

CHAPTER 4

THE NEMATIC-ISOTROPIC PHASE TRANSITION IN A SYSTEM OF SPHEROCYLINDERS: APPLICATION OF THE SCALED PARTICLE THEORY.

4.1 Introduction

As we have discussed in chapter 1, asymmetry of the molecular shape is essential for a substance to exhibit liquid crystalline properties. The relative importance of short-range intermolecular repulsions as compared to long range anisotropic intermolecular attractions in stabilizing the nematic phase has formed the subject matter of several papers.

A good summary of hard rod models of the nematic-isotropic (NI) transition has been given by Cotter (1976, 1979). In all such hard rod theories, the fluid is considered to be made up of long thin rods having no forces between them other than the one preventing their interpenetration. In such a system one may expect that at low densities, the rods can take all possible orientations and hence the fluid to be isotropic. As the density increases, it is more and more difficult for a given molecule to take random orientations with reference to its neighbours and if the density is high enough, the

rods will be packed efficiently only if they are approximately parallel to one another. In other words the system undergoes a transition to a more ordered anisotropic phase having uniaxial symmetry. Many theories have been developed on the basis of this idea.

Onsager (1949) for the first time treated the equilibrium properties of dilute solutions of hard-rod macromolecules which have a well-defined length and diameter. This theory was meant to study the phase separation of ordered and disordered phases in solutions of very long molecules like polymers, etc. The ordered phase in such a system is an orientationally ordered phase, analogous to the nematic phase. However typical compounds forming the thermotropic nematic phase in which we are interested have relatively short molecules with a length to breadth ratio $x \simeq 3-5$. Most of the hard-rod theories proposed for studying nematic-isotropic (NI) transition are indeed developments based on Onsager's approach. Hence we give this theory in some detail.

Considering a fluid of N-rod like molecules in a volume V, with intermolecular pair potential

$$U_{ij} = U(r_{ij}, \hat{r}_i, \hat{r}_j) = \begin{cases} \infty, & \text{if } i \text{ and } j \text{ overlap} \\ 0, & \text{otherwise} \end{cases}$$

where $r_{ij} = r_i - r_j$, r_i and r_j the vectors representing the positions of the molecules i and j (for convenience, the vector ^{notation} is not shown explicitly), and Ω_i and Ω_j are the polar coordinates describing the orientations of the molecules i and j with respect to a space fixed coordinate system. Since we are only interested in the angular distribution of the particles in the mean field approximation we can write the configurational partition function Q_N for such a system as

$$Q_N = \frac{1}{N!(4\pi)^N} \int [dr^N] \int [d\Omega^N] \exp(-U_N/kT) \quad (1)$$

where $(4\pi)^{-N}$ is a normalization factor, k the Boltzmann constant, T the absolute temperature, and U_N is the configurational potential energy of the N -particle system. Assuming additivity of pairwise interactions, U_N can be written as

$$U_N = \sum_{(1 < i < j < N)} U_{ij} \quad (2)$$

By restricting the molecules to n discrete orientations, Q_N can be written as

$$Q_N = \frac{1}{N!(4\pi)^N} \sum_{N_1} \dots \sum_{N_n} \frac{N!(\Delta\Omega)^N}{N_1!N_2!\dots N_n!} \times \int dr^N \exp[-U_N(r^N, N_1 \dots N_n)/kT] \quad (3)$$

where $\Delta\Omega = 4\pi/n$, $[N_1, N_2 \dots N_n]$ stands for the number of molecules oriented in the directions $[1, 2 \dots n]$ respectively subject to the constraint

$$\sum_{m=1}^n N_m = N .$$

By retaining only the term with the configuration $[\bar{N}_1, \bar{N}_2, \dots \bar{N}_n]$ which maximizes the partition function Q_N , we can write the Helmholtz free energy of a molecule as

$$\begin{aligned} \frac{A_c}{NkT} &= -\frac{1}{N} \ln Q_N \\ &= \sum S_i \ln S_i + \ln \rho + \varphi_N(\bar{N}_1, \bar{N}_2 \dots \bar{N}_n)/NkT - 1 \end{aligned} \quad \dots (4)$$

and where $S_i = \bar{N}_i/N$, $\rho = N/V$. A_0 is the configurational Helmholtz free energy of the hard rod system and φ_N is given by (Zwanzig 1963)

$$\varphi_N(\bar{N}_1 \dots \bar{N}_n) = -kT \ln \left\{ V^{-N} \int dr^N \exp[-U_N(r^N, \bar{N}_1 \dots \bar{N}_n)/kT] \right\}. \quad (5)$$

φ_N is the excess Helmholtz free energy of the system of N molecules relative to an ideal mixture of $N_1, N_2 \dots N_n$ molecules. By changing over to a continuum of orientations, eq.(4) can be written as

$$\frac{A_G}{NkT} = \ln \rho + \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega + \varphi_H[f(\Omega)]/NkT - 1 \quad (6)$$

where $f(\Omega)$ is the normalized single particle distribution function. By knowing the excess free energy φ_H , the form of $f(\Omega)$ which minimizes the free energy (eq. 6) can be obtained with the constraint $\int f(\Omega) d\Omega = 1$ and hence the properties of the systems can be studied.

In Onsager's approach, ρ is assumed to be sufficiently small and the excess free energy is expanded in a cluster or virial expansion in density (see Cotter, 1979), i.e.,

$$\begin{aligned} \frac{\varphi_H}{NkT} &= \frac{A_G(\text{excess})}{NkT} \\ &= \sum_{j \geq 2} (j-1)^{-1} B_j(S_1, \dots, S_n) \rho^{(j-1)} \end{aligned} \quad (7)$$

where B_j is the j^{th} virial coefficient. Since U_H is the sum of pair-wise interactions, the virial coefficients can be written in terms of the Mayer functions

$$f_{ij}^{\sigma\sigma'}(r_{ij}) = \exp(-U_{ij}^{\sigma\sigma'}) - 1$$

where $U_{ij}^{\sigma\sigma'}$ is the potential energy between molecules i and j which have orientations Ω_σ and $\Omega_{\sigma'}$, respectively. Using these Mayer functions, B_2 and B_3 can be written

$$B_2 = -\frac{1}{2} \sum_{\sigma'=1}^n \sum_{\sigma=1}^n S_{\sigma} S_{\sigma'} \int dr_{ij} f_{ij}^{\sigma\sigma'}(r_{ij})$$

and

$$B_3 = -\frac{1}{6} \sum_{\sigma''=1}^n \sum_{\sigma'=1}^n \sum_{\sigma=1}^n S_{\sigma} S_{\sigma'} S_{\sigma''} \iint dr_{ij} dr_{ik} f_{ij}^{\sigma\sigma'} f_{ik}^{\sigma\sigma''} f_{jk}^{\sigma'\sigma''} \dots (8)$$

The other virial coefficients, viz., $B_4, B_5 \dots B_n$ can be written in a similar manner. Retaining only the first term in the expansion for $\rho V/NkT$ (i.e., in eq. 7) and substituting in eq. (4), we get after simplification

$$\frac{A_c}{NkT} = \sum S_i \ln S_i + \ln \rho - 1 - \frac{\rho}{2} \sum_{\sigma} \sum_{\sigma'} S_{\sigma} S_{\sigma'} \int r_{ij} f_{ij}^{\sigma\sigma'}(r_{ij}) \dots (9)$$

f_{ij} is equal to -1 when $U_{ij}^{\sigma\sigma'} = \infty$ and is zero when $U_{ij}^{\sigma\sigma'} = 0$.

Hence the eq. (9) can be written as

$$\frac{A_c}{NkT} = \sum S_i \ln S_i + \ln \rho - 1 + \frac{\rho}{2} \sum_{\sigma} \sum_{\sigma'} S_{\sigma} S_{\sigma'} V(\Omega_{\sigma}, \Omega_{\sigma'}) \dots (10)$$

where $V(\Omega_{\sigma}, \Omega_{\sigma'})$ is the volume excluded to the centre of molecule with an orientation Ω_{σ} due to the presence of a molecule with orientation $\Omega_{\sigma'}$, and vice versa.

In the limit of continuous orientations, the free energy

takes the form

$$\frac{A_c}{NkT} = \int d\Omega f(\Omega) \ln[4\pi f(\Omega)] + \ln \rho - 1 + \frac{\rho}{2} \iint d\Omega d\Omega' f(\Omega) f(\Omega') V(\Omega, \Omega') \quad (11)$$

To calculate $V(\Omega, \Omega')$, Onsager assumed the molecule to be of the form of a spherocylinder, i.e., a cylinder capped at both ends by a hemisphere of the same radius. He showed that

$$\begin{aligned} V(\Omega, \Omega') &= \frac{32}{3} \pi r^3 + 8\pi r^2 l + 4rl^2 |\sin(\Omega, \Omega')| \\ &= 8v_0 + 4rl^2 |\sin(\Omega, \Omega')| \end{aligned} \quad (12)$$

where r and l are the radius and the cylindrical height of a spherocylinder, v_0 its volume, (Ω, Ω') is the angle between the long axes of molecules orienting in the directions Ω and Ω' respectively. Eq.(12) is substituted in eq. (11) for A_0/NkT and the distribution function $f(\Omega)$ which minimizes this free energy is obtained by solving the variational equation

$$\delta[A_0/NkT - \epsilon \int d\Omega f(\Omega)]/\delta f = 0$$

along with the constraint

$$\int d\Omega f(\Omega) = 1.$$

We get

$$f(\Omega) = \frac{\exp[-4r\ell^2\rho \int d\Omega' f(\Omega') |\sin(\Omega, \Omega')|]}{\int \exp[-4r\ell^2\rho \int d\Omega' f(\Omega') |\sin(\Omega, \Omega')|] d\Omega} \quad (13)$$

This gives a set of non-linear integral equations for $0 < \Omega < \pi/2$. This distribution function along with eq. (11) for the Helmholtz free energy can be used to determine all the thermodynamic properties of the system.

Onsager (1949) gave an approximate variational solution to eq. (13). For large values of length to breadth ratio $x (= \frac{\ell}{2r} + 1)$, the relative change in volume $\Delta V/V$ and the orientational long range order parameter

$\langle P_2 \rangle$ at the transition point are found to be 0.343 and 0.84 respectively (see de Gennes, 1974). The packing fraction $\delta (= v_0 \rho)$ of ordered (d_n) and disordered (d_i) phases are $4.5/x$ and $3.3/x$ respectively. Isihara (1951) also got a similar value for d_n (~ 4) for both spheroids and right circular cylinders. However both Onsager and Isihara considered only the second virial coefficient in the virial expansion and hence the results obtained are strictly applicable only when the density is very

Flory (1956) has overcome this restriction by means

of a lattice model which is applicable for a wide range of densities. This theory yields, for $x = 200$, $\Delta V/V = 0.56$, $d_n = 12.5/x$ and $d_1 = 8.0/x$. Further the calculations could be made down to $x = 6.7$ for which it appears that $\Delta V/V = 0$. Flory and Ronca improved this lattice model in 1979 and got $\Delta V/V = 0.465$ and $d_n = 7.8937/x$ for $x = \infty$ and the critical value of x has come down to 6.4166 from 6.7. The long range order parameter $\langle P_2 \rangle$ at ^{the} transition point for $x = 6.4166$ was found to be 0.9473.

