

CHAPTER V

THE NEMATIC-ISOTROPIC PHASE TRANSITION IN A SYSTEM OF SPHEROCYLINDERS: APPLICATION OF THE ANDREWS METHOD

5.1 Introduction

The importance of both the attractive and the repulsive contributions to the intermolecular potential in determining the properties of nematic phase has been discussed in the previous chapter. As we have mentioned in the previous chapter, there are several computer simulation studies on a fluid of spherocylindrical hard molecules in the isotropic phase. In table I we give the results of computer simulation studies on the equation of state made by Vieillard-Baron (1974), Monson and Rigby (1978), and Cornahan and Starling (1960) for $x = 3, 2$ and 1 respectively and compare them with the results of SPZ. Though the comparison is quite good at the lowest densities, SPZ overestimates the pressure as the density is increased and the discrepancy also increases with increase of density. This trend implies that SPZ calculations would be quite inaccurate in the nematic phase.

It would of course be interesting to extrapolate the essentially 'exact' results of the computer studies

TABLE I

Equation of state in the isotropic phase

(i) Pv_0/kT for $x = 3$

d	Computer simulation ^a	Martha-Cotter ^b	Present calculation
0.54	12.6 ± 0.2	15.56	12.69
0.50	9.0 ± 0.2	10.56	9.04
0.45	5.85 ± 0.07	6.6	5.94
0.40	3.84 ± 0.04	4.17	3.89
0.35	2.51 ± 0.04	2.63	2.53
0.30	1.62 ± 0.04	1.65	1.62

(ii) Pv_0/kT for $x = 2$

0.3351	5.53 ± 0.14		5.55
0.3879	7.57 ± 0.26	7.88	7.53
0.4460	10.74 ± 0.24	11.53	10.75
0.5096	16.80 ± 0.90	18.12	16.35

continued..

Table I continued

(iii) Pv/dkt for $x = 1$

z^0	Computer simulation ^a	SPT ^d	Present calculation
0.10	1.36	1.36	1.36
0.20	1.89	1.89	1.89
0.30	2.68	2.70	2.68
0.40	3.90	3.97	3.90
0.50	5.83	6.04	5.84
0.55	7.23	7.55	7.24
0.60	9.06	9.57	9.10
0.625	10.18	10.82	10.25
0.65	11.48	12.28	11.60
0.67	12.66	13.62	12.83
0.68	13.32	14.36	13.52
0.69	14.01	15.15	14.26
0.70	14.75	15.99	15.05

^a Computer simulation values from Vieillard Baron (1974) for $x = 3$, Manson and Rigby (1978) for $x = 2$, and Carnahan and Starling (1968) for $x = 1$.

^b from M.A. Cotter (1977a).

^c $z = 6d/(\pi\sqrt{2})$

^d SPT results which are the same as Percus-Yevick results are from Andrews (1975).

on the isotropic phase to the region of nematic-isotropic phase transition. We found that the model proposed by Andrews (1975) for calculating the equation of state of an assembly of hard spheres ($x = 1$) can be extended to the case of spherocylinders. Further the extended model provides a suitable scheme for making calculations in the ordered (nematic) phase also.

5.2 The Andrews Method

Andrews developed a scheme for deriving the equation of state for a system of hard spheres by using an intuitive physical interpretation of the 'activity' of a classical fluid. The results obtained for the compressibility factor agreed better than those of SPZ with the Monte Carlo calculations. The scheme can be easily extended to a system of spherocylinders, as we shall see below.

Let the ensemble consist of N molecules which can take n discrete orientations such that N_1 molecules have orientation 1, N_2 molecules have orientation 2, etc. Then choosing the configuration $\{N_1 \dots N_n\}$ so as to maximise the partition function, the maximum term of the ensemble partition function is given by

$$Q_N(N_1, \dots, N_n, V, T) = (N_1! \dots N_n!)^{-1} \int \dots \int d^3r_1 \dots d^3r_N d^3\Omega_1 \dots d^3\Omega_N \exp\{-U_N(r_1 \dots r_N; \Omega_1 \dots \Omega_N)/kT\} \quad (1)$$

where V is the volume, T the temperature, $N = \sum_{k=1}^n N_k$ and U_N is the energy of the N particle system. The chemical potential of the molecule which is in the direction Ω_1 is given by

