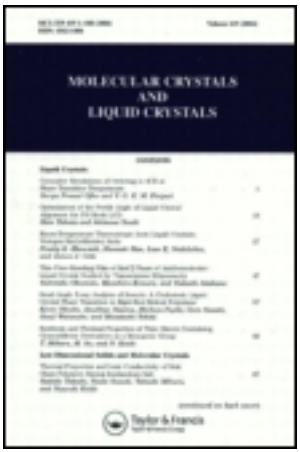

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The Nematic-Isotropic Phase Transition: Application of the Andrews Method

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The Nematic-Isotropic Phase Transition: Application of the Andrews Method

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We have extended the Andrews method to derive the thermodynamic properties of an ensemble of spherocylinders. In the case of *hard* spherocylinders, by using the virial coefficients of the isotropic phase which agree with the results of recent computer simulation studies, we have determined several properties near the nematic-isotropic phase transition point in the mean field approximation. Including the attractive part of the potential, the values derived from the model are in reasonably good agreement with experimental data and in fact show considerable improvements over the currently available model calculations. In particular, the results are compared with those based on the scaled particle theory.

1 INTRODUCTION

The importance of both the attractive and repulsive contributions to the intermolecular potential in determining the properties of nematic phase has been recognised for the past few years.[1–11] Of late, there have been several attempts to develop models of nematic liquid crystals including both the factors.[12–28] Of these, the scaled particle theory as developed recently by Martha Cotter[13] appears to be the most significant, since it considers a continuous distribution of anisotropic molecules, assumed to be of the form of spherocylinders of realistic length to breadth ratios (x). Cotter has made calculations in the mean field approximation for spherocylinders with $x = 3$. She found that the qualitative features of the N–I transition could be reproduced. However, comparing the theoretical results with the data on paraazoxyanisole (PAA) for which all the relevant experimental values are available, it was found that the theoretical packing fraction was too low and further, the calculated values of the second derivatives of the

thermodynamic potential, viz., specific heat (C_p and C_v), coefficient of thermal expansion α, etc., were significantly higher than the experimental values.

There have been several computer simulation studies[29–34] on systems of hard spherocylinders with $x = 2$ and 3. The equation of state as well as several virial coefficients have been evaluated in such studies. The calculations have all been made in the isotropic phase of such a system, somewhat away from the nematic-isotropic transition point. (As the density approaches the value at the phase-transition, the calculations become more and more time consuming and impractical.) A comparison between the results of scaled particle theory (SPT) on hard spherocylinders and those of computer studies shows that while SPT gives reasonably good values at low densities, it overestimates the pressure as the density is increased. The discrepancy also increases at higher densities. Consequently, we may expect that even for a system of *hard* spherocylinders, the results of SPT in the nematic state are not likely to be accurate.

It would of course be interesting to extrapolate the essentially "exact" results of the computer studies to the region of nematic-isotropic phase transition. We found that the model proposed by Andrews[35] for calculating the equation of state of an assembly of hard spheres can be extended to the case of spherocylinders. Further, the extended model provides a suitable scheme for making calculations in the ordered (nematic) phase also.

In the next section of this paper, we present some results of our calculations based on the SPT of Martha Cotter[13] for different values of the length to breadth ratio x. As we shall see, for a value of $x \simeq 1.75$, the packing fraction at the nematic-isotropic transition and many other properties agree reasonably well with experimental data. However the second derivatives still do not agree with experiment; the calculated values are significantly lower than the data on PAA.

In Section 3, we will present an extension of the Andrews model to the case of spherocylinders. We have made calculations in the mean field approximation, both for hard spherocyclinders as well as for spherocylinders with a specific form of attractive potential between them. The results of all the calculations are compared with the experimental data on PAA.

2 CALCULATIONS BASED ON SPT

We used the theoretical expressions derived by Martha Cotter[13] in all our calculations. Assuming that the attractive potential is of the form[36]

$$u_i = -\vartheta_0 \rho - \vartheta_2 \rho \eta P_2(\cos \theta_i), \tag{1}$$

where

$$\eta = \frac{\int_0^{\pi} P_2(\cos\theta)\exp\left\{\left[\Lambda(\rho) + \frac{\vartheta_2\rho}{kT}\right]\eta P_2(\cos\theta)\right\}\sin\theta\, d\theta}{\int_0^{\pi}\exp\left\{\left[\Lambda(\rho) + \frac{\vartheta_2\rho}{kT}\right]\eta P_2(\cos\theta)\right\}\sin\theta\, d\theta}, \tag{2}$$

