$

where θ_{ij} is the angle between the long axes of the molecules i and j . The outer molecule of the Bethe cluster is subjected to a mean field potential $V(\theta_j)$ due to the rest of the medium. Several approximations, namely, (i) Chang's consistency condition, (ii) Krieger-James (KJ) approximation, (iii) Bethe-Peierls-Weiss (BPW) approximation, and (iv) constant coupling (CC) approximation have been proposed

for solving Bethe's cluster model. We have examined these approximations at some length and emphasized that satisfying the KJ relation as accurately as possible is essential to achieve thermodynamic consistency. For this purpose, the long range mean field potential $V(\theta_j)$ of an outer molecule j is taken as

$$V(\theta_j) = \sum_{n=0}^{\infty} B_{2n} P_{2n}(\cos \theta_j) .$$

For a given value of z , various properties of the nematic and isotropic phases and T^{NI} are calculated by retaining terms up to $P_2(\cos \theta_j)$, $P_4(\cos \theta_j)$ and $P_{12}(\cos \theta_j)$ in the expansion for $V(\theta_j)$. The calculations are repeated for $z = 3, 4, 8$ and 12 .

We have found that the error in satisfying KJ relation is extremely small when terms up to $P_{12}(\cos \theta_j)$ are included. In this case, the ratio $(T_{\text{NI}} - T^{\text{NI}})/T_{\text{NI}}$ decreases from 0.117 to 0.031 as z decreases from ∞ (mean field) to 3. The value of a given long range order parameter $\langle P_{2n} \rangle$ is lower for lower values of z particularly near T_{NI} . Further the rate of decrease of $\langle P_{2n} \rangle$ with temperature increases for lower values of z . The calculated values of $\langle P_2 \rangle = \langle P_4 \rangle$ and $\langle P_4 \rangle / \langle P_2 \rangle$ for $z = 3$ are in good agreement with the experimental data. We

observe that C_V (specific heat at constant volume) at T_{HI} as well as ΔC_V increase as we go from the mean field limit ($z = \infty$) to $z = 4$ in agreement with expectations. At temperatures sufficiently far off from T_{HI} , C_V is lower if z is lower.

The part played by permanent dipoles in determining the nematic liquid crystalline properties has been studied in chapter III. There are a large number of nematogenic compounds with a nitrile ($-C\equiv N$) group fixed to one end of the molecule. Since the nematic director is apolar, there is an equal probability for the dipoles to point in either direction. Further for strongly polar molecules, the interaction energy between neighbouring dipoles is comparable with the dispersion energy. Madhusudana and Chandrasekhar (1973b) showed that near neighbours of such strongly polar molecules will favour an antiparallel arrangement. However the absence of long range translational order in nematic liquid crystals precludes the possibility of antiferroelectric long range order.

We have refined Bath's cluster model developed for a system of polar molecules (Madhusudana and Chandrasekhar, 1973c) in the light of results obtained for non-polar molecules. $B(\theta_{ij})$ and $V(\theta_j)$ are taken as

$$E(\theta_{ij}) = A^{\mathbb{M}} P_1(\cos \theta_{ij}) - B^{\mathbb{M}} P_2(\cos \theta_{ij})$$

$$V(\theta_j) = -B_2 P_2(\cos \theta_j) - B_4 P_4(\cos \theta_j)$$

We have made numerical calculations by assuming that $A^{\mathbb{M}}/B^{\mathbb{M}} = 0.5$. For $z = 3, 4$ and 6 , various properties of the nematic and isotropic phases and $T^{\mathbb{M}}$ are calculated. The dielectric constants ($\epsilon_{||}$ and ϵ_{\perp}) along and perpendicular to the unique axis of the nematic phase are also calculated for the same values of z .

The variation of $(T_{\text{NI}}^{\mathbb{M}} - T^{\mathbb{M}})/T_{\text{NI}}^{\mathbb{M}}$ is found to be similar to that observed for the system of non-polar molecules. The values of $\langle P_2 \rangle$ of a typical cyanobiphenyl compound (Miyano, 1978) agrees well with the theoretical values for $z = 3$ and 4 . However, the experimental $\langle P_4 \rangle$ values of such compounds are lower than the theoretical values even for $z = 3$. As in the system of non-polar molecules, Q_v and ΔQ_v at $T_{\text{NI}}^{\mathbb{M}}$ increase systematically as z decreases from ∞ to 4 . The calculated dielectric anisotropy is comparable to the experimental value. An interesting consequence of the theory is that the mean dielectric constant should increase by a few per cent on going from the nematic to the isotropic phase because of the discontinuous decrease in value of $\langle P_1(\cos \theta_{ij}) \rangle =$

This is found to be the case experimentally in a number of strongly positive materials.