$$\mu_1/kT = - \frac{\partial \ln Q_N}{\partial N_1} = \ln(s_1 \rho) - \ln a_1^{-1}(\rho, T) \quad (2)$$

where $\rho = N/V$ is the number density, $s_1 = N_1/N$, the fraction of the total number of molecules of 1th type in the medium. Hence $\sum_{i=1}^n s_i = 1$. The reciprocal activity of the 1th species is given by (Andrews, 1975)

$$a_1^{-1} = \frac{1}{Z_N} \int \dots \int \prod_{\alpha=1}^N d^3r_\alpha \int \dots \int \prod_{\alpha=1}^N d\Omega_\alpha \times \exp\left\{-\frac{1}{kT} \sum_{\alpha=1}^N U_{N+1,\alpha}(r_{N+1}, r_\alpha; \Omega_1, \Omega_\alpha)\right\} \times \exp\left\{-U_N(r_1 \dots r_N; \Omega_1 \dots \Omega_N)/kT\right\} \quad (3)$$

where

$$Z_N = \int \dots \int \prod_{\alpha=1}^N d^3r_\alpha \int \dots \int \prod_{\alpha=1}^N d\Omega_\alpha \times \exp\left\{-U_N(r_1 \dots r_N; \Omega_1 \dots \Omega_N)/kT\right\}$$

where r_{N+1} is the position of the $(N+1)$ th molecule in

the i^{th} direction introduced into a system of N molecules and Ω_i represents its angular coordinates, and $\sum_{\alpha=1}^N U_{N+1,\alpha}(x_{N+1}, x_{\alpha}, \Omega_i, \Omega_{\alpha})$ its energy. Assuming that the equilibrium structure is unaffected by the introduction of the new particle, we can write

$$4\pi v_{\Omega_i}^{-1} = \left(d^3 x_{N+1} \exp\left\{-\frac{1}{kT} \sum_{\alpha} U_{N+1,\alpha}(x_{N+1}, x_{\alpha}, \Omega_i, \Omega_{\alpha})\right\} \right) \quad \dots (4)$$

This means that in the fixed, most probable configuration of the N particle system, the added molecule is allowed to wander throughout the system subject to the weighting function given by eq. (4). For hard spherocylinders, $U_{N+1,\alpha}$ is ∞ if the two particles come into contact and zero if they do not. In that case, the reciprocal activity is merely the probability of inserting a spherocylinder without overlapping with any other spherocylinders. Adapting Andrews method (1975) to the present case, we can write it as a product of two terms. The first is the probability that an arbitrarily chosen point x_{N+1} does not lie within the core of any of the N molecules. This is given by

$$(1 - v_0 \rho) = 1 - (4/3 \pi r^3 + \pi r^2 l) \rho \quad (5)$$

where v_0 is the volume of a spherocylinder of radius r and cylindrical length l . Finding such a point ensures that

there is no spherocylinder whose centre lies within a volume v_0 around this point. The second part in calculating a_1^{-1} consists of finding the probability, conditional on the first, that the hole around the given point can actually accommodate the introduced particle. This means that the centre of any other spherocylinder say of k^{th} type should not lie within the excluded volume of the introduced particle, i.e., within the additional volume

$$v_{\text{add}}^{1k} = 8\pi r^2 l + \frac{32}{3} \pi r^3 + 4r l^2 |\sin \theta_{1k}| - (4/3 \pi r^3 + \pi r^2 l) \dots (6)$$

where θ_{1k} is the angle between the long axes of the introduced molecule and the solvent molecule of the k^{th} type.

Following Andrews, the probability P_k that all N_k molecules lie outside v_{add}^{1k} is the N_k^{th} power of the probability that one of them lies outside v_{add}^{1k} . Assuming that the available free volume is independent of the species, we may write for large values of N_k

$$P_k = \left(1 - \frac{v_{\text{add}}^{1k}}{v - \sum_{k=1}^n N_k \omega}\right)^{N_k} \rightarrow \exp\left(-\frac{v_{\text{add}}^{1k} N_k}{v - \sum_{k=1}^n N_k \omega}\right) \quad (7)$$

where $(v - \sum_{k=1}^n N_k \omega)$ is the 'free' volume available to the molecules. ω can be expected to be of the order of the

average volume occupied by a molecule when they are close-packed. Following Andrews, we assume that ω is actually dependent on the density, increasing somewhat as the density is lowered.