$$\Lambda(\rho) = 5\pi Rd\left[\frac{1 - (1-q)d/3}{8(1-d)^2}\right], \tag{3}$$

$d = v_0\rho$; $R = 6(x-1)^2/\pi(3x-1)$; $q = 2/(3x-1)$; ϑ_0 and ϑ_2 are the strengths of the isotropic and the anisotropic parts of the potential, ρ is the number density, v_0 is the molecular volume and d is the packing fraction. The pressure P is given by the relation

$$Pv_0/kT = \pi^* - \frac{1}{2}\frac{d^2}{kT}\left[\frac{\vartheta_0}{v_0} + \frac{\vartheta_2}{v_0}\eta^2\right]$$

where

$$\pi^* = \frac{d[1 + d + 2/3(1 + q - q^2/2)d^2 + \pi rd/2\{1 + (1+2q)d/3\}(1 - \frac{5}{8}\eta^2)]}{(1-d)^3}$$

The chemical potential μ_c is given by

$$\frac{\mu_c}{kT} = \langle \ln 4\pi f(\Omega)\rangle + \ln\{\rho/(1-d)\} + 6d[1 + \pi R(1 - 5/8\eta^2)/6]/(1-d) + 4d^2(1 + q/2)[1 - q/4 + \pi R(1 - 5/8\eta^2)/4]/(1-d)^2 + \pi^* - \left(\frac{\vartheta_0}{v_0} + \frac{\vartheta_2}{v_0}\eta^2\right)d/kT \tag{5}$$

For a system of hard spherocylinders, $\vartheta_0 = \vartheta_2 = 0$. The results of calculations on this system are shown in Table I and will be discussed later. In such a case the coefficient γ defined as

$$\gamma = \left[\frac{\partial \ln T}{\partial \ln \rho}\right]_{\eta = \text{constant}} \tag{6}$$

is infinity since the order parameter of the system does not directly depend on temperature. (γ is a measure of the relative importance of volume compared to that of temperature in determining the variation of η of the medium near T_{NI}.) On the other hand, if we consider only the attractive potential given by the Eq. (1), and do not take into account the hard-rod feature of the molecules, $\gamma = 1$. The experimental value is $\gamma = 4$ for PAA.[37,38] This shows

TABLE I

Results for hard spherocylinders

$x = \frac{1}{2r} + 1$	3.0		2.5		2.0		1.5	
	Andrew's method	SPT	Andrew's method	SPT	Andrew's method	SPT	Andrew's method	SPT
$T^{\circ}_{NI}K$	409	409	409	409	409	409	409	409
$\langle P_2(\cos\theta)\rangle$	0.4718	0.4914	0.4605	0.4799	0.4464	0.4648	0.4291	0.4454
$(v_0\rho)_{nem}$	0.6126	0.5588	0.6753	0.6147	0.7483	0.6884	0.7991	0.7964
$(v_0\rho)_{iso}$	0.6083	0.5531	0.6726	0.6105	0.7473	0.6860	0.7991	0.7957
$\Delta\rho/\rho$	0.0071	0.0104	0.0039	0.0068	0.0014	0.0035	0.0001	0.0009
$(C_P/Nk)_{nem}$	9.400	8.890	11.076	10.3296	14.308	13.563	16.464	26.336
$(C_P/Nk)_{iso}$	6.869	5.795	8.696	7.168	12.350	10.313	16.007	22.960
$\alpha_{nem} \times 10^4/^{\circ}C$	5.855	6.863	4.127	5.343	2.175	3.842	0.1410	2.069
$\alpha_{iso} \times 10^4/^{\circ}C$	4.249	4.421	3.227	3.745	1.875	2.911	0.1371	1.802
$\beta_{nem} \times 10^{12}$ cm^2/dyne	40.591	64.451	15.520	31.705	3.011	10.774	0.01031	1.392
$\beta_{iso} \times 10^{12}$ cm^2/dyne	29.455	41.576	12.137	21.850	2.595	8.164	0.001002	1.212

the necessity for incorporating *both* the attractive and hard-rod features in the theory.

Apart from the length to breadth ratio x, there are essentially two adjustable parameters in the theory, viz., the parameters of the attractive potential, ϑ_0 and ϑ_2. ϑ_0 is the parameter describing the average or isotropic attraction between the centres of mass of the spherocylinders, while ϑ_2 is the parameter describing the anisotropic part of the attractive potential. They may be assumed to arise essentially from the dipole-dipole part of the dispersion forces. In any case, ϑ_0 and ϑ_2 are both only "effective" parameters since the potential has been taken to be proportional to the density (see Eq. 1) to satisfy thermodynamic consistency.[36]

We have made calculations for various values of x. The criterion adopted for selecting the values of ϑ_0 and ϑ_2 was to adjust T_{NI} and the packing fraction (d_{nem}) of the nematic phase at T_{NI} to 409°K and 0.62 which are the experimental values for PAA. At T_{NI}, the pressures of the nematic and isotropic phases were adjusted to be equal to the atmospheric pressure. The chemical potentials of the two phases were also adjusted to be the same. The results of calculations on the order parameter η at T_{NI}, the density change $\Delta\rho/\rho$, the heat of transition are shown in Table II for various values of x. The second derivatives, viz., the specific heat at constant pressure C_p, the specific heat at constant volume C_v, the coefficient of thermal expansion α, and the isothermal compressibility β are shown at T_{NI} for both the N and I phases. Further, the coefficient γ is also listed in the table.