Because of strong antiparallel correlations between near neighbours, now it is known that cyano compounds form a bilayer structure. This has some important consequences like the occurrence of re-entrant nematic phase, smectic A_1 -smectic A_2 transition, etc.

In the above theories the anisotropy of the molecular shape which is an important factor in determining whether or not a substance exhibits liquid crystalline phase is not taken into account. In other words the short range intermolecular repulsions are not considered. In chapter IV we give a summary of different hard rod theories proposed so far. We have also discussed hybrid models which in addition to the repulsive force, also take into account the long range anisotropic ^{attractive} interaction between molecules. Of them Cotter's model (1977) developed on the basis of the scaled particle theory (SPT) for a system of spherocylinders gives a comparatively better description of the nematic phase. SPT was originally developed by Reiss et al (1959) for a system of hard spheres. The equation of state of a system of hard spheres given by SPT is identical to the compressibility equation of state obtained by the Percus-

Ievick (P-I) theory. The theory provides a means of deriving approximate expressions for the chemical potential μ and pressure P of a hard particle fluid by considering the reversible work necessary to insert a scaled particle (i.e., a 'solute' particle which is a scaled replica of the 'solvent' particles) at some arbitrary point in the fluid. The chemical potential of a spherical particle of radius αa is written as (Reiss et al, 1959; Cotter and Martire, 1970a,b,c)

$$\mu/kT = \ln(\rho \Lambda^3) + w(\xi, \rho)/kT \quad (7)$$

where Λ^3 is the reciprocal of the particle translational momentum partition function, $\rho = N/V$ is the number density, $w(\xi, \rho)$ is the reversible work necessary to create a spherical cavity of radius at least equal to $\xi = (\alpha + 1)a$ into a fluid of N spherical molecules of radius a . It is related to the probability $P_0(\xi, \rho)$ of observing a fluctuation in which such a cavity can be found, where

$$P_0(\xi, \rho) = \exp[-w(\xi, \rho)/kT] \quad (8)$$

The chemical potential of the solvent particle is obtained by setting $\xi = 2a$ in eq.(7). The pressure of the system is given by

$$\frac{P}{kT} = 1 - \frac{\alpha \rho}{3} \left[\frac{\ln P_0(\xi, \rho)}{\partial \xi} \right]_{\xi = 2a} \quad (9)$$

Cotter and Martire (1970a,b,c) showed that when α is sufficiently small so that three 'regular' spheres cannot simultaneously be in contact with the scaled sphere, P_0 can be written as

$$P_0(\xi, \rho) = 1 - \frac{4}{3} \pi a^3 \rho [1 + 3\alpha + 3\alpha^2 + \alpha^3]. \quad (10)$$

In the other extreme when α is very large, W must approach the reversible PV work of creating a macroscopic spherical cavity in the liquid, i.e.,

$$\lim_{\alpha \rightarrow \infty} [W] = \frac{4}{3} \pi a^3 \alpha^3 P. \quad (11)$$

This suggests that $\ln P_0(\xi, \rho)$ can be expanded as

$$-\ln P_0(\xi, \rho) = C_0 + C_1 \alpha + C_2 \alpha^2 + \left(\frac{4}{3} \pi a^3 P\right) \alpha^3, \quad \alpha \geq 0.$$

The coefficients C_m are determined from eq. (10) together with

$$C_m = \frac{-1}{m!} \left[\frac{\partial^m \ln P_0(\xi, \rho)}{\partial \alpha^m} \right]_{\alpha=0}. \quad (12)$$

The pressure P is then obtained by using equation (9) together with equation (12) to get

$$\frac{Pv_0}{kT} = \frac{d + d^2 + d^3}{(1-d)^3}, \quad d = \frac{4}{3} \pi a^3 \rho. \quad (13)$$

The Gibbs free energy and the Helmholtz free energy are given by

$$\mu/kT = G_c/kT = \ln \rho + W/kT, \quad (14)$$

$$A_0/kT = G_0/kT - P/\rho kT \quad (15)$$

As we have already mentioned, equation (15) is nothing but the P-V equation of state of hard spheres. This gives exact second and third virial coefficients and reasonable values for the higher virial coefficients also.