Di Marzio (1961), Cotter and Martire (1969), Wulf and de Rocco (1971), Alben (1971) and others have also developed some lattice models for the hard rod system. Alben (1971) made extensive calculations using the lattice model developed essentially on the basis of Flory's approximation. In this model space is considered as a simple cubic array of cells. A rod of length x is a series of x full cells running along one of the three cubic directions. The system consists of N rods and M cells. The free energy of the system can be written in terms of the number of ways of arranging the molecules. Then for a given value of density N/M , the orientational distribution function is obtained by minimizing the free energy. Alben calcu-

lated the equilibrium values of density and $\langle P_2 \rangle$ as functions of pressure P and temperature T . By restricting the expansion to the second virial coefficient, the results for large values of x are $\langle P_2 \rangle = 0.915$, $\Delta V/V = 0.523$ and $d_n = 3.85/x$. There was a tendency of getting smaller values of $\langle P_2 \rangle$ and $\Delta V/V$ by taking into account higher order virial coefficients. The calculations were possible down to $x = 3.652$. For $x = 3.85$, he has studied $\langle P_2 \rangle$, $\Delta V/V$ and the coefficient of thermal expansivity α as functions of temperature. In this case $\langle P_2 \rangle = 0.754$ and $\Delta V/V = 0.157$ at the NI transition points. Alben also studied transition properties for a van der Waals fluid. This again leads to large value of $\langle P_2 \rangle$ and $\Delta V/V$. But in all these lattice models, it is inherent to restrict the molecules to a discrete set of lattice sites and the long axes of the molecular cores to three discrete and mutually orthogonal directions. However these are not realistic assumptions for the nematic phase and further the properties predicted from lattice models differ very much from the experimental results.

Zwanzig (1963) simplified Onsager's theory and evaluated the virial coefficients to a much higher order, allowing spatial freedom but restricting the molecules to take discrete orientations along three mutually perpendicular

axes. Hummel and Colvin (1970) developed a Padé analysis of Zwanzig model. They found that inclusion of a higher order approximation does not affect the character of NI transition.

The scaled particle theory (SPT) is a scheme which has been applied to study the statistical thermodynamic properties of nematic liquid crystals by considering the continuous orientational distribution and realistic densities. As we have mentioned in the introduction, SPT was originally developed by Reiss et al (1959) for a system of hard spheres. The equation of state obtained from SPT was exactly identical to the compressibility equation of state obtained by the Percus-Yevick (P-Y) theory of hard sphere liquids. Cotter and Martire (1970 a,b,c) extended the SPT for a system of hard rods. Initially they studied the thermodynamic properties of the system for the isotropic phase with $\langle P_2 \rangle = 0$ (Cotter and Martire 1970a) and for the completely ordered phase with $\langle P_2 \rangle = 1$ (Cotter and Martire 1970 b). Later Cotter and Martire (1970c) made calculations by restricting the molecular axes to three perpendicular directions. The order parameter $\langle P_2 \rangle$ of the nematic phase was found to decrease as x decreased. However the values of $\langle P_2 \rangle$ (~ 0.66 for $x = 3$) was much larger than the experimental

In the hard rod models, the properties of the systems are too density-dependent. The pressure, configuration-

We will discuss this method in a later section.

(1977a) used a different approach to overcome this problem. Way of choosing the additional term, Gorter subsequently suitable term in the expansion. Since there is no unique results of Gorter et al for $x = 1$, Gorter (1974) added a satisfying Maxwell's relation as well as to recover the (see Gorter 1974). To overcome the inconsistency in suggested to give unrealistic results for shorter rods for hard spheres when $x = 1$ and thus the truncation is expression does not reduce to the corresponding expression $0.1, d_{\text{new}} = 0.74$ and $\langle P_2 \rangle = 0.6$. However this truncated values of x . For instance, for $x = 2.75$, he got $\Delta V/V =$ inconsistency, Gorter made calculations for a range of Dropping the term which leads to this thermodynamic

$$(14) \quad \frac{\partial \epsilon(\nu^j)}{\partial \mu_j} = \frac{\partial \epsilon(\nu^i)}{\partial \mu_i} ; i \neq j$$

the following Maxwell's relation chemical potential obtained from GOR does not satisfy distribution of orientations. He also found that the three orientations and developed GOR for a continuous value. Gorter (1970) removed the restriction to only

rational entropy and chemical potential, etc. are directly proportional to the absolute temperature and the long range order parameter $\langle P_2 \rangle$ is independent of temperature at constant density.

Defining the parameter γ by the equation (Alben, 1971)

$$\gamma = - \left[\frac{\partial \ln T}{\partial \ln V} \right] \langle P_2 \rangle = \text{const.} \quad (15)$$

it is clear that γ is a measure of the relative importance of volume V compared to that of temperature T in determining the variation of $\langle P_2 \rangle$ of the medium. Experimentally McColl and Shih (1972) found that $\gamma = 4$ at the NI transition point for para-azoxyanisole (PAA). On the other hand all the hard rod models give $\gamma = \infty$. Thus purely hard rod models do not give a good description of nematic liquid crystals.

As we have discussed in chapter II, theories of the nematic phase have also been developed by assuming that it is stabilized by anisotropic attractive interactions. In the mean field approximation, the simplest form of the potential energy of a molecule can be written as

$$\Psi = -A(V) \langle P_2 \rangle P_2(\cos \theta) \quad (16)$$

where θ is the angle between the molecular axis and the nematic director and $\langle P_2 \rangle$ is the ensemble average second order Legendre polynomial $P_2(\cos \theta)$ (Maier and Saupe, 1957, 1958, 1959, 1960). In all these theories, though not explicitly stated, the molecules have essentially a spherical shape and the excluded volume effects are not taken into account. To get $\gamma = 4$ from theories, it is required that $A(V) \propto V^{-4}$ (see Chandrasekhar and Madhusudana, 1971, 1973; Humphries et al, 1972; Humphr and Luckhurst, 1972). But as Cotter (1977b) proved later, thermodynamic consistency demands that all the coefficients in such a potential, viz., $A(V)$ should be proportional to V^{-1} and hence these theories lead to $\gamma = 1$. Thus the theories based on attractive forces alone cannot be realistic representations of nematic liquid crystals. Hence it is clear that a combination of both short range intermolecular repulsions and long range anisotropic attractions is necessary to provide a proper description of nematic liquid crystals (Cotter 1977a; Gelbart and Baron, 1977, 1978).

There have been several 'hybrid' models in which both repulsive and attractive interactions are taken into account. Cotter and Martire (1969) applied a quasi-chemical

treatment to a system in which four independent segment interaction energies are considered.

People and Karasz (1961) developed a model which can be applied to study both crystal-nematic and nematic-isotropic transitions. The positions and the orientations of molecules are allowed to be in either 'right' or 'wrong' situations. The energies of interactions between neighbouring molecules in different configurations are considered. Using a Lennard-Jones potential and taking V^{-4} dependence for repulsive interactions and V^{-2} dependence for attractive interactions, they found that the agreement between the calculated values and the experimental results on nematic liquid crystals was not good. By changing the volume dependence of attractive interactions to V^{-3} , Chandrasekhar et al (1970, 1972) got considerably improved results. Since the molecules are restricted to only two types of orientations, the theory can reproduce only the qualitative behaviour of the properties of the nematic phase. Hijikuro et al (1974), Boehm and Martire (1978) and Cotter (1976) also studied lattice models in which the orientations and the positions of the molecules are again restricted to a discrete number of sets.

Alben (1971) has studied some lattice models as

well as some continuum models of hard rod liquids both with and without superposed attractive interactions.

continuum models, he has considered a hard rod fluid with (i) density independent isotropic energy (steric model), (ii) density independent isotropic and anisotropic energies (balanced model), and (iii) a hard sphere fluid with a volume dependent anisotropic energy of the form $-(w/v^2) \langle P_2 \rangle^2$. He has calculated $\langle P_2 \rangle$, d_{nem} , $\Delta V/V$, ΔH as well as the second derivatives of the chemical potential like isobaric expansivity α , isothermal compressibility β , specific heat at constant pressure C_p and the parameter γ . It was found that in all the three models considered, $\Delta V/V$ is somewhat smaller than the experimental value whereas ΔH and $\langle P_2 \rangle$ are larger. The calculated values of the second derivatives, viz., α , β , C_p , etc. are in reasonable agreement with the experimental results. He also made calculations by considering a cluster of m molecules as a single unit and taking both v^{-2} and v^{-4} dependence for the attractive energies. For $m = 10$ and with v^{-4} dependence for attractive energies, the results obtained were in good agreement with the experimental data. However it is clear that Cotter's (1977b) argument about volume dependence of the attractive potential is applicable to all these models. This would

affect very much the calculated values of γ , whereas the other results would not be affected much.

Kimura (1974a,b) rewrote Onsager's model by including an attractive energy in a mean field approximation. However to get $\gamma = 4$, Kimura had to take $d_{nem} = 0.97$ which is much larger than the close-packed density of spherocylinders of any length to breadth ratio.

Ypsa and Vertogen (1977a,b,c) have developed a few different models of the nematic liquid crystals. In the simplest model the molecules are assumed to be hard spheres. The nematic order is thus thought of as resulting from the anisotropic attractive interactions alone. P-Y compressibility equation of state is used for the pressure of the hard sphere system. The attractive energy is introduced in a mean field approximation. Calculations were made by using (i) a distance dependent, and (ii) distance independent potentials, viz.,

$$-\Psi_{ij} = \Psi_0(r_{ij}) + \Psi_2(r_{ij})P_2(\cos \theta_{ij}) \quad (17)$$

$$-\Psi_i = \mathcal{V}_0 \rho + \mathcal{V}_2 \rho \langle P_2 \rangle P_2(\cos \theta_i) \quad (18)$$

where r_{ij} is the distance between the centres of molecules i and j and θ_{ij} the angle between their long axes. With the potential given in eq. (17), the average of the spatial

part of the interactions was carried out by using the hard sphere distribution with the aid of Laplace transformation. The resulting values of T_{HI} , d_{nem} , $\langle P_2 \rangle$, $\Delta P/\bar{p}$, $\Delta S/Nk$ were in reasonably good agreement with the experimental data. But the calculated value of γ is too low. By allowing the molecule to have a slightly non-spherical shape, they were able to get $\gamma = 4$ (see Ypma and Vertogen 1977b). In this model, they have assumed that the molecular shapes are only slightly non-spherical so that they could treat the effect of the anisotropic shape as a perturbation over the hard sphere fluid following a method developed by Bellenans (1968). Ypma and Vertogen (1977c) also included the near-neighbour orientational correlations and the resulting theory led to a remarkably good agreement with ^{the} experimental data. Thus the calculated values of γ , dT/dP , $\langle P_2 \rangle$ and ΔH agrees well with the experimental values. (These authors have not calculated the second derivatives of the thermodynamic potential.) Nevertheless the theory is unsatisfactory for the following reasons. As Flapper and Vertogen (1980) pointed out, the theory does not use ^{the} actual length to breadth ratio x . It is possible to estimate roughly the value of x from the eccentricity parameter a_2 as defined by Ypma and Vertogen (1977). The estimated value of x turns out to

be 1.05. Thus to get good agreement with experiment, they have to assume $x = 1.05$ (see Ypma and Vertogen 1977c), while x of a typical molecule forming liquid crystals is in the range 3-5. Further in this theory, the coefficient γ is far too sensitive a function of the anisotropy parameter. It is 1 for a spherical unit ($x = 1$) and 4 for $x = 1.05$. Moreover the authors have taken into account only the first order perturbation approximation. According to Bellemans (1968) at liquid densities, the second order perturbation becomes important - indeed the second order term tends to have a somewhat larger magnitude than the first order term and, more importantly, ^{it} has the opposite sign. In view of these observations, we believe that the good agreement that these authors find with experimental data to be fortuitous.