The probability that an introduced molecule can be accommodated in the N molecule system is now given by

$$\prod_{k=1}^n P_k = \exp\left(-\frac{\sum_{k=1}^n v_{\text{add}}^{ik} N_k}{V - N\omega}\right) = \exp\left(-\frac{\rho \sum_{k=1}^n v_{\text{add}}^{ik} S_k}{1 - \omega\rho}\right).$$

Hence we can write

$$a_1^{-1} = (1 - v_0\rho) \exp\left(-\frac{\rho \sum_{k=1}^n S_k v_{\text{add}}^{ik}}{1 - \omega\rho}\right). \quad (8)$$

Using the relations (2) and (8), the Gibbs free energy of the hard spherocylinder system can be written as

$$\begin{aligned} G_c^*/NkT &= \langle \mu_1/kT \rangle = \sum_{i=1}^n S_i \mu_1/kT \\ &= \ln[d/(1-d)] + \sum_{i=1}^n S_i \ln S_i + \frac{Ad}{1-(\omega/v_0)d} \end{aligned} \quad (9)$$

where

$$A = \frac{14 + 21(x-1) + 6(x-1)^2 + \frac{4}{\pi} \sum_{i=1}^n \sum_{k=1}^n |\sin \theta_{ik}| S_i S_k}{(3x - 1)}.$$

As in the previous chapter, we expand $|\sin \theta_{ik}|$ in terms of Legendre polynomials. Retaining terms up to $P_{10}(\cos \theta_{ik})$ only and ignoring correlations between the i and k molecules

in the mean field theory, we can write

$$\begin{aligned}
 |\sin \theta_{1k}| \approx & \frac{\pi}{4} - \frac{5\pi}{32} P_2(\cos \theta_1) P_2(\cos \theta_k) \\
 & - \frac{9\pi}{(16)^2} P_4(\cos \theta_1) P_4(\cos \theta_k) \\
 & - \frac{65\pi}{(16)^3} P_6(\cos \theta_1) P_6(\cos \theta_k) \\
 & - \frac{595\pi}{(16)^4} P_8(\cos \theta_1) P_8(\cos \theta_k) \\
 & - \frac{6174\pi}{(16)^5} P_{10}(\cos \theta_1) P_{10}(\cos \theta_k) \quad (10)
 \end{aligned}$$

The pressure is given by

$$\begin{aligned}
 \frac{P^M v_0}{dkT} &= 1 - \frac{1}{\rho} \int_0^\rho \frac{\partial}{\partial \rho'} \left[\sum_{i=1}^n s_i \ln s_i^{-1} \right] \frac{-\rho'}{d} \\
 &= -\frac{1}{d} \ln(1-d) + \frac{Ad}{1-(\omega/v_0)d} - \frac{A}{d} \int_0^d \frac{y dy}{1-(\omega/v_0)y} \quad (11)
 \end{aligned}$$

The Helmholtz free energy

$$\begin{aligned}
 \frac{A_c^M}{NkT} &= \frac{G_c^M}{NkT} - \frac{P^M v_0}{dkT} = \ln d - \frac{(1-d)}{d} \ln(1-d) \\
 &+ \sum_{i=1}^n s_i \ln s_i + \frac{A}{d} \int_0^d \frac{y dy}{1-(\omega/v_0)y} \quad (12)
 \end{aligned}$$

ω can be expected to depend on the density (see Andrews, 1975) and is assumed to be of the form $\omega = \sum_{n=0}^{\infty} \omega_n \rho^n$.

For the close packed solid,

$$\omega_{\text{solid}} = \frac{1}{\rho_0} = \sqrt{3} \times 2 v_0 (x-1 + \sqrt{2/3}) / [\pi(x - \frac{1}{3})]. \quad (13)$$