Cotter (1970a,b,c) has extended this theory to a system of hard spherocylinders. The reversible work ΔW written in terms of the volume excluded to the centre of a regular spherocylinder with orientation k by the presence of the scaled spherocylinder which is ⁱⁿ the orientation l , is a function of $|\sin \theta_{lk}|$. By retaining terms up to $P_2(\cos \theta)$ in the expansion of $|\sin \theta|$, Cotter made the calculation for $x (= 1/4 l/2r) = 3$ by treating the hard rod repulsive interactions in terms of SPT and subjecting each molecule to a mean field attractive potential of the form

$$\psi_1 = -v_0 \rho - v_2 \rho \langle P_2 \rangle P_2(\cos \theta_1)$$

where v_0 and v_2 are the strengths of the isotropic and anisotropic interactions.

We have extended the calculations for various values of x for a system of hard spherocylinders as well as for a system with a superposed attractive potential. By comparing

the various transition properties obtained for a system of hard spherocylinders with the experimental data on PAA, we have found that $x \simeq 2.5$ gives a good overall agreement. Including terms up to $P_{12}(\cos \theta)$ in $|\sin \theta|$ expansion, there is a considerable increase in the values of $\langle P_2 \rangle$, density change $\Delta \rho / \bar{\rho}$ and entropy change $\Delta S / Nk$ at NI transition. Properties obtained for $x \simeq 2.5$ are again in relatively better agreement with the experimental results than for other values of x .

Including the attractive potential Ψ_1 , we have made calculations by fixing ϕ (packing fraction) = 0.62 at $T_{NI} = 409^\circ K$. Truncating $|\sin \theta|$ expansion at $P_2(\cos \theta)$ various transition properties and $\gamma = -[\partial \ln T / \partial \ln V]_{\langle P_2 \rangle}$ calculated for different values of x are compared with the experimental results on PAA. γ which is equal to 1 when $x = 1$ increases as x increases, first slowly and then rapidly. It attains the experimental value ~ 4 for $x \simeq 1.75$. The order parameter $\langle P_2 \rangle$ and $\Delta \rho / \bar{\rho}$ increase with x as expected. $\Delta S / Nk$ is not much affected by the value of x and is of the order of 0.5 which is considerably larger than the experimental value (~ 0.17). C_p decreases with x whereas α and β do not vary much. Calculations beyond $x \sim 2.45$ are not possible if we choose to retain the correct values for

d and T_{NI} . For $x \simeq 1.75$, many properties are in an overall agreement with the experimental results. Retaining terms up to $P_{12}(\cos \theta)$ in the $|\sin \theta|$ expansion, there is a substantial increase in the values of $\langle P_2 \rangle$, $\Delta P/\bar{p}$ and $\Delta S/Rk$. On comparison with the experimental data, a value of x lying between 1.2 and 1.5 would appear to give a relatively better agreement than for other values of x .

The theory also enables us to study the thermodynamic properties of nematic and isotropic phases at the NI transition as functions of pressure. By retaining terms up to $P_{12}(\cos \theta)$ in the $|\sin \theta|$ expansion, we have calculated phase transition properties for $x = 1.75$ by varying the pressure from one bar to 6.5 kbar. The results are compared with the experimental results on PAA (see for example Chandrasekhar and Shashidhar, 1979) $(dT/dP)^\circ K/kbar \simeq 30$ up to 1kbar, whereas the experimental value ~ 47 . dT/dP decreases as T_{NI} increases, which is in qualitative agreement with the experimental trend noticed by Stishov et al for PAA and Horn (1978) for methoxybenzylidene-butylaniline (MBBA) and 4-n-pentyl-4'-cyanobiphenyl (5CB). Variation of molar volume of the nematic phase (V_n) as a function of T_{NI} is of the same order as that of experimental variation. $\langle P_2 \rangle$ is practically constant, varying slowly from 0.499 to 0.511

when T_{HI} changes from 409° to 572°K . γ the slope of the curve obtained by plotting $\ln V$ versus $\ln T_{HI}$ varies from 4.0 to 6.5 as T_{HI} increases from 409°K to 572°K . Apart from this, the theory is able to reproduce the qualitative behaviour of ΔS , internal energy change (ΔU), molar volume of nematic (V_n) and isotropic (V_i) phases, the change in molar volume (ΔV), etc., as functions of pressure.