Shih et al (1976) have used the familiar HGY (Born-Green-Kirkwood-Yvon) equation for s classical isotropic liquid consisting of spherical molecules superposed with an orientation dependent pair potential. The internal energy, entropy and the pressure of the system have been written in the mean field approximation. The theory has too many parameters with not many equations. Lee and Woo (1977) developed a similar theory by adapting

the coupled BBGKY (Bogoliubov-Born-Green-Kirkwood-Yvon) equation.

Gelbart and Baron (1977, 1978) have developed a generalized Van der Waals theory. The molecules assumed to have a spherocylindrical core. The hard rod contribution is calculated using scaled particle and the attractive energy is assumed to be distance dependent and of the form given in eq. (17). The Helmholtz free energy of system is obtained as a function of d , T , the coefficients of attractive potential and the molecular shape. The results obtained for \bar{z}_{HI} , d_{nm} , $\Delta P/\bar{p}$, dT/dP are in reasonable agreement with experiments, but the values of $\langle P_2 \rangle$ and $\Delta S/Nk$ are very much larger compared to the experimental values. Cotter (1977b) reexamined this theory and came to the conclusion that statistical thermodynamic consistency can be achieved by the potential given in eqn. (18) but not by that given in eq. (17).

Very recently Flory and Ronca (1979a,b) also made some calculations for a system of cylinders by using a lattice model and taking the attractive energy in the mean field approximation. It reduces to the Maier-Saups's theory for $x = 0$. The theory has been developed for a system at constant volume.

Apart from all these models, Monte Carlo simulation studies have also been made for a fluid of non-spherical hard molecules. The main aim of all these methods is to calculate either the virial coefficients or the equation of state. Viillard-Baron (1974) calculated the compressibility factor Pv/kT as function of d in the isotropic phase of a fluid consisting of spherocylinder with length to breadth ratio equal to 3. Doublik et al (1976) made similar calculations for $x = 2$. The first five virial coefficients have been calculated by many authors like Rigby (1970), Nezbeda (1976a,b) and Monson and Rigby (1978). Nezbeda (1976b) also proposed an (essentially empirical) analytical expression for calculating the virial coefficients of a fluid of hard spherocylinders. The first six virial coefficients given by this relation are in good agreement with the Monte-Carlo calculation of Monson and Rigby (1978) for $x \leq 3$. We will have an occasion to refer to this in the next chapter.

We consider the model developed by Martha Cotter (1977a) as the best available theory. In this theory, the hard rod repulsions are treated in terms of SPT and the long range attractive forces are taken in the mean field approximation. Cotter has made calculations for

spherocylinders with $x = 3$. We have made calculations on several properties at T_{HI} for different values of x by the SPT as developed by Cotter. The results are presented for ~~both~~ hard rod system as well as for a system superposed with an attractive potential of the Maier-Saupe type. We have also calculated all these properties by an improved evaluation of the angle dependent term of the excluded volume (eq. 12). Further the calculations have been extended to study the phase transition properties at higher pressures.

4.2 The Method

Consider again a multicomponent system, each component consisting of molecules with a particular orientation. The thermodynamic activity Z_i of component i is then written as (Widom, 1963)

$$Z_i = \rho_i / \langle \langle \exp(-\Psi_i/kT) \rangle \rangle$$

where $\rho_i = N_i/V$, $\Psi_i(\vec{r}_1, \dots, \vec{r}_N)$ is the total potential energy of interaction of a molecule of i^{th} type located at \vec{r}_i with the rest of the medium. $\langle \langle \rangle \rangle$ denotes the ensemble average over ^{the} $(N-1)$ particle system $2, 3, \dots, N$ and an averaging over \vec{r}_i as well giving equal weights to equal volume elements in the latter instance. The molecules are assumed

to move in a uniform mean field potential

$$\bar{\Psi}_i = -\nu_0 \rho^m - \nu_2 \rho^m \langle P_2 \rangle P_2(\cos \theta_i)$$

where

$$\langle P_2 \rangle = \frac{1}{N} \sum_{i=1}^n N_i P_2(\cos \theta_i).$$

Then

$$\frac{\rho_i}{Z_i} = \langle \langle \exp(-\Psi_i/kT) \rangle \rangle = \frac{\rho_i}{Z_i^*} \exp(-\bar{\Psi}_i/kT)$$

where Z_i^* is the activity of the component i with the attractive potential turned off. Thus

$$\begin{aligned} Z_i &= Z_i^* \exp(\bar{\Psi}_i/kT) \\ \ln Z_i &= \ln Z_i^* - \frac{\nu_0 \rho^m}{kT} - \frac{\nu_2 \rho^m}{kT} \langle P_2 \rangle P_2(\cos \theta_i) \end{aligned} \quad (19)$$

and hence the configurational Gibbs free energy is given by

$$\begin{aligned} \frac{G_c}{NkT} &= \sum_i S_i \ln Z_i^* - \frac{\nu_0 \rho^m}{kT} - \frac{\nu_2 \rho^m}{kT} \langle P_2 \rangle^2 \\ &= \frac{G_c^*}{NkT} - \frac{\nu_0 \rho^m}{kT} - \frac{\nu_2 \rho^m}{kT} \langle P_2 \rangle^2. \end{aligned} \quad (20)$$

The internal energy U of the system is given by

$$\frac{U}{N} = -\frac{1}{2} \nu_0 \rho^m - \frac{1}{2} \nu_2 \rho^m \langle P_2 \rangle^2. \quad (21)$$

Using equations (19-21), we get the pressure and Helmholtz free energy as

$$P = P^* - \frac{1}{2} \vartheta_0 \rho^{m+1} - \frac{1}{2} \vartheta_2 \rho^{m+1} \langle P_2 \rangle^2 \quad (22)$$

$$\frac{A_c}{NkT} = \frac{A_c^*}{NkT} - \frac{1}{2} \frac{\vartheta_0 \rho^m}{kT} - \frac{1}{2} \frac{\vartheta_2 \rho^m}{kT} \langle P_2 \rangle^2 \quad (23)$$

and

$$\frac{\varphi_H}{N} = \frac{\varphi_H^*}{N} - \frac{1}{2} \vartheta_0 \rho^m - \frac{1}{2} \vartheta_2 \rho^m \langle P_2 \rangle^2. \quad (24)$$

All the quantities with asterisk refer to a fluid of hard spherocylinders. To calculate the properties of the hard rod system the scaled particle theory has been adopted.

For this purpose, in a system of hard spherocylinders described above, a scaled spherocylinder of radius αr and cylindrical length λl is introduced. If $w_i(\alpha, \lambda)$ is the reversible work of adding such a scaled particle to the fluid at some arbitrary fixed point in the i^{th} direction, the configurational chemical potential μ_{ci} can be written as (Cotter 1977a)

$$\mu_{ci}/kT = \ln Z_i = \ln \rho_i + w_i(\alpha, \lambda)/kT. \quad (25)$$

For small values of α and λ , when three 'regular' spherocylinders cannot simultaneously be in contact with the scaled spherocylinder, Cotter and Martire (1970) showed that

$$\exp[-W_1(\alpha, \lambda)/kT] = 1 - \rho \sum_{k=1}^n S_k v_{ik} \quad (26)$$

where v_{ik} is the volume excluded to the centre of a regular spherocylinder with orientation k by the presence of the scaled spherocylinder which is in i^{th} direction and it is given by (Onsager, 1949)

$$v_{ik} = \pi r^2 l (1+\alpha)^2 (1+\lambda) + \frac{4}{3} \pi r^3 (1+\alpha)^3 + 2r l^2 (1+\alpha) \lambda |\sin \theta_{ik}| \quad (27)$$

On the other hand, when α and λ are very large, $W_1(\alpha, \lambda)$ must approach the reversible PV work of creating a macroscopic spherocylindrical cavity in the fluid, i.e.,

$$\lim_{\alpha \rightarrow \lambda \rightarrow \infty} W_1(\alpha, \lambda) = [\pi(\pi r)^2 \lambda l + \frac{4}{3} \pi(\pi r)^3] P^* \quad (28)$$

$W_1(1, 1)$ is obtained by interpolating between $W_1(0, 0)$ and $W_1(\infty, \infty)$. Knowing the work function $W_1(1, 1)$, the chemical potential μ_1 can be obtained by using the relation (25). Substituting for the chemical potential in the Maxwell's relations (eq. 14) we get

$$\int f(\Omega_k) |\sin \theta_{ik}| d\Omega_k = \int f(\Omega_k) |\sin \theta_{jk}| d\Omega_k$$

Since in the nematic phase, Ω_i and Ω_j in general represent two different directions, the above equality is not valid. Thus the chemical potential obtained from SPT

does not satisfy Maxwell's relations. As we have discussed earlier, a suitable term has been added or excluded for overcoming this problem. Cotter avoided the problem by considering only the average chemical potential and deriving all thermodynamic properties from that. (However, we should note that the problem is just avoided but not solved.)