ω_{solid} is the high density limit. To calculate the low density limit of ω , the pressure relation in the isotropic phase, viz.,

$$\left[\frac{P^* v_0}{dkT} \right]_{\text{iso}} = -\frac{1}{d} \ln(1-d) + \frac{A_0 d}{1-\omega\rho} - \frac{A_2}{d} \int_0^d \frac{y dy}{1 - \frac{\omega}{v_0} y} \quad (14)$$

where $A_0 = (6x^2 + 9x - 1)/(3x - 1)$, is expanded in powers of ρ . Andrews used terms up to the third virial coefficient in his calculations on spheres, i.e., he assumed that $\omega = \omega_0 + \omega_1 \rho$. However, by using this restricted expansion, the compressibility factors $P^* v_0 / kT$ of the isotropic phase of spherocylinders are not in good agreement with the computer calculations for $x = 3$ (Vicillard-Baron, 1974) ^{and} $x = 2$ (Manson and Rigby, 1978). Hence we took the higher order terms in the expansion of ω and found that 7 terms of the ω expansion are sufficient to give reasonable agreement with the computer calculations. To calculate the coefficients ω_n , $n = 0, 1, \dots, 6$, we proceed as follows:

$$\omega_{\text{solid}} = \sum_{n=0}^6 \omega_n \rho_0^n \quad (15)$$

where ω_{solid} and ρ_0 are given by the relation (13).

The pressure relation (14) is expanded in powers of ρ and the first eight virial coefficients (i.e., $B_1, B_2, B_3, B_4 \dots B_8$) are obtained in terms of ω_n :

$$B_1 = 1$$

$$B_2 = (1 + \Lambda_0)/2 \\ = (3x^2 + 6x - 1)/(3x - 1) \text{ which is an exact value}$$

$$v_0 B_3 = (v_0 + 2\Lambda_0 \omega_0)/3$$

$$v_0^2 B_4 = (v_0^2 + 3\Lambda_0 \omega_1 + 3\Lambda_0 \omega_0^2)/4$$

$$v_0^3 B_5 = (v_0^3 + 4\Lambda_0 \omega_2 + 8\Lambda_0 \omega_0 \omega_1 + 4\Lambda_0 \omega_0^3)/5$$

$$v_0^4 B_6 = (v_0^4 + 5\Lambda_0 \omega_3 + 10\Lambda_0 \omega_0 \omega_2 + 15\Lambda_0 \omega_0^2 \omega_1 \\ + 5\Lambda_0 \omega_1^2 + 5\Lambda_0 \omega_0^4)/6$$

$$v_0^5 B_7 = (v_0^5 + 6\Lambda_0 \omega_4 + 12\Lambda_0 \omega_0 \omega_3 + 12\Lambda_0 \omega_1 \omega_2 \\ + 18\Lambda_0 \omega_0^2 \omega_2 + 18\Lambda_0 \omega_0 \omega_1^2 + 24\Lambda_0 \omega_0^3 \omega_1 + 6\Lambda_0 \omega_0^5)/7$$

$$v_0^6 B_8 = (v_0^6 + 7\Lambda_0 \omega_5 + 14\Lambda_0 \omega_1 \omega_3 + 14\Lambda_0 \omega_0 \omega_4 + 21\Lambda_0 \omega_0^2 \omega_3 \\ + 7\Lambda_0 \omega_2^2 + 42\Lambda_0 \omega_0 \omega_1 \omega_2 + 7\Lambda_0 \omega_1^3 + 28\Lambda_0 \omega_2 \omega_0^3 \\ + 42\Lambda_0 \omega_0^2 \omega_1^2 + 35\Lambda_0 \omega_0^4 \omega_1 + 7\Lambda_0 \omega_0^6)/8$$

The last 6 equations along with eq.(15) are solved for $\omega_n, n = 0, 1, \dots, 6$ as functions of x and the virial coefficients. Indeed, utilizing the above expressions

leads to a much better agreement with the equation of state of the hard sphere fluid than that given by the original calculations of Andrews (1975). Nazbada (1976) has proposed the following (essentially empirical) analytical expression for calculating the virial coefficients of a fluid of hard spherocylinders.

$$B_n = (4n^2 - 13n + 13)\epsilon + (-2n^2 + 11n - 14)\epsilon^2 + (3n - n^2 - 1) \quad (17)$$

where $\epsilon = x(x + 1)/(3x - 1)$. The first 6 virial coefficients given by the above equation are in very good agreement with ^{the} Monte Carlo calculations made by Hanson and Rigby (1978) for $x \leq 3$. Furthermore, the expression can be utilised to calculate the virial coefficients for any arbitrary value of x .