The isotropic fluid state of hard spherocylinders has also been studied with the aid of computers (Vieillard Baron, 1974; Monson and Rigby, 1978; Carnahan and Starling, 1969). The results of SPF in the isotropic phase for $x = 1, 2$ and 3 are in good agreement with the results of computer studies for low densities. However SPF overestimates the pressure as the density is increased and the discrepancy also increases with increase of density.

It is of interest to extrapolate the essentially 'exact' results of the computer studies to the region of nematic-isotropic phase transition. We found that a model proposed by Andrews (1975) for calculating the equation of state of an assembly of hard spheres can be extended to the case of spherocylinders. Further the extended model provides a suitable scheme for making calculations in the ordered phase also. We will present here a brief summary of Andrews

approach developed for a system of spheres. The activity of a fluid of spheres of diameter σ is computed as a product of two terms. The first term is the probability that a point x chosen at random within a volume V does not lie inside the core of one of the N -molecules. The second term is the probability conditional on the first, that the hole around the given point can actually accommodate the introduced molecule. This demands that there should be no other molecule within the additional volume $\frac{4}{3}\pi\sigma^3 - \frac{1}{6}\pi\sigma^3 = \frac{7}{6}\pi\sigma^3$. If ω gives the value of the average volume taken up by each molecule when they are crowded together, then the reciprocal activity can be written as

$$a^{-1} = \left(1 - \frac{1}{6}\pi\sigma^3\rho\right) \exp\left[-\frac{7\pi\sigma^3\rho}{6(1-\omega\rho)}\right] \quad (16)$$

Andrews assumed that $\omega = \omega_0 + \omega_1\rho$. At low densities, the value of ω_0 is obtained from the third virial coefficient of a dilute fluid of spheres. In the other extreme, when the density is very large, the crystal clearly has the close-packed volume of $\omega_{\text{solid}} = 1/\rho_0 = \sigma^3/2$. Under these two conditions, the coefficients ω_0 and ω_1 are calculated. The simplified expression for the pressure of the system of spheres will be

$$\frac{P}{\rho kT} = \frac{5.1834 Z}{(1 - 1.534 Z + 0.534 Z^2)} - \frac{1.3504}{Z} \ln(1 - 0.7405 Z) - \frac{4.8534}{Z} \ln(1 - 1.534 Z + 0.534 Z^2) - \frac{15.977}{Z} \ln\left(\frac{1 - 0.534 Z}{1 - Z}\right) \quad (17)$$

where $Z = \rho/\rho_0$ is the scaled density relative to the close-packed density. Compared to the results of SPT, the values of $P/\rho kT$ obtained from equation (17) are in better agreement with the molecular dynamics data of Alder and Wainwright (1960). Further unlike in SPT, the unphysical calculations beyond $\rho > \rho_0$ are not admissible since $P/\rho kT$ (see eq. 17) tends to take infinite value as ρ approaches ρ_0 .

We extended the Andrews approach to a system of spherocylinders. We found that the two term expansion of ω is inadequate to reproduce the value of $P/\rho kT$ obtained from the computer calculations. Hence we expanded ω as $\omega = \sum_{n=0}^6 \omega_n \rho^n$. The coefficients $\omega_0, \omega_1, \dots, \omega_6$ are derived by using ρ_0 of a close packed system of spherocylinders and the first eight virial coefficients got by Monte Carlo calculations of Monson and Rigby (1978).

As in SPT, we have made calculations for a system

of hard spherocylinders as well as for a system which includes an attractive potential, by retaining terms up to $P_2(\cos \Theta)$, and $P_{12}(\cos \Theta)$ in the $|\sin \Theta|$ expansion (see chapter V). On comparing with the results of SPT, we have found that the present calculations improve upon the values of x as well as other results, particularly the second derivatives of the chemical potential.

As we have already noted, disc-like molecules also exhibit liquid crystalline phases which can be broadly classified as columnar and nematic phases. Transition between columnar, nematic and isotropic phases have been observed in a number of discotic mesogens.