Following Cotter (1977a), the average work function \bar{W} can be written as

$$\bar{W} = \sum_{i=1}^n s_i w_i(1,1)$$

Hence

$$\begin{aligned} \frac{\bar{W}}{kT} = & -\ln(1-d) + \left[\frac{2d(1+q/2)}{(1-d)} \right] \alpha + \left[\frac{d[1-q+2R \langle |\sin \theta_{1j}| \rangle]}{(1-d)} \right] \lambda \\ & + 2 \left[\frac{d(1-q+R \langle |\sin \theta_{1j}| \rangle)}{(1-d)} + \frac{d^2(1+q/2)(1-q+2R \langle |\sin \theta_{1j}| \rangle)}{(1-d)^2} \right] \alpha \lambda \\ & + \left[\frac{d(1+2q)}{(1-d)} + \frac{2d^2(1+q/2)^2}{(1-d)^2} \right] \alpha^2 \lambda + (1-q) \frac{Pv_0}{kT} \alpha^2 \lambda + q \frac{Pv_0}{kT} \alpha^3 \\ & \dots (29) \end{aligned}$$

$$\begin{aligned} \frac{G_c^E}{NkT} = & \langle \ln f(\Omega) \rangle + \ln[\rho/(1-d)] + \frac{6d[1 + \frac{2R}{3} \langle \sin \theta_{1j} \rangle]}{(1-d)} \\ & + \frac{4d^2(1 + Q/2)(1 - Q/4 + R \langle \sin \theta_{1j} \rangle)}{(1-d)^2} \\ & + \frac{d[1+d + \frac{2}{3}d^2(1+Q-\frac{Q^2}{2}) + 2Rd \{1+(1+2Q)\frac{d}{3}\} \langle \sin \theta_{1j} \rangle]}{(1-d)^3} \end{aligned} \quad \dots \dots (30)$$

$$\frac{P^E v_0}{kT} = \frac{d[1+d + \frac{2}{3}d^2(1+Q-\frac{Q^2}{2}) + 2Rd \{1+(1+2Q)\frac{d}{3}\} \langle \sin \theta_{1j} \rangle]}{(1-d)^3} \quad \dots (31)$$

$$\begin{aligned} \frac{A_c^E}{NkT} = -\frac{S_c}{Nk} = & \langle \ln f(\Omega) \rangle + \ln\left(\frac{\rho}{1-d}\right) + \frac{3d}{1-d} - 1 \\ & + \frac{[(4+Q-\frac{Q^2}{2})d^2/3 + 2Rd \{1-(1-Q)d/3\} \langle \sin \theta_{1j} \rangle]}{(1-d)^2} \end{aligned} \quad \dots (32)$$

where

$$\langle \sin \theta_{1j} \rangle = \iint f(\Omega_1) f(\Omega_2) |\sin \theta_{1j}| d(\Omega_1) d(\Omega_2) \quad \dots \dots (33)$$

$$\begin{aligned} Q &= 2/(3x - 1), \\ R &= 6(x-1)^2/\pi(3x - 1), \\ x &= \frac{1}{2r} + 1, \\ d &= v_0 \rho \end{aligned}$$

and

$$v_0 = \pi r^2 l + \frac{4}{3} \pi r^3$$

The excess Helmholtz free energy ϕ_H^E is now given by

$$\begin{aligned}
 \frac{\phi_K^m}{NkT} &= \frac{A_c}{NkT} - \left(\frac{A_c}{NkT}\right)_{\text{ideal}} \\
 &= \frac{A_c}{NkT} - \langle \ln(\rho f(\Omega)) \rangle - 1 \\
 &= -\ln(1-d) + \frac{3d}{1-d} \\
 &\quad + \frac{[(4+q-q^2/2)d^2/3 + 2Bd \{1-(1-q)d/3\} \langle |\sin \theta_{1j}| \rangle]}{(1-d)^2} \quad \dots (34)
 \end{aligned}$$

By substituting for G^m , P^m and A_c^m in equations (20-23), we get the total configurational Gibb's free energy, pressure and the Helmholtz free energy of the system. To obtain the value of index m , Cotter (1977b) considered the thermodynamic identity, viz.,

$$\frac{U}{N} + p \left[\frac{\partial(U/N)}{\partial p} \right]_{T, f(\Omega)} = \int f(\Omega) \left[\frac{\partial \ln Z_1}{\partial (1/kT)} \right]_{T, f(\Omega)} d\Omega \quad (35)$$

where U/N and $\ln Z_1$ are as given in equations (21) and (9). Substituting them in eq. (19), we get, after simplification,

$$\frac{1}{2} \psi_0^m (m-1) + \frac{1}{2} \psi_2^m (m-1) \langle P_2 \rangle^2 = 0$$

For the above equation to be satisfied both for $\langle P_2 \rangle = 0$ and $\langle P_2 \rangle \neq 0$, m must be equal to 1. To calculate $f(\Omega)$, Cotter approximated $\langle |\sin \theta_{1j}| \rangle$ as

$$\langle |\sin \theta_{1j}| \rangle \approx \frac{\pi}{4} - \frac{5\pi}{32} \langle P_2 \rangle^2 \quad (36)$$

and obtained $f(\Omega)$ by solving the functional relation

$$\frac{\delta [\Lambda_0 / kT - \epsilon \int f(\Omega) d\Omega]}{\delta f(\Omega)} = 0 \quad (37)$$

which yields

$$f(\Omega) = \frac{\exp \{ [\Lambda(\rho) + \frac{U_2 \rho}{kT}] \langle P_2 \rangle P_2(\Omega) \}}{\int \exp \{ [\Lambda(\rho) + \frac{U_2 \rho}{kT}] \langle P_2 \rangle P_2(\Omega) \} d\Omega} \quad (38)$$

where

$$\Lambda(\rho) = \frac{5\pi R d [1 - (1 - d)/3]}{8(1 - d)^2} \quad (39)$$

She made calculations for $x = 3$, the results of which are given in table I. However, the expansion of $\langle |\sin \theta_{1j}| \rangle$ given in eq. (36) is a relatively crude one. To make it more exact, we have also expanded $\langle |\sin \theta_{1j}| \rangle$ up to the tenth order Legendre polynomial to get

$$\begin{aligned} \langle |\sin \theta_{1j}| \rangle &= \frac{\pi}{4} - \frac{5\pi}{32} \langle P_2 \rangle^2 - \frac{9\pi}{(16)^2} \langle P_4 \rangle^2 - \frac{65\pi}{(16)^3} \langle P_6 \rangle^2 \\ &\quad - \frac{595\pi}{(16)^4} \langle P_8 \rangle^2 - \frac{6174\pi}{(16)^5} \langle P_{10} \rangle^2. \end{aligned} \quad (40)$$

This equation along with equations (23), (32) and (37) gives

TABLE I

Comparison of various theoretical results with the experimental results

Experi- ments on PAA	hr ^a ; x = 3		hr ^b + attr; x = 1		hr + attr.		Cotter's result for x = 3 v ₀ = 230 Å ³
	Present calc. v ₀ = 230 Å ³	Baron & Gelbart v ₀ = 262 Å ³	Present calc. v ₀ = 230 Å ³	Baron & Gelbart v ₀ = 230 Å ³	Present calc. x = 2.45 v ₀ = 230 Å ³	Baron & Gelbart x = 2.50 v ₀ = 295 Å ³	
T _{NI} °K	-	-	409	383	409	491.4	410.4
$\langle P_2 \rangle$	0.4	0.49	0.43	0.67	0.50	0.93	0.54
v ₀ \bar{p}	0.62	0.556	0.619	0.569	0.617	0.55	0.445
ρ_{nem} (10 ²¹ cm ⁻³)	2.678	2.430	2.696	2.49	2.696	1.94	1.975
ρ_{iso} (10 ²¹ cm ⁻³)	2.669	2.405	2.689	2.46	2.668	1.80	1.896
$\Delta p / \bar{p}$	0.0035	0.010	0.0026	0.012	0.010	0.074	0.040
$\frac{\Delta S}{NK}$	0.17	0.33	0.522	1.22	0.502	3.25	0.887
$(\frac{dT}{dP})_{p=1atm}$ °K/kbar	48	94.04	15.31	110	55.45	128	175

a a hard rod fluid

b a hard sphere fluid

$$f(\Omega) = \frac{\exp[F(\varphi, \Omega)]}{\int \exp[F(\varphi, \Omega)] d\Omega} \quad (41)$$

where

$$F(\varphi, \Omega) = \frac{v_{2p}}{kT} \langle P_2 \rangle P_2(\Omega) + \frac{4\pi i d(1 - (1-q)d/3)}{(1-d)^2} \chi(\Omega) \quad (42)$$

where

$$\begin{aligned} \chi(\Omega) = & \frac{5}{32} \langle P_2 \rangle P_2(\Omega) + \frac{9}{(16)^2} \langle P_4 \rangle P_4(\Omega) \\ & + \frac{65}{(16)^3} \langle P_6 \rangle P_6(\Omega) + \frac{595}{(16)^4} \langle P_8 \rangle P_8(\Omega) \\ & + \frac{6174}{(16)^5} \langle P_{10} \rangle P_{10}(\Omega) \end{aligned}$$

with

$$P_2(\Omega) = (3\Omega^2 - 1)/2$$

$$P_4(\Omega) = (35\Omega^4 - 30\Omega^2 + 3)/8$$

$$P_6(\Omega) = (231\Omega^6 - 315\Omega^4 + 105\Omega^2 - 5)/16$$

$$P_8(\Omega) = (6435\Omega^8 - 12012\Omega^6 + 6930\Omega^4 - 1260\Omega^2 + 35)/128$$

$$P_{10}(\Omega) = (184756\Omega^{10} - 437580\Omega^8 + 360360\Omega^6 - 120120\Omega^4 + 13860\Omega^2 - 252)/1024$$

$$\text{and } \langle P_{2n} \rangle = \int P_{2n}(\Omega) f(\Omega) d\Omega \quad (43)$$

For the sake of completeness we give the following expressions for β , α , C_V and C_P

$$\beta = -\frac{1}{V} \left[\frac{\partial V}{\partial P} \right]_{N,T} , \quad (44)$$

$$\alpha = \frac{1}{V} \left[\frac{\partial V}{\partial T} \right]_{N,P} , \quad (45)$$

$$C_V = \left[\frac{\partial U}{\partial T} \right]_{N,V} , \quad (46)$$

and

$$\frac{C_P}{Nk} = \frac{C_V}{Nk} + \frac{T\alpha^2}{\rho k\beta} . \quad (47)$$

The detailed expressions for these parameters are given in Appendix III.

4.3 Results and Discussion

Apart from the length to breadth ratio x , there are essentially two adjustable parameters in the theory, viz., the parameters of the attractive potential \mathcal{V}_0 and \mathcal{V}_2 . In principle, when $|\sin \theta_{1j}|$ is expanded up to $P_{10}(\cos \theta_{1j})$ the attractive potential could also have been expanded as follows.

$$\overline{\Psi}_1 = -\mathcal{V}_0 \rho - \rho \sum_{n=1}^5 \mathcal{V}_{2n} \langle P_{2n} \rangle P_{2n}(\cos \theta_1) .$$

This leads to four more adjustable parameters. To avoid a large number of parameters, we have taken only the first two terms in $\bar{\Psi}_1$.