It is obvious that the Andrews method is not a fully self-contained theory of the liquid phase, since it does not give an independent method for the calculation of the virial coefficients. However, it does provide a convenient scheme for calculating the properties near the nematic-isotropic phase transition point, utilising the available computer calculations in the isotropic phase. The equation of state in the isotropic phase of hard spherocylinders with $x = 2$ and 3 have been given in table I. As

is to be expected, the results are in very good agreement with computer calculations.

As we have already discussed in the previous chapter, a hard spherocylinder fluid would have $\gamma = \infty$. We will now introduce an attractive potential to the Andrews model exactly as has been done in the case of SPT.

As in the previous chapter, we derive all the thermodynamic functions of the system by introducing a mean field attractive potential of the form

$$\Psi_1 = -\nu_0 \rho - \nu_2 \rho \langle P_2 \rangle P_2(\cos \theta) \quad (19)$$

where ν_0 and ν_2 are the strengths of the isotropic and anisotropic interactions respectively. Taking the limit of continuous orientations with the corresponding distribution function denoted by $F(\cos \theta)$, the configurational Gibb's free energy takes the form

$$\frac{G_c}{NkT} = \frac{G_c^h}{NkT} - \frac{\nu_0 d}{v_0 kT} - \frac{\nu_2 d}{v_0 kT} \langle P_2 \rangle^2. \quad (20)$$

The internal energy of the system is given by

$$\frac{U}{N} = -\frac{1}{2} \frac{\nu_0 d}{v_0} - \frac{1}{2} \frac{\nu_2 d}{v_0} \langle P_2 \rangle^2. \quad (21)$$

The pressure is given by

$$\frac{Pv_0}{kT} = \frac{P^h v_0}{kT} - \frac{1}{2} \frac{\nu_0 d^2}{v_0 kT} - \frac{1}{2} \frac{\nu_2 d^2}{v_0 kT} \langle P_2 \rangle^2. \quad (22)$$

Substituting for G_o^M and P^M from the relations (9) and (11), we can obtain the configurational Gibbs free energy and the pressure relations. The Helmholtz free energy is given by

$$\frac{A_o}{NkT} = \ln\left(\frac{d}{1-d}\right) + \frac{\ln(1-d)}{d} + \langle \ln P(\cos \theta) \rangle + \frac{A}{d} \int_0^d \frac{y dy}{1 - \sum_{n=0}^6 \frac{\omega_n y^{n+1}}{v_o^{n+1}}} - \frac{1}{2} \frac{v_o^d}{v_o kT} - \frac{1}{2} \frac{v_o^d}{v_o kT} \langle P_2 \rangle^2 \quad (23)$$

The normalised distribution function $F(\cos \theta)$ which minimizes this Helmholtz free energy is given by

$$F(\cos \theta) = \frac{\exp\left\{\frac{v_o^d}{kT} \langle P_2 \rangle P_2(\cos \theta) + \frac{48(x-1)^2}{d(3x-1)} \chi(\cos \theta)\right\} \int_0^d \frac{y dy}{1 - \sum_{n=0}^6 \frac{\omega_n y^{n+1}}{v_o^{n+1}}}}{\int_0^d \exp\left\{\frac{v_o^d}{kT} \langle P_2 \rangle P_2(\cos \theta) + \frac{48(x-1)^2}{d(3x-1)} \chi(\cos \theta)\right\} \int_0^d \frac{y dy}{1 - \sum_{n=0}^6 \frac{\omega_n y^{n+1}}{v_o^{n+1}}}} d(\cos \theta) \quad \dots (24)$$

where

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

and the self-consistency relation reads as follows:

$$\langle P_{2n} \rangle = \int_0^1 P_{2n}(\cos \theta) F(\cos \theta) d(\cos \theta). \quad (25)$$

For the sake of completeness, we give the following relations for the second derivatives. (The detailed expressions are given in appendix IV):

$$\beta = \left[P \left(\frac{\partial P}{\partial \rho} \right)_{N,T} \right]^{-1}, \quad (26)$$

$$\alpha = \frac{1}{V} \left[\frac{\partial V}{\partial T} \right]_{N,T}, \quad (27)$$

$$\frac{C_V}{Nk} = \left[\frac{\partial (U/Nk)}{\partial T} \right]_{N,V}, \quad (28)$$

$$\frac{C_P}{Nk} = \frac{C_V}{Nk} + \frac{T\alpha^2}{\rho k\beta}. \quad (29)$$

5.3 Results and Discussion

a. Hard rod fluid

For a system of hard spherocylinders, $\nu_0 = \nu_2 = 0$. As in the previous chapter, we have studied the transition properties as functions of x by approximating the expansion of $|\sin \theta_{1j}|$ to different orders.