$x = 1$ gives a spherical shape to the molecules, i.e., there is no geometrical anisotropy. In this case again $\gamma = 1$. As the value of x is increased, γ value also increases, first slowly and then very rapidly. The ratio of ϑ_0/ϑ_2 also increases in a similar manner. C_p decreases with x, whereas α and β are not influenced very much by changing x. The order parameter at T_{NI} increases slowly with x. Calculations are not possible beyond $x \simeq 2.45$ if we want to retain the value of packing fraction $d = 0.62$ at $T_{NI} = 409$°K. Martha Cotter had to lower the value of d to 0.445 to be able to calculate for $x = 3$ and adjust ϑ_0 and ϑ_2 suitably to get $\gamma = 4$. Further in this case, the second derivatives turn out to be too high[13] compared to the experimental data.

If we choose to retain the correct value of the packing fraction (Table II), we see that $x = 1.75$ yields $\gamma \simeq 4$. It is also seen that the overall agreement with experiment is reasonably good for this value of x. In this case, however, the second derivatives are all underestimated, though they are closer to the experimental values compared to the results for $x = 3$. Returning to the hard spherocylinder fluid, we give in Table III the comparison between the equation of state as got by computer simulation studies and results of SPT in the *isotropic* phase for $x = 1$, 2, and 3. ($x = 1$ defines a system of hard spheres). Though the comparison is quite good at the lowest densities, the

TABLE II

Results of scaled particle theory for different values of x

$x = \frac{1}{2r} + 1$	2.45	2.20	2.0	1.80	1.75	1.50	1.2	1.0	Experimental values
ϑ_0/ϑ_2	1299.09	88.87	49.11	33.26	30.70	22.11	17.01	15.87	
ϑ_2/v_0k	48.815	675.868	1168.99	1648.03	1764.53	2315.92	2845.51	2999.81	
T_{NI}K	409	409	409	409	409	409	409	409	409
η	0.5012	0.4821	0.4688	0.4574	0.4548	0.4442	0.4363	0.4345	0.36
$(v_0\rho)_{nem}$	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
$(v_0\rho)_{iso}$	0.61364	0.61475	0.61557	0.61632	0.61650	0.61733	0.61815	0.61840	
$\Delta\rho/\rho$	0.01031	0.0085	0.0072	0.0060	0.0057	0.0043	0.0030	0.0026	0.0035
γ_{iso}	241.518	14.791	7.324	4.337	3.853	2.216	1.227	1.000	
γ_{nem}	254.452	15.402	7.561	4.440	3.938	3.244	1.230	1.000	4
$\Delta U/NkT$	0.5024	0.5046	0.5056	0.5079	0.5084	0.5135	0.5200	0.5224	0.17
$(C_P/Nk)_{nem}$	7.112	7.991	8.942	10.092	10.406	12.067	13.917	14.495	72.9 (at $T_c - 1$)
$(C_P/Nk)_{iso}$	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	
$\alpha_{nem} \times 10^4/°K$	3.590	3.752	3.837	3.870	3.869	3.806	3.637	3.562	12.65 (at $T_c - 1$)
$\alpha_{iso} \times 10^4/°K$	2.846	2.846	2.847	2.849	2.850	2.853	2.857	2.859	
$\beta_{nem} \times 10^{12}$ cm^2/dyne	19.926	20.102	20.257	20.448	20.504	20.843	21.327	21.502	82.3 (at $T_c - 1$)
$\beta_{iso} \times 10^{12}$ cm^2/dyne	16.248	17.091	17.842	18.654	18.864	19.930	21.058	21.398	

TABLE III

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/NkT for $x = 2$

0.3351	5.53 ± 0.14	5.70	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

(iii) PV/NkT for $x = 1$

Z[c]	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 Ref. 29 for $x = 3$, Ref. 33 for $x = 2$, and Ref. 44 for $x = 1$.

[b] Ref. 13.

[c] $Z = 6d/(\sqrt{2}\pi)$.

[b] SPT results which are the same as Percus-Yevick results are from Ref. 35.

SPT overestimates the pressure as the density is increased and the discrepancy also increases with increase of density. This trend implies that the SPT calculations would be quite inaccurate in the nematic phase.