All the calculations were made on an IBM-360 computer in double precision. The integrals are calculated by using 32-points Gaussian quadrature method.

a. Results for the purely hard rod system

For a purely hard rod system ($\nu_0 = \nu_2 = 0$), the calculations for a given value of x are made as follows. Assuming a reasonable value for d_{nem} , equations (43) are satisfied to get self-consistent values of long range order param $\langle P_{2n} \rangle$. Then the pressure of the nematic phase is calculated by using the equation (51). Equating this to the pressure of the isotropic phase, d_{iso} is calculated. Gibb's free energy (eq. 30) is calculated for both nematic and isotropic phases. The assumed value of d_{nem} is adjusted by an iterative procedure to equalize the Gibb's free energy of both the phases. The Clausius-Claperan equation is used to calculate dP/dT :

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

where ΔV is the volume change at NI transition and the entropy change at NI transition is given by

$$\frac{\Delta S}{Nk} = - \frac{Pv_0}{kT} \left\{ \frac{d_{nem} - d_{iso}}{d_{nem} d_{iso}} \right\} .$$

This procedure has been repeated for various values of x . The different transition properties like order parameter $\langle P_2 \rangle$, NI transition temperature T_{NI} , d_{nem} , d_{iso} , $\Delta P/\bar{p}$, dT/dP and the second derivatives, viz., C_p , α and β , etc. of both nematic and isotropic phases are tabulated in table II for x ranging from 1.5 to 3.0. These results are obtained by using the two term expansion of $|\sin \theta|$ (eq. 36). The order parameter $\langle P_2 \rangle$, $\Delta P/\bar{p} = \Delta S/Nk$ and dT/dP increases with x and d_{nem} , Pv_0/kT decrease as x increases. C_p/Nk decreases whereas α increases slowly and β increases rapidly as x increases. Comparing these results with the experimental data for PAA (given in table I), $x = 2.5$ gives an overall good agreement for most of the properties.

Results obtained by including higher order terms up to $P_{10}(\cos \theta_{1j})$ in the expansion of $|\sin \theta_{1j}|$ (eq.40) are given in table III for x ranging from 1.25 to 6.0. Comparing these results with the corresponding results obtained from the two term expansion of $|\sin \theta_{1j}|$, we find that the long range order parameter $\langle P_2 \rangle$ increases

TABLE II

Results for hard spherocylinders $|\sin \theta_{1j}| = \sum_{n=0}^1 a_{2n} P_{2n}(\cos \theta_{1j})$

$x = \frac{1}{2r} + 1$	1.5	2.0	2.5	3.0
T_{HI} °K	409	409	409	409
$\langle P_2 \rangle$	0.4454	0.4648	0.4799	0.4914
d_{nem}	0.7964	0.6884	0.6147	0.5588
d_{iso}	0.7957	0.6860	0.6105	0.5531
$\Delta \rho / \bar{\rho}$	0.0009	0.0035	0.0068	0.0104
$(\sigma_p / Nk)_{nem}$	26.336	13.563	10.330	8.890
$(\sigma_p / Nk)_{iso}$	22.960	10.313	7.168	5.795
$\alpha_{nem} \times 10^4 / ^\circ K$	2.069	3.842	5.343	6.863
$\alpha_{iso} \times 10^4 / ^\circ K$	1.802	2.911	3.745	4.421
$\beta_{nem} \times 10^{12} \text{ cm}^2 / \text{dyne}$	1.392	10.774	31.705	64.451
$\beta_{iso} \times 10^{12} \text{ cm}^2 / \text{dyne}$	1.212	8.164	21.850	41.576
$\Delta s / Nk$	0.288	0.305	0.319	0.330
dT/dP °K/kbar	6.726	28.046	58.343	94.037
Pv_0 / kT	247.810	59.426	28.567	17.724

Table III

Results for hard spherocylinders. $|\sin \theta_{1j}| = \sum_{n=0}^5 a_{2n}^2 P_{2n}(\cos \theta_{1j})$

x	1.25	1.50	2.00	2.50	3.00	4.00	5.00	6.00
$\langle P_2 \rangle$	0.5532	0.5700	0.6009	0.6256	0.6448	0.6722	0.6905	0.7039
$\langle P_4 \rangle$	0.2304	0.2449	0.2740	0.2986	0.3136	0.3489	0.3705	0.3867
$\langle P_6 \rangle$	0.0804	0.0882	0.1050	0.1200	0.1329	0.1534	0.1688	0.1807
$\langle P_8 \rangle$	0.0250	0.0284	0.0359	0.0432	0.0496	0.0605	0.0689	0.0759
$\langle P_{10} \rangle$	0.0072	0.0084	0.0114	0.0144	0.0171	0.0220	0.0261	0.0295
d_{nem}	0.8756	0.7943	0.6861	0.6127	0.5575	0.4776	0.4207	0.3774
d_{180}	0.8753	0.7930	0.6817	0.6050	0.5467	0.4618	0.4014	0.3558
$\Delta \rho/\bar{\rho}$	0.0003	0.0016	0.0063	0.0126	0.0196	0.0336	0.0468	0.0588
$\Delta S/\bar{S}$	0.4587	0.4785	0.5217	0.5589	0.5895	0.6359	0.6695	0.6950
$(\frac{d^2}{dt^2})^\circ \text{K/kbar}$	1.36	7.04	29.55	61.84	100.16	187.68	283.86	385.24
P_T/kT	1228.94	236.83	56.40	26.95	16.64	8.83	5.87	4.33

by $\sim 30\%$ in $x = 3$ and $\sim 28\%$ for $x = 1.5$. Indeed Cotter herself had noted that excluding higher order terms in the expansion of $|\sin \theta_{ij}|$ would underestimate the value of order parameter $\langle P_2 \rangle$. Further d_{nem} decreases slightly whereas $\Delta\rho/\bar{\rho}$ [$\bar{\rho} = (\rho_{nem} + \rho_{iso})/2$] increases by a factor of two. Correspondingly $\Delta S/Nk$ also increases by the same factor. df/dP increases slightly whereas the compressibility factor Pv_0/kT decreases. Apart from that, all these properties as functions of x are similar to those calculated using the two term expansion.

b. Systems superposed with an attractive potential.

Including the attractive potential as given in eq. (18), we have two adjustable parameters ψ_0 and ψ_2 . The criterion adapted for selecting the values of ψ_0 and ψ_2 was to adjust T_{NI} and the packing fraction of the nematic phase (d_{nem}) at T_{NI} to $409^\circ K$ and 0.62 respectively, which are the experimental values for PAA.

For a given value of x , we start with some value of ψ_2/v_0k and satisfy the consistency relations (eqs. 43) to get self-consistent values of $\langle P_{2n} \rangle$. The pressure of the nematic phase calculated from equations (22 and 31) is equated to the atmospheric pressure to determine the

value of ϑ_0/v_0k . The pressure of the isotropic phase calculated by using the same equations (and setting $\langle P_{2n} \rangle = 0$) is equated to that of the nematic phase to obtain d_{iso} . Knowing all these quantities, the Gibb's free energy (equations 20 and 30) of both nematic and isotropic phases are calculated. The assumed value of ϑ_2/v_0k is iterated to make them equal. The change in the internal energy ΔU and the entropy ΔS of the system at T_{NI} transition point are obtained by using the relations

$$\frac{\Delta U}{NkT} = \frac{1}{2} \frac{\vartheta_0}{v_0kT} (d_{nem} - d_{iso}) + \frac{1}{2} \frac{\vartheta_2}{v_0kT} d_{nem} \langle P_2 \rangle^2$$

$$\frac{\Delta S}{Nk} = \frac{\Delta U}{NkT} - \frac{Pv_0}{kT} \left(\frac{d_{nem} - d_{iso}}{d_{nem} d_{iso}} \right)$$

and

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} .$$

Various transition properties for a range of values of x are calculated by using $|\sin \theta_{ij}|$ expansions as given in equation (36) and equation (40). They are compared with the data on PAA for which all the relevant experimental values are available. (~~see table IV~~)

We have shown the results obtained by Cotter (1977) for $x = 3$ in the table I. For this value of x she was able to reproduce most of the qualitative features of the

85 transition. However comparing the results with the experimental data on PAA (see table I), it is seen that the theoretical packing fraction (d_{nem}) is too low and further the calculated values of the second derivatives of the thermodynamic potential, viz., C_p , C_v , α and β were significantly larger than the experimental values.

Our calculations for various transition properties determined by using two term expansion of $|\sin \theta_{ij}|$ (eq. 36) for different values of x ranging from 1.0 to 2.45 are given in table IV. $x = 1$ gives a spherical shape to the molecules, i.e., there is no geometrical anisotropy. In this case $\gamma = 1$. As the value of x is increased, γ value also increases, first slowly and then rapidly. $\gamma \simeq 4$ for $x = 1.75$. The ratio v_0/v_2 also increases with x slowly at first and rapidly as x increases further. The order parameter $\langle P_2 \rangle$ and $\Delta \rho/\bar{\rho}$ increase with x as expected. The internal energy change $\Delta U/NkT$ unexpectedly decreases slowly as x is increased, and is of the order ~ 0.5 which is almost 3 times the experimental value (~ 0.17) for PAA. C_p decreases with x , whereas α and β are not changed much. Calculations are not possible beyond $x \simeq 2.45$ if we want to retain the value of $d = 0.62$ at $T_{HI} = 409^\circ K$. Martha Cotter had to lower the value of d to 0.445 to be able to

Table IV. Results for a system including an attractive potential

$$|\sin \theta_{1j}| = \sum_{n=0}^1 a_{2n} P_{2n}(\cos \theta_{1j})$$

x	2.45	2.20	2.0	1.80	1.75	1.50	1.20	1.0	expt.
v_0/v_2	1299.09	88.87	49.11	33.26	30.70	22.11	17.01	15.87	
v_2/v_0	48.815	675.868	1168.99	1648.03	1764.53	2315.92	2845.51	2999.81	
T_{HI}^*	409	409	409	409	409	409	409	409	409
$\langle z^2 \rangle$	0.5012	0.4821	0.4688	0.4574	0.4548	0.4442	0.4363	0.4345	0.36
d_{nem}	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
d_{iso}	0.61364	0.61475	0.61557	0.61632	0.61650	0.61733	0.61815	0.61840	
$\Delta P/P$	0.01031	0.0085	0.0072	0.0060	0.0057	0.0043	0.0030	0.0026	0.0035
Y_{nem}	254.452	15.402	7.561	4.440	3.938	3.244	1.230	1.000	4
Y_{iso}	241.518	14.791	7.324	4.337	3.853	2.216	1.227	1.000	
$\Delta U/NkT$	0.5024	0.5046	0.5056	0.5079	0.5084	0.5135	0.5200	0.5224	0.17
$\Delta S/Nk$	0.5025	0.5047	0.5056	0.5079	0.5084	0.5135	0.5200	0.5224	
$(dT/dP)^* K/kbar$	55.449	45.491	38.259	31.600	30.016	22.640	15.471	13.313	48
$(C_p/Nk)_{nem}$	7.112	7.991	8.942	10.092	10.406	12.067	13.917	14.495	72.9 (at $T_{HI}-1$)
$(C_p/Nk)_{iso}$	5.540	5.256	5.031	4.813	4.760	4.510	4.276	4.210	
$(C_v/Nk)_{nem}$	0.0014	0.2932	0.9524	2.041	2.380	4.425	7.098	8.006	
$\alpha_{nem} \times 10^4 / ^\circ K$	3.590	3.752	3.837	3.870	3.869	3.853	3.637	3.562	12.65 (at $T_{HI}-1$)
$\alpha_{iso} \times 10^4 / ^\circ K$	2.846	2.846	2.847	2.849	2.850	2.853	2.857	2.859	
$\beta_{nem} \times 10^{12} \text{ cm}^2/\text{dyne}$	19.926	20.102	20.257	20.448	20.504	20.843	21.327	21.502	82.3 (at $T_{HI}-1$)
$\beta_{iso} \times 10^{12} \text{ cm}^2/\text{dyne}$	16.248	17.091	17.842	18.654	18.864	19.930	21.058	21.398	

calculate for $x = 3$ and adjust v_0 and v_2 suitably to get $\gamma = 4$. Further in this case, the second derivatives turn out to be too high compared to the experimental data on P44 (see Arnold, 1964; Kapustin and Bykova, 1966 and & Saue, 1960). From our calculations, it is seen that the overall agreement with experimental results is reasonably good for $x \approx 1.75$. In this case, however, the second derivatives are all underestimated, though they are closer to the experimental values compared to Cotter's results for $x = 3$.