Restricting the expansion of $|\sin \theta_{1j}|$ (eq. 10) to the first two terms only, calculations are made for x ranging from 1.5 to 3.0. The transition properties like $\langle P_2 \rangle$, $d_{nem} \Delta \rho / \bar{\rho}$ [$\bar{\rho} = (\rho_{nem} + \rho_{iso})/2$], entropy change

ΔS , dT/dP , the second derivatives of the chemical potential like Q_p , Q_v , α and β are given in table II. It is seen that most of the present results are indeed comparable to experimental data (given in table IV) for $x = 3$, whereas in SPT such a comparison can be made for $x = 2.5$.

Including terms up to $P_{10}(\cos \theta_{1j})$ in the expansion of $|\sin \theta_{1j}|$, we find that (see table III) as in the case of SPT, $\langle P_2 \rangle$, $\Delta P/\bar{P}$ and $\Delta S/kx$ increase substantially whereas dT/dP increases and Pv_0/kT decreases slightly. The second derivatives have not been calculated since the calculations become tedious after including higher order terms in the expansion of $|\sin \theta_{1j}|$. Most of the results are now comparable to experimental data on PAA, for $x = 3$, whereas in the case of SPT $x \approx 2.5$ would give a reasonable agreement with the data. Hence the Andrews model gives a somewhat improved length to breadth ratio even in the case of hard spherocylinders.

b. System superposed with an attractive potential

Taking into account the attractive part of the potential, calculations have been made for different values of μ by retaining terms up to $P_2(\cos \theta_{1j})$ and $P_{10}(\cos \theta_{1j})$ in the expansion of $|\sin \theta_{1j}|$ (see eq. 10). As in SPT, we

TABLE II

Results at T_{NI} for hard spherocylinders

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

x	3.0	2.5	2.0	1.5
$T_{NI}^* K$	409	409	409	409
$\langle P_2 \rangle$	0.4718	0.4605	0.4464	0.4291
d_{nem}	0.6126	0.6753	0.7483	0.7991
d_{iso}	0.6083	0.6726	0.7473	0.7990
$\Delta \rho / \bar{\rho}$	0.0071	0.0039	0.0014	0.0001
$\Delta S / Nk$	0.2740	0.2665	0.2123	0.1251
$(dT/dP)^* K / kbar$	70.28	58.57	14.08	1.664
Pv_0 / kT	23.71	44.84	118.42	1001.5
$(\sigma_p / Nk)_{nem}$	9.400	11.076	14.308	16.464
$(\sigma_p / Nk)_{iso}$	6.869	8.696	12.350	16.007
$\alpha_{nem} \times 10^4 / ^\circ K$	5.855	4.127	2.175	0.1410
$\alpha_{iso} \times 10^4 / ^\circ K$	4.249	3.227	1.875	1.1371
$\beta_{nem} \times 10^{12} \frac{cm^2}{dyne}$	40.591	15.520	3.011	0.0103
$\beta_{iso} \times 10^{12} \frac{cm^2}{dyne}$	29.455	12.137	2.595	0.0010

TABLE IIIResults at T_{NI} for hard spherocylinders

$$|\sin \theta_{1j}| \approx \sum_{n=0}^5 a_{2n} P_{2n}(\cos \theta_{1j})$$

x	3.0	2.5	2.0
T_{NI} °K	409	409	409
$\langle P_2 \rangle$	0.6128	0.5945	0.5730
$\langle P_4 \rangle$	0.2857	0.2679	0.2479
$\langle P_6 \rangle$	0.1121	0.1014	0.0899
$\langle P_8 \rangle$	0.0393	0.0343	0.0291
$\langle P_{10} \rangle$	0.0127	0.0107	0.0087
d_{nem}	0.6096	0.6721	0.7457
d_{iso}	0.6017	0.6674	0.7439
$\Delta\rho/\bar{\rho}$	0.0129	0.0071	0.0025
$\Delta S/k$	0.4835	0.4423	0.3767
(dT/dP) °K/kbar	73.704	39.886	14.683
Pv_0/kT	22.613	41.786	113.514

again fix $T_{NI} = 409^{\circ}\text{K}$ and d_{nem} (at T_{NI}) = 0.62.