In chapter VI, we extend the SPT to study properties at the nematic-isotropic transition of disc-like mesogens. In order to be able to compare the results on disc-like molecules with those on rod-like molecules, the shape of the molecule is taken to be a right circular cylinder. If r is the radius of the cylinder and l its height, the shape factor $R = r/l > 0.5$ for disc-like molecules and < 0.5 for rod-like molecules. The excluded volume in this case involves three different functions of Θ_{ik} , viz., $|\sin \Theta_{ik}|$, $|\cos \Theta_{ik}|$ and $\int_0^{\pi/2} \sqrt{1 - \sin^2 \Theta_{ik} \sin^2 \varphi} d\varphi$. By retaining terms up to $P_2(\cos \Theta_{ik})$, $P_4(\cos \Theta_{ik})$ and $P_6(\cos \Theta_{ik})$ in

their expansions, properties of rod-like and disc-like particles are studied for a system of hard particles as well as for a system superposed with an attractive potential. The results obtained are compared with the experimental data. Our calculations demonstrate that it is necessary to retain higher order terms, at least up to $P_4(\cos \theta)$ in the expansion of angle dependent terms in order to get qualitatively correct results. The phase transition properties of a nematic medium of disc-like molecules are essentially analogous to those of rod-like molecules, when they are plotted as functions of the ratio (larger dimension/smaller dimension) of the cylinder.

In chapter VII, we have extended the McMillan's (1971) model of smectic A phase to the columnar phase exhibited by disc-like molecules. As we have already noted, in the smectic A phase the molecules are upright in each layer, with their centres irregularly spaced ^{within the layer.} The director (say Z-axis) also represents the direction of the layer normal (or the vector of the density wave). McMillan has proposed a simple description of this phase by extending the Maier-Saupe theory to include an additional order parameter for characterizing the one-dimensional translational periodicity of the layered structure. To start with he has considered a pair potential of the form

$$V_{12}(r_{12}, \cos \theta_{12}) = - \frac{V_0}{\pi r_0^3} \frac{3}{2} \exp(-(r_{12}/r_0)^2) P_2(\cos \theta_{12})$$

where r_{12} is the distance between the molecular centres and θ_{12} the angle between the symmetry axes of the molecules 1 and 2. r_0 is of the order of the length of the rigid part of the molecule and V_0 the strength of the anisotropic interaction. By retaining the leading terms in the Fourier expansion, the single particle potential in the mean field approximation turns out to be

$$V_1(Z, \cos \theta) = -V_0 [\langle P_2 \rangle + \alpha \cos(2\pi Z/d)] P_2(\cos \theta)$$

where $\alpha = 2 \exp[-(\pi r_0/d)^2]$ is the model parameter.

We have extended this mean field model to describe the columnar phase exhibited by disc-like molecules by treating the density wave to be periodic in two dimensions. The theory is developed for a face-centered rectangular (FCR) lattice composed of liquid-like columns, taking the molecular cores to be circular discs normal to the columnar axes. The FCR lattice is described by a superposition of three density waves with wave vectors say \vec{A} , \vec{B} and $\vec{C} = \vec{A} + \vec{B}$ defined as in fig. 12. Unlike in the smectic A phase of rod-like molecules, the director is parallel to the columnar axis (Z-axis say), whereas the wave vectors \vec{A} , \vec{B} and \vec{C} are

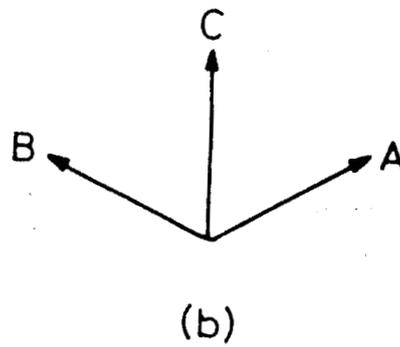
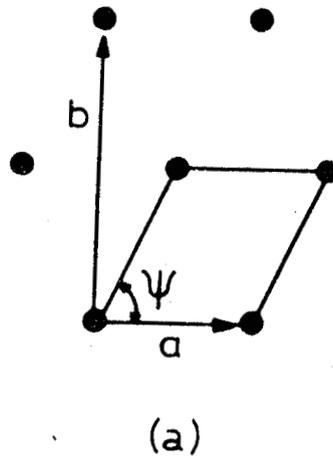


FIG.12: Two-dimensional face-centered rectangular lattice showing (a) the lattice parameters a and b , and the primitive cell of the direct lattice, (b) the reciprocal lattice vectors \vec{A} , \vec{B} , and \vec{C} .