Results obtained by including higher order terms up to $P_{10}(\cos \theta_{1j})$ in the $|\sin \theta_{1j}|$ expansion (eq. 40) are given in table V for x ranging from 1.0 to 2.45. Comparing the results with those obtained by restricting $|\sin \theta_{1j}|$ to the first two terms only (table IV), we notice the following differences. For spherical molecules ($x = 1$) with angle independent excluded volume, obviously there is no change in the calculated values. As x is increased, the inclusion of higher order terms leads to an increase in the strength of the transition; the values of $\langle P_2 \rangle$, $\Delta P / \rho$ and $\Delta U / NkT$ go up, the relative increase being higher for larger values of x . Further, we also see that the internal energy change increases considerably as x

TABLE V

5

Results of a system including an attractive potential $|\sin \theta_{1j}| = \sum_{n=0}^{\infty} a_{2n} P_{2n}(\cos \theta_{1j})$

x	2.45	2.20	2.0	1.80	1.75	1.50	1.20	1.0	expt
v_0/v_2	1571.86	90.38	49.61	33.48	30.88	22.17	17.62	15.68	
$v_2/v_0 k$	38.704	649.775	1142.08	1625.69	1743.80	2303.96	2842.88	2999.81	
$T_{HI} \text{ } ^\circ K$	409	409	409	409	409	409	409	409	409
$\langle P_2 \rangle$	0.6574	0.5895	0.5440	0.5070	0.4990	0.4659	0.4407	0.4345	0.36
$\langle P_4 \rangle$	0.3319	0.2562	0.2119	0.1792	0.1725	0.1461	0.1275	0.1230	0.07
$\langle P_6 \rangle$	0.1415	0.0916	0.0664	0.0497	0.0466	0.0348	0.0271	0.0254	
$\langle P_8 \rangle$	0.0540	0.0288	0.0180	0.0117	0.0107	0.0068	0.0046	0.0041	
$\langle P_{10} \rangle$	0.0191	0.0083	0.0044	0.0025	0.0022	0.0012	0.0006	0.0005	
d_{non}	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
d_{iso}	0.6080	0.6117	0.6138	0.6154	0.6157	0.6170	0.6181	0.6184	
$\Delta P/\bar{p}$	0.0195	0.0135	0.0100	0.0075	0.0070	0.0048	0.0031	0.0026	0.0035
$\Delta U/NkT$	0.9017	0.7658	0.6853	0.6253	0.6130	0.5645	0.5305	0.5224	0.17
$\Delta S/Nk$	0.9018	0.7659	0.6853	0.6254	0.6130	0.5646	0.5305	0.5224	
(dT/dP) $^\circ K/kbar$	58.60	47.53	39.59	32.40	30.71	22.91	15.52	13.32	48

is increased which is a trend to be expected. As we noted earlier, if the expansion of $|\sin \theta_{ij}|$ is confined to the $P_2(\cos \theta_{ij})$ term, a trend though weak, is observed (see table IV), bringing out importance of the higher order terms in the expansion. Comparing the calculated values of $\langle P_2 \rangle$, $\Delta P/\bar{P}$ and $\Delta U/HkT$ with the experimental data on PAA, a value of x lying between 1.2 and 1.5 would appear reasonable agreement, even though the calculated values of both $\langle P_2 \rangle$ and $\Delta U/HkT$ would still be considerably higher than the experimental data. However we know from the calculations made by retaining terms only up to $P_2(\cos \theta_{ij})$ in the $|\sin \theta_{ij}|$ expansion (table IV), that γ would agree with the experimental value on PAA for $x \simeq 1.75$. Further dT/dP value would also be in better agreement with the experimental data on PAA for $x \simeq 1.75$ than for $x \simeq 1.2 - 1.5$. Hence we have chosen $x = 1.75$ for our calculations on the phase transition properties at high pressures. The results are presented in the next section.

c. Results at higher pressures

The theory also enables us to study the properties of nematic and isotropic phases at NI transition such as T_{NI} , molar volume of nematic (V_n) and isotropic (V_i)

phases, entropy change (ΔS), internal energy change (ΔU) at NI transition, etc. as functions of pressure. We have studied these properties as the pressure is changed from one bar to 6.5 kbar for $x = 1.75$, by using the six term expansion of $|\sin \theta_{1j}|$. To calculate the phase transition properties at a pressure of say n bars, we proceed as follows: For $x = 1.75$, fixing v_2 and v_0 to the appropriate values listed in table V and starting from some value of T and d , the consistency conditions for the long range order parameters (eq. 43) are satisfied. The pressure of the nematic phase is calculated from equations (22) and (31). The assumed value of d is adjusted by an iterative procedure to make the pressure equal to n bars. The pressure of the isotropic phase calculated by setting $\langle P_{2n} \rangle = 0$ in equations (22) and (31) is also equated to n bars and d_{iso} is calculated. Then the Gibb's free energies of both the nematic and isotropic phases are calculated by using equations (20) and (30). The assumed value of T is adjusted by an iterative procedure to equalize the Gibb's free energy of both the phases. This procedure has been repeated for n ranging from 1 to 6500. The different properties calculated as functions of pressure are tabulated in table VIa and VIb. The corresponding experimental results given by Kachinaki et al (1978)

TABLE VIa

Theoretical results at various pressures

T_{HI} °K	P_H bars	V_n cm ³ / mole	ΔV cm ³ / mole	$\Delta V/V_n$ $\times 10^{-3}$	$\Delta S/R$	ΔU cal/ mole
409	1	223.43	1.56	7.00	0.613	498.05
416.63	250	222.45	1.50	6.75	0.606	492.38
424.09	500	221.53	1.45	6.54	0.600	487.67
431.36	750	220.68	1.40	6.35	0.594	483.74
438.47	1000	219.89	1.36	6.18	0.589	480.44
445.42	1250	219.14	1.32	6.03	0.585	477.65
452.25	1500	218.45	1.29	5.90	0.581	475.46
458.95	1750	217.79	1.26	5.80	0.578	473.26
465.55	2000	217.17	1.23	5.68	0.574	471.54
478.44	2500	216.03	1.19	5.49	0.569	468.81
490.99	3000	215.00	1.15	5.33	0.564	466.82
503.24	3500	214.07	1.11	5.20	0.560	465.38
515.23	4000	213.21	1.08	5.08	0.556	464.38
526.99	4500	212.42	1.06	4.98	0.553	463.71
535.56	5000	211.69	1.04	4.89	0.550	463.30
549.95	5500	211.01	1.02	4.81	0.548	463.11
561.18	6000	210.38	1.00	4.74	0.545	463.08
572.25	6500	209.79	0.98	4.68	0.543	463.19

TABLE VIIb

Theoretical Results at various Pressures

T_{HI} °K	dT/dP °K/kbar	$\langle P_2 \rangle$	$\langle P_4 \rangle$ x 10 ₁	$\langle P_6 \rangle$ x 10 ₁	$\langle P_8 \rangle$ x 10 ₁	$\langle P_{10} \rangle$ x 100
409.00	30.71	0.4990	0.1725	0.4657	0.1063	0.2163
416.63	29.83	0.4993	0.1729	0.4680	0.1073	0.2192
424.09	29.05	0.4997	0.1733	0.4705	0.1083	0.2223
431.36	28.36	0.5001	0.1738	0.4731	0.1093	0.2253
438.47	27.75	0.5005	0.1742	0.4757	0.1103	0.2284
445.42	27.20	0.5010	0.1747	0.4783	0.1113	0.2314
452.25	26.70	0.5015	0.1752	0.4810	0.1123	0.2345
458.95	26.24	0.5019	0.1757	0.4836	0.1133	0.2376
465.55	25.82	0.5026	0.1764	0.4863	0.1143	0.2406
478.44	25.09	0.5034	0.1772	0.4915	0.1160	0.2466
490.99	24.46	0.5044	0.1781	0.4966	0.1183	0.2526
503.24	23.92	0.5054	0.1791	0.5017	0.1201	0.2584
515.23	23.44	0.5064	0.1800	0.5067	0.1220	0.2642
526.99	23.02	0.5074	0.1810	0.5115	0.1238	0.2698
535.56	22.65	0.5083	0.1819	0.5162	0.1257	0.2754
549.95	22.31	0.5092	0.1827	0.5209	0.1274	0.2809
561.18	22.01	0.5102	0.1836	0.5254	0.1291	0.2862
572.25	21.73	0.5110	0.1845	0.5298	0.1308	0.2915

are listed in table VII.

We have plotted the pressure P , dT/dP , V_n and A ($\Delta V = V_n - V_i$) in figures 1-3. Experimental data on PAA for the variation of T_{NI} , V_n and $\Delta V/V_n$ with P plotted for the sake of comparison. As we can see from figure 1, the calculated value of $dT/dP \sim 30^\circ\text{K}/\text{kbar}$ up to 1 kbar, whereas the experimental value is ~ 47 for PAA (see McColl, 1972; Chandrasekhar et al, 1973; Stishov et al, 1976; Kachinskii et al, 1978; Chandrasekhar and Shashidhar, 1979). The ratio dT/dP decreases as T increases which is in qualitative agreement with the experimental data on PAA, *N*-*p*-methoxybenzylidene-*p'*-butylaniline (MBBA) (Horn, 1978; Kuss, 1978), *p*-*n*-pentyl-*p'*-cyanobiphenyl (5CB) (flora, 1978) and *N*-*p*-ethoxybenzylidene-*p'*-butylaniline (EBBA) (Kuss, 1978; Kachinskii et al, 1979). Variation of the molar volume of the nematic phase V_n as a function of pressure (figure 2) is in good agreement with the experimental results given by Stishov et al (1976) and Kachinskii et al (1979) on PAA. The theoretical values of $\Delta V/V_n$ (figure 3), $\Delta U/NkT$ and $\Delta S/Nk$ are much larger than the experimental values, but their variations with P are in qualitative agreement with the experimental trends.