Various transition properties like $\langle P_{2n} \rangle$, $\Delta\rho/\bar{\rho}$, $\Delta S/k$, $\Delta U/kT$, dT/dP , C_p , C_v , α , β , etc. are calculated as functions of x .

Results obtained by including terms only up to $P_2(\cos \theta_{ij})$ in the $|\sin \theta_{ij}|$ expansion are listed in table IV. It is obvious from table IV that the calculations based on the extended Andrews model can be carried out up to $x = 2.9$, while similar calculations based on SPT could only be made up to $x = 2.45$. The trends of different physical quantities as functions of x are similar to those given by SPT. For example, $\Delta U/kT$ again decreases slowly as x increases. But in the case of the Andrews model, $\gamma = 4$ P us $x = 2.075$, which is a reasonable improvement over $x = 1.75$ of SPT. Further, it is obvious from table IV that the new theoretical values of the second derivatives, viz., C_v , C_p , α and β are considerable improvements over those of SPT. In fact they come quite close to the experimental data given by Maier and Saupe (1960), Arnold (1964), Kupustina and Bykova (1966). However, the volume change at the transition, $\Delta\rho/\bar{\rho}$ and ΔU , still remain somewhat larger than the experimental values. The latter result is a consequence of using the mean field approximation (see Chandrasekhar and Madhusudana, 1971,

TABLE IV: Results for a system including an attractive potential: $\text{lain } \theta_{ij} \approx \sum_{n=0}^{\infty} P_{2n}(\cos \theta_{ij})$

$x = \frac{1}{2r} + 1$	2.90	2.50	2.075	2.05	2.00	1.50	1.00	Experimental values
ψ_0/ψ_2	589.46	62.72	30.79	29.86	28.15	18.02	15.99	
$\psi_2/v_0 k$	92.09	833.23	1610.60	1655.12	1743.53	2552.15	2998.85	
$T_{NI} \cdot K$	409	409	409	409	409	409	409	409
$\langle P_2 \rangle$	0.4915	0.4713	0.4549	0.4541	0.4524	0.4397	0.4332	0.36
d_{nem}	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
d_{iso}	0.61329	0.61483	0.61617	0.61624	0.61639	0.61767	0.61875	
$\Delta P/\bar{p}$	0.01088	0.0084	0.0062	0.0061	0.0058	0.0038	0.0021	0.0035
γ_{nem}	107.260	9.933	4.022	3.850	3.533	1.632	1.000	4.0
γ_{iso}	102.617	9.617	3.939	3.773	3.467	1.621	1.000	
$\Delta U/NkT$	0.4621	0.4703	0.4846	0.4855	0.4874	0.4947	0.5000	0.17
$\Delta S/Nk$	0.4621	0.4703	0.4846	0.4855	0.4874	0.4947	0.5000	
$(dT/dP) \cdot K/kbar$	64.380	48.000	34.956	34.329	32.513	20.982	11.837	48
$(C_p/Nk)_{nem}$	16.984	20.487	21.475	21.461	21.414	20.074	17.882	72.9 (at $T=T_{NI}-1$)
$(C_p/Nk)_{iso}$	10.468	9.636	8.762	8.711	8.608	7.578	6.319	
$(C_v/Nk)_{nem}$	0.0052	0.476	1.982	2.105	2.363	5.563	8.086	
$\alpha_{nem} \times 10^4 / ^\circ K$	9.793	10.018	9.381	9.322	9.200	7.633	5.338	12.65 (at $T=T_{NI}-1$)
$a_{iso} \times 10^4 / ^\circ K$	6.288	5.997	5.734	5.720	5.690	5.335	4.259	
$\beta_{nem} \times 10^{12} \frac{cm^2}{dyne}$	61.102	55.146	49.634	49.366	48.845	44.145	31.985	82.3 (at $T=T_{NI}-1$)
$\beta_{iso} \times 10^{12} \frac{cm^2}{dyne}$	41.977	41.377	41.524	41.546	41.592	41.446	31.618	

Cotter, 1977). Short-range order effects in the medium have to be taken into account to correct for the discrepancies.