in the orthogonal XY plane. Therefore, we couple each density wave to the appropriate component of the orientational order parameter along \vec{A} , \vec{B} and \vec{C} , rather than to the component along Z . The single particle potential in the mean field approximation is written in terms of α_1 , α_2 and order parameters η_1 , η_2 , σ_1 and σ_2 , by retaining only the leading terms in the Fourier expansion of the density wave. α_1 is an interaction strength related to the density wave along \vec{C} and α_2 that along \vec{A} and \vec{B} . η_2 and η_1 are the orientational order parameters measured along the X and Y axes, and σ_2 and σ_1 are the order parameters coupling the orientational and translational order along the \vec{A} (or \vec{B}) and \vec{C} directions respectively. The single particle distribution function and the free energy are written in the mean field approximation. These equations give rise to four possible solutions corresponding to biaxial rectangular columnar, biaxial smectic, uniaxial nematic and isotropic phases.

We have studied the phase diagram as well as the transition entropies for $\frac{b}{a} = 1.5, 1.6, \sqrt{3}, 1.85$ and 1.95 . For $\frac{b}{a} = \sqrt{3}$, the phase diagram is exactly identical to the one presented by Feldkamp et al (1981) for hexagonal lattice. The hexagonal-nematic transition is always first order. The

phase diagrams for values of $\frac{b}{a} < \sqrt{3}$ are very similar to that for the hexagonal lattice and lead to a first order transition between a biaxial rectangular columnar phase and a uniaxial nematic phase. The temperature range of the nematic phase decreases with increasing α_1 and for values of α_1 higher than some value say α_0 , the columnar phase transforms directly to the isotropic phase. If as in McMillan's theory, α_1 is interpreted to be a measure of the chain length, these results are in qualitative accord with the experimental results.

If $\frac{b}{a}$ is slightly greater than $\sqrt{3}$ say equal to 1.85, the phase diagram is again rather similar to that for the hexagonal lattice. However as the asymmetry of the lattice is increased, we get solutions corresponding to a smectic phase also. For $\frac{b}{a} = 1.95$ we find that for $\alpha_1 < 0.52$, the rectangular columnar phase transforms to a biaxial smectic 4 phase (with the layer normal along \vec{C}) which in turn undergoes a second order transition to a uniaxial nematic phase at a higher temperature.

By comparing the phase diagrams for $1.5 < \frac{b}{a} < 1.95$, we find that the value of α_0 increases as $\frac{b}{a}$ increases. The temperature variation of order parameters in different phases show that larger the asymmetry of the lattice,

stronger is the biaxial order of the rectangular columnar phase.

Some of the results discussed in this thesis are reported in the following publications.

- 1 Short range orientational order in nematic liquid crystals (N.V.Madhusudana, K.L.Savithramma and S. Chandrasekhar) Pramana **8**, 22 (1977).
- 2 The nematic-isotropic phase transition: Application of the Andrews method (K.L.Savithramma and N.V.Madhusudana) Mol. Cryst. Liq. Cryst. **62**, 63 (1980).
- 3 Scaled particle theory of a system of hard right circular cylinders (K.L.Savithramma and N.V.Madhusudana) - presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980 - Mol. Cryst. Liquid Cryst. **74**, 245 (1981).
- 4 Extension of McMillan's model to liquid crystals of disc-like molecules (S. Chandrasekhar, K.L.Savithramma and N.V.Madhusudana) - Presented at the Fourth International Symposium on Liquid Crystals and Ordered Fluids, Las Vegas, March 28-April 2, 1982 (Plenum Press)
- 5 Scaled particle theory of a system of right circular cylinders subjected to an attractive potential (K.L.Savithramma and N.V.Madhusudana) - Mol. Cryst. Liq. Cryst. (in press). 1982 MCLC 90 35-45
- 6 Extension of the scaled particle theory calculations on a system of spherocylinders to high pressures 1983 (K.L.Savithramma and N.V.Madhusudana) (under preparation).

MCLC 97 407-415

The following paper on magnetism has some discussions relevant to the chapter II of the thesis.

- 7 Equivalence of the Krieger-James approximation and the constant-coupling approximation in magnetism (K.L.Savithramma and H.V.Madhusudana) - Prasanna 10, 349 (1978).

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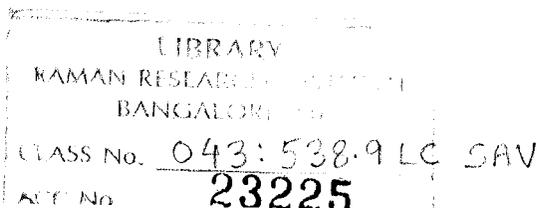
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