Experiments on PAA carried out for the pressure

TABLE VII

Experimental data for PAA at various pressures

T_{HI} °K	P_H bars	V_H cm ³ / mol	ΔV cm ³ / mol	$\Delta S/R$	ΔU cal/ mol
408.75	1	225.04	0.72	0.172	140
408.85	1	225.02	0.72	0.173	142
410.61	39	224.80	0.71	0.171	139
412.70	81	224.53	0.70	0.171	139
416.55	161	224.97	0.69	0.173	140
420.78	249	223.49	0.68	0.173	140
427.55	398	222.70	0.65	0.170	
435.25	564	221.92	0.66	0.171	140
435.23	564	221.92	0.61	0.166	135
448.21	862	220.65	0.59	0.168	138
452.66	968	220.29	0.57	0.164	134
458.23	1104	219.80	0.54	0.160	131

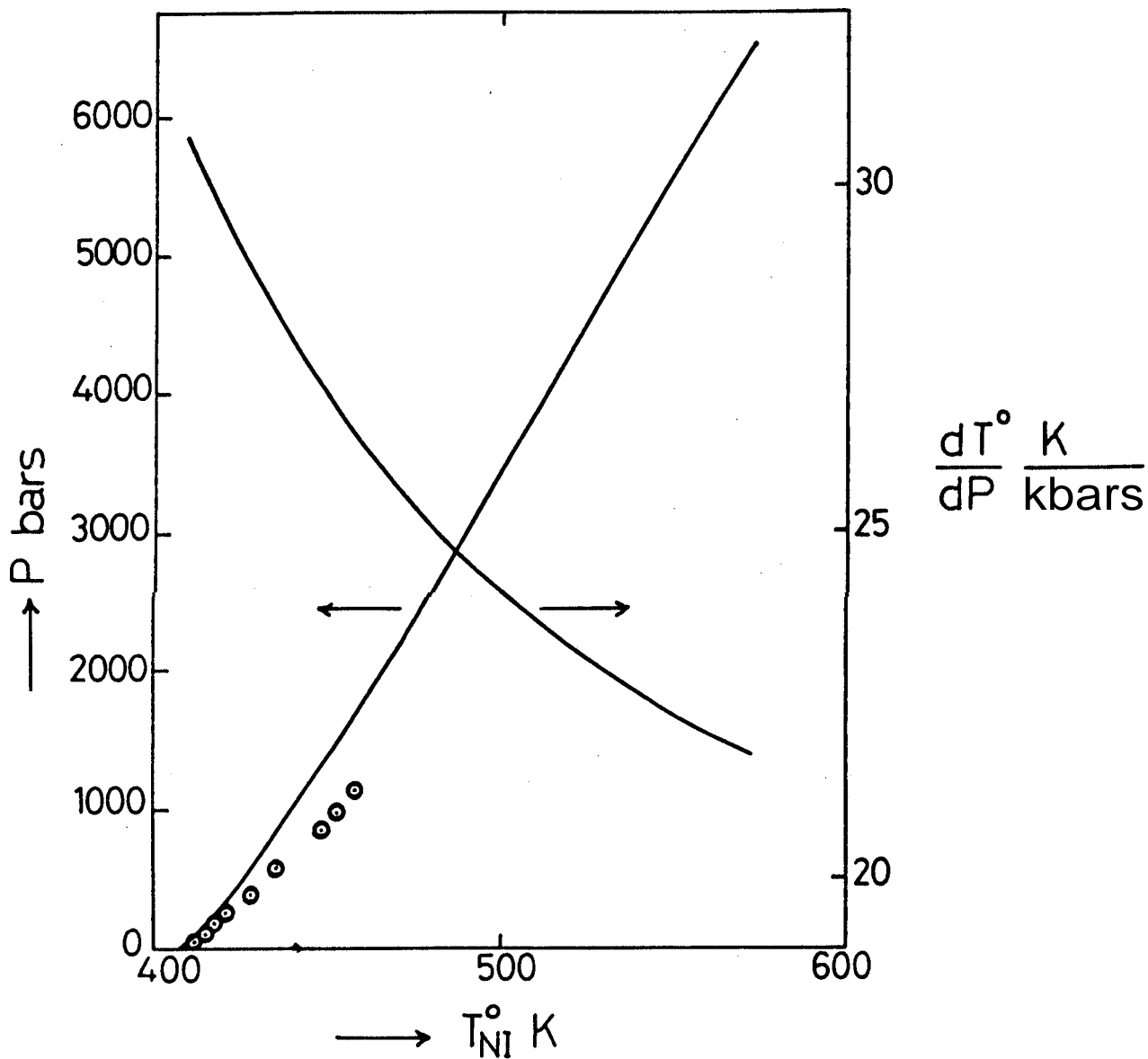


FIG.1: Theoretical variation of P at T_{NI} and of (dT/dP) with the NI transition temperature (T_{NI}). Circles indicate experimental data on PAA.

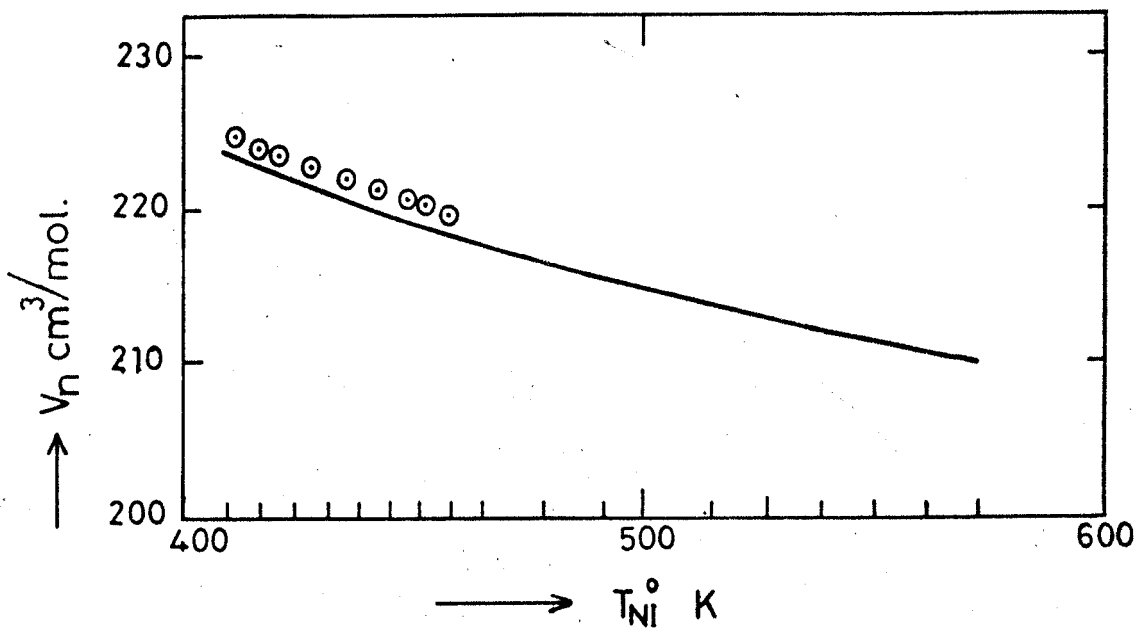


FIG.2: Theoretical variation of the molar volume of the nematic phase with the NI transition temperature. \odot represents the experimental values of PAA by Stishov et al (1976).

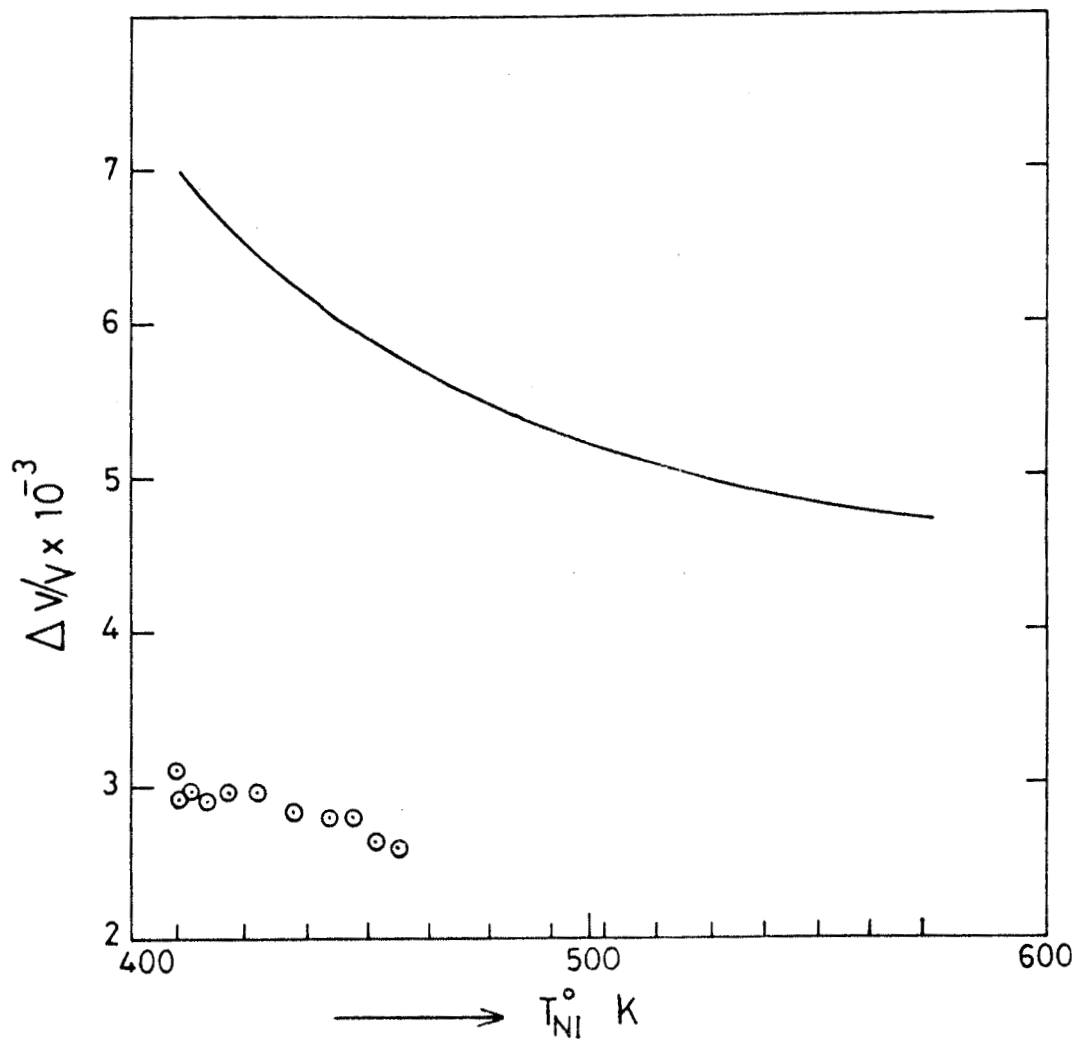


FIG.3: Theoretical variation of the relative change in volume with the NI transition temperature. Circles indicate experimental data on PAA.

varying from 1 to 2 kbar shows that $\langle P_2 \rangle$ is constant along the NI transition. The theoretical value of $\langle P_2 \rangle$ is almost constant, increasing very slightly from 0.499 to 0.503 over the same range of pressures (see table VIb). For 5CB and MBBA, Horn and Faber (1979) observed that $\langle P_2 \rangle$ is not constant along the NI transition. Indeed in this case $\langle P_2 \rangle$ decreases as the pressure is increased, which is a trend opposite to the theoretical trend.