Including terms up to $P_{10}(\cos \theta_{ij})$ in the expansion of $|\sin \theta_{ij}|$, the results obtained for various transition properties are given in table V. As was noticed for the purely hard rod model, the inclusion of higher order terms to increase the accuracy of the value of $|\sin \theta_{ij}|$ also increases the value of $\langle P_2 \rangle$, $\Delta\rho/\bar{\rho}$, $\Delta U/NkT$, $\Delta S/Nk$ and dT/dP . For $x = 1$, the inclusion of higher order terms does not affect any of the transition properties, since there is no shape anisotropy. For $x = 2.9$, the value of $\langle P_2 \rangle$ increases by $\sim 30\%$; $\Delta\rho/\bar{\rho}$ increases by $\sim 84\%$; dT/dP increases slightly by $\sim 4\%$. As in SPT, $\Delta U/NkT$ now increases with x , - a trend opposite to that obtained with the two term expansion. Again second derivatives of the chemical potential are not calculated in the present case. $x \simeq 2.05$ still gives a reasonable agreement with the experimental data.

in the previous chapter

In conclusion, our calculations have shown that SPT leads to very reasonable results which can be compared with experimental data on PAA for $x = 1.75$. We can improve upon x as well as other results, particularly the second derivatives, by using an extension of the Andrews method along

TABLE V: Results for a system including an attractive potential $|\sin \theta_{1j}| \approx \sum_{n=0}^5 a_{2n} P_{2n}(\cos \theta_{1j})$

x	2.90	2.50	2.075	2.05	2.00	1.50	1.00
ν_{obs}	761.24	63.974	31.019	30.08	28.34	18.05	15.99
$\nu_2/\nu_0 k$	68.834	802.860	1587.255	1632.412	1722.137	2544.137	2998.945
$\Sigma_{HI}^* k$	409	409	409	409	409	409	409
$\langle P_2 \rangle$	0.6400	0.5660	0.5059	0.5029	0.4972	0.4533	0.4333
$\langle P_4 \rangle$	0.3128	0.2336	0.1786	0.1761	0.1714	0.1367	0.1223
$\langle P_6 \rangle$	0.1287	0.0787	0.0496	0.0484	0.0462	0.0309	0.0252
$\langle P_8 \rangle$	0.0473	0.0232	0.0117	0.0113	0.0105	0.0057	0.0041
$\langle P_{10} \rangle$	0.0167	0.0063	0.0025	0.0024	0.0021	0.0009	0.0005
d_{nem}	0.62	0.62	0.62	0.62	0.62	0.62	0.62
d_{1so}	0.60767	0.61220	0.61515	0.61529	0.61554	0.61751	0.61875
$\Delta P/\bar{P}$	0.0201	0.0126	0.0078	0.0076	0.0072	0.0040	0.0020
$\Delta U/NkT$	0.8112	0.6844	0.5996	0.5958	0.5886	0.5361	0.5001
$\Delta S/Nk$	0.8288	0.6954	0.6064	0.6024	0.5948	0.5396	0.5019
$(dT/dP)^* k/\text{bar}$	67.228	50.609	35.318	34.556	33.056	20.098	10.837

with the computer results on hard spherocylinders in the isotropic phase. However, as in the original Maier-Saupe model in which only the attractive part of the potential was taken into account, the order parameter at T_{NI} as well as the heat of transition remain considerably higher than the experimental values. For cylindrically symmetric rods that we have considered here, inclusion of short-range effects in the development of the theory can be expected to improve the predictions just as inclusion of such effects improves the Maier-Saupe theory (see N.V. Madhusudana et al, 1977).

However, considering a nematogenic molecule as a cylindrically symmetric rod is at best an approximation. Most real nematogens have a lower symmetry, and, of late, there have been some attempts to take into account deviations from cylindrical symmetry in the mean field approximation. Alben (1972, 1973) showed that such deviations can account for the lowering of order parameter at T_{NI} . This result has been confirmed by more recent calculations due to Straley (1974) and Luckhurst et al (1975) who used a suitable extension of the Maier-Saupe model. Very recently, Galbart and Barbov (1979) have discussed a theory in which the shape-factor has been taken into account in a model with a few fixed orientations. They have again

showed that the results based on cylindrically symmetric rods can be improved. Developing a model in which such molecules are allowed to take all possible orientations and with the appropriate attractive potential superposed on them is obviously of great interest.

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