The value of γ evaluated by taking the slope of curve obtained by plotting $\ln T$ vs $\ln V_n$ is found to be ~ 4 (see figure 4) for pressures ranging from 1 bar to 2 kbar, which is again in very good agreement with the result on PAA. However as the pressure is increased say to 6.5 kbar, the theoretical value of γ increases to ~ 6.5 (see figure 4). Experimental values of γ have been obtained for MBBA also but the values quoted by different authors vary from 2.6 to 5.3 (see Horn, 1978; Kuss, 1978 and Keyes and Daniels, 1979).

In conclusion, restricting $|\sin \theta_{1j}|$ to a two term expansion, for purely hard rod fluid, the SPT gives a reasonably good agreement with the experimental result for $x = 2.5$. Including the attractive potential, the best agreement is obtained for $x = 1.75$. Inclusion of

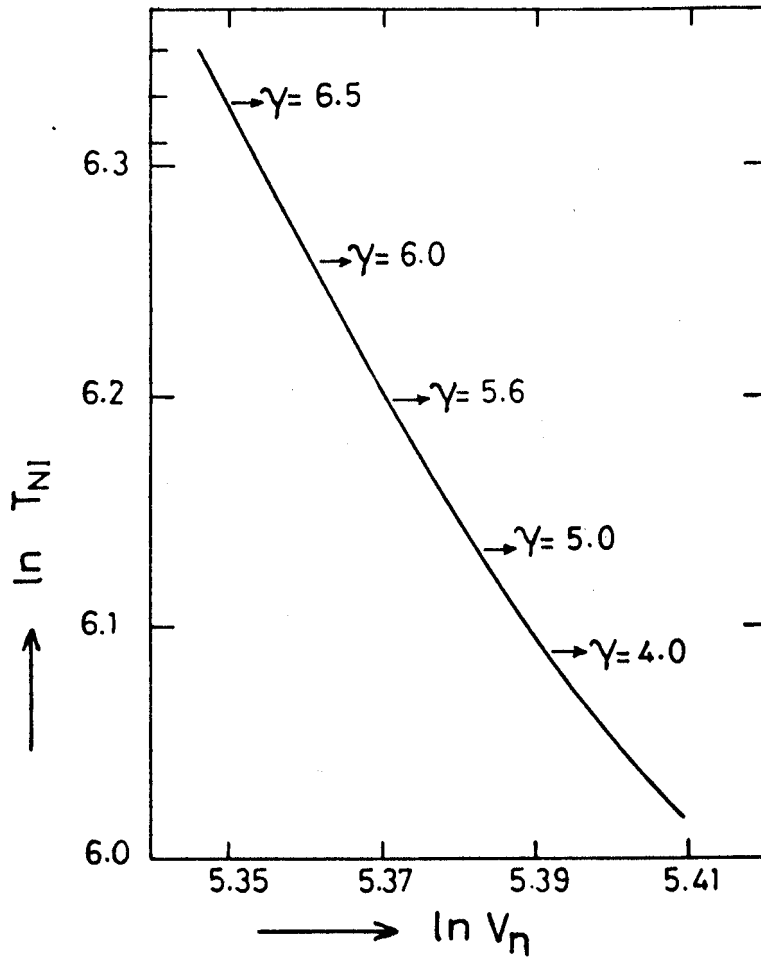


FIG.4: Variation of $\ln V_n$ with $\ln T_{NI}$. γ is the slope of the curve.

higher order terms in $|\sin \theta_{ij}|$ expansion up to $P_2(\cos \theta_{ij})$ will have the principal effect of strengthening the NI transition, &**** it increases the values of $\langle P_2 \rangle$, $\Delta P/\bar{P} = \Delta U/NkT$, dT/dP , etc. For higher pressure, the theory is able to reproduce qualitative behaviour of most of the transition properties like ΔS , ΔU , dP/dT , $\Delta V/v_n$, v_n , etc.

References

- Alben, R. 1971 Mol. Cryst. Liq. Cryst. 13, 193.
- Andrews, P.C. 1975 J. Chem. Phys. 62, 272.
- Arnold, H. 1964 Z. Phys. Chem. 226, 146.
- Baron, B. and Gelbart, W.M. 1978 J. Chem. Phys. 67, 5795.
- Bellemans, A 1968 Phys. Rev. Lett. 21, 527.
- Boehm, R.E. and Martire, D.E. 1978 Mol. Phys. 36, 1
- Boublik, T., Nezbeda, I. and Tynko, O. 1976 Czech. J. Physics 1326, 1081.
- Chandrasekhar, S. and Madhusudana, N.V. 1971 Acta Cryst. A27, 305.
- Chandrasekhar, S. and Madhusudana, N.V. 1973 Mol. Cryst. Liq. Cryst. 24, 179.
- Chandrasekhar, S., Ramaseshan, S., Resharwala, A.S., Sadashiva, B.K., Shashidhar, R. and Surendranath, V. 1973 Proc. Int. Liq. Cryst. Conf., Bangalore, Pramana Suppl. 1, p. 117
- Chandrasekhar, S. and Shashidhar, R. 1979 Advances in Liquid Crystals 4, 83.
- Chandrasekhar, S., Shashidhar, R. and Tara, N. 1970 Mol. Cryst. Liq. Cryst. 10, 337.
- Chandrasekhar, S., Shashidhar, R. and Tara, N. 1972 Mol. Cryst. Liq. Cryst. 12, 245.

- Cotter, M.A. 1974 Phys. Rev. A10, 625.
- Cotter, M.A. 1976 Mol. Cryst. Liq. Cryst. 35, 33.
- Cotter, M.A. 1977a J. Chem. Phys. 66, 1098.
- Cotter, M.A. 1977b Mol. Cryst. Liq. Cryst. 39, 173.
- Cotter, M.A. 1979 'The Molecular Physics of Liquid Crystals', Ed. G.R.Luckhurst and G.W. Gray, Academic Press Inc., London, Chap. 7, p.169.
- Cotter, M.A. and Martire, D.E. 1969 Mol. Cryst. Liq. Cryst. 7, 295.
- Cotter, M.A. and Martire, D.E. 1970a J. Chem. Phys. 52, 1902.
- Cotter, M.A. and Martire, D.E. 1970b J. Chem. Phys. 52, 1909.
- Cotter, M.A. and Martire, D.E. 1970c J. Chem. Phys. 53, 4500.
- de Gennes, P.G. 1974 'The Physics of Liquid Crystals', Oxford University Press.
- Di Marzio, E.A. 1961 J. Chem. Phys. 35, 658.
- Flapper, S.D.P. and Vertogen, G. 1980 Phys. Lett. 79A, 87.
- Flory, P.J. 1956 Proc. Royal Soc. A234, 75.
- Flory, P.J. and Ronca, G. 1979a Mol. Cryst. Liq. Cryst. 54, 289.
- Flory, P.J. and Ronca, G. 1979b Mol. Cryst. Liq. Cryst. 54, 311.
- Gelbart, W.M. and Baron, B. 1977 J. Chem. Phys. 66, 207.
- Hijikuro, N., Miyakawa, K. and Mori, H. 1974 J. Phys. Soc. Japan 37, 928.

- Horn, R.G. 1978 J. de Physique 39, 167.
- Horn, R.G. and Faber, T.E. 1979 Proc. Roy. Soc. London, A368, 199.
- Humphries, R.L., James, P.G. and Luckhurst, G.R. 1972 Faraday Soc. Trans. II 68, 1031.
- Humphries, R.L. and Luckhurst, G.R. 1972 Chem. Phys. Lett. 17, 514.
- Isihara, A. 1951 J. Chem. Phys. 19, 1142.
- Kachinskii, V.N., Ivanov, V.A., Zisman, A.R. and Stishov, S.M. 1979 Sov. Phys. JETP 48, 273.
- Kapustin, A.P. and Bykova, N.F. 1966 Soviet Physics Crystallography 11, 297.
- Karasz, F.E. and Pople, J.A. 1961 J. Phys. Chem. Solids 20, 294.
- Keyes, P.H. and Daniels, W.B. 1979 J. de Physique, 40, C3-380.
- Kimura, H. 1974a J. Phys. Soc. Japan 37, 1204.
- Kimura, H. 1974b Phys. Lett. 47A, 173.
- Kuss, E. 1978 Mol. Cryst. Liq. Cryst. 47, 71.
- Lasher, G. 1970 J. Chem. Phys. 53, 4141.
- Lee, M.A. and Woo, C.W. 1977 Phys. Rev. A16, 750.
- Maier, W. and Saupe, A. 1957 Z. Naturforsch. 12a, 668.
- Maier, W. and Saupe, A. 1958 Z. Naturforsch. 13a, 564.

- Maier, W. and Saupe, A. 1959 Z.Naturforsch 14a, 882.
- Maier, W. and Saupe, A. 1960 Z.Naturforsch. 15a, 287.
- McCull, J.R. 1972 Phys. Lett. 38A, 55.
- McCull, J.R. and Shih, C.S. 1972 Phys.Rev.Lett. 34, 1076.
- Monson, P.A. and Rigby, M. 1978 Mol. Phys. 35, 1337.
- Nezbeda, I. 1976a Czech.J.Chem.Phys. B26, 355.
- Nezbeda, I. 1976b Chem.Phys.Lett. 41, 55.
- Onsager, L. 1949 Ann. N.Y.Acad. Sci. 51, 627.
- Pople, J.A. and Karasz, F.E. 1961 J.Phys.Chem.Solids, 18, 28.
- Reiss, H., Frisch, H.L. and Lebowitz, J.L. 1959 J. Chem. Phys. 31, 369.
- Rigby, M. 1970 J.Chem.Phys. 53, 1021.
- Runnels, L.K. and Colvin, C. 1970 J.Chem.Phys. 53, 4219.
- Shih, Y.M., Lin-Liu, Y.R. and Woo, C.W. 1976 Phys.Rev. A14, 1895.
- Stishov, S.M., Ivanov, V.A. and Kachinskii, V.N. 1976 JETP Lett. 24, 297.
- Vieillard-Baron, J. 1974 Mol. Phys. 28, 809.
- Widom, B. 1963 J.Chem.Phys. 39, 2808.
- Wulf, A. and De Rocco, A.G. 1971 J.Chem.Phys. 55, 12.
- Ypma, J.G.J. and Vertogen, G. 1977a Phys. Lett. 60A, 212.

- Ypma, J.G.J. and Vertogen, G. 1977b Phys.Lett. 61A, 45.
- Ypma, J.G.J. and Vertogen, G. 1977c Phys. Lett. 61A, 125.
- Zwanzig, R. 1963 J. Chem. Phys. 39, 1714.