It would indeed be interesting to extrapolate up to the phase transition point the "exact" values got by computer simulation studies. We found it convenient to extend Andrews method for this purpose.

3 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 agreed better than those of SPT 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 m discrete orientations such that N_1 molecules have orientation 1, N_2 have orientation 2, etc. Then, choosing $N_1 \cdots N_m$ so as to maximise the partition function, the maximum term of the ensemble partition function is given by

$$Q_N(N_1 \cdots N_m, V, T) = (N_1! \cdots N_m!)^{-1} \int \cdots \int d^3r_1 \cdots d^3r_N$$

$$d^3\Omega_1 \cdots d^3\Omega_N \exp\{-U_N(r_1 \cdots r_N; \Omega_1 \cdots \Omega_N)/kT\} \quad (7)$$

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

$$\frac{\mu_i}{kT} = -\frac{\partial \ln Q_N}{\partial N_i} = \ln(f(\Omega_i)\rho) - \ln a_i^{-1}(\rho, T) \quad (8)$$

where $\rho = N/V$ is the number density, $f(\Omega_i) = N_i/N$, the fraction of the total number of molecules of ith type in the medium. Hence $\sum_{i=1}^{m} f(\Omega_i) = 1$. The reciprocal activity of the ith species is given by[35]

$$a_i^{-1} = \frac{1}{Z_N} \int \cdots \int \prod_{\alpha=1}^{N} d^3r_\alpha \int d^3r_{N+1} \int \cdots \int \prod_{\alpha=1}^{N} d\Omega_\alpha$$

$$\exp\left\{-\frac{1}{kT} \sum_{\alpha=1}^{N} U_{N+1,\alpha}(r_{N+1}, r_\alpha; \Omega_i, \Omega_\alpha)\right\} \exp\{-U_N(r_1 \cdots r_N; \Omega_1 \cdots \Omega_N)/kT\} \quad (9)$$

where

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

where r_{N+1} is the position of the $(N+1)$th molecule in the ith direction introduced into a system of N molecules and Ω_i represents its angular coordinates, and $\sum_{\alpha=1}^{N} U_{N+1,\alpha}(r_{N+1}, r_\alpha; \Omega_i, \Omega_\alpha)$ its energy. Assuming that the equilibrium structure is unaffected by the introduction of the new

particle, we can write

$$4\pi V a_i^{-1} = \int d^3 r_{N+1} \exp\left\{ -\frac{1}{kT} \sum_{\alpha} U_{N+1,\alpha}(r_{N+1}, r_\alpha; \Omega_i, \Omega_\alpha) \right\}. \quad (10)$$

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. (10). 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 spherocylinder. Adapting Andrews method[35] to the present case, we can write it as a product of two terms. The first is the probability that an arbitrarily chosen point r_{N+1} does not lie within the core of any of the N molecules. This is given by

$$(1 - v_0\rho) = 1 - (4/3\pi r^3 + \pi r^2 l)\rho \quad (11)$$

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_i^{-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 kth type should not lie within the excluded volume of the introduced particle, i.e., within the *additional* volume

$$v_{\text{add}}^{ik} = 8\pi r^2 l + \tfrac{32}{4}\pi r^3 + 4rl^2 \sin\theta_{ik} - (4/3\pi r^3 + \pi r^2 l) \quad (12)$$

where θ_{ik} is the angle between the long axes of the introduced molecule and the solvent molecule of the kth type. Following Andrews, the probability P_k that all N_k molecules lie outside v_{add}^{ik} is the N_kth power of the probability that one of them lies outside v_{add}^{ik}. Assuming that the available free volume is independent of the species, we may write for large values of N_k

$$P_k = \left(1 - \frac{v_{\text{add}}^{ik}}{V - \sum_{k=1}^{m} N_k \omega}\right)^{N_k} \to \exp\left(-\frac{v_{\text{add}}^{ik} N_k}{V - \sum_{k=1}^{m} N_k \omega}\right) \quad (13)$$

where $(V - \sum_{k=1}^{m} N_k \omega)$ 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

$$\prod_{k=1}^{m} p_k = \exp\left(-\frac{\sum_{k=1}^{m} v_{\text{add}}^{ik} N_k}{V - N\omega}\right) = \exp\left(-\frac{\rho \sum_{k=1}^{m} v_{\text{add}}^{ik} f(\Omega_k)}{1 - \omega\rho}\right).$$

Hence we can write

$$a_i^{-1} = (1 - v_0\rho)\exp\left(-\frac{\rho\sum_{k=1}^{m} f(\Omega_k)v_{\text{add}}^{ik}}{1 - \omega\rho}\right) \tag{14}$$

Using the relations (8) and (14), the Gibbs free energy of the hard spherocylinder system can be written as

$$G_c^*/NkT = \langle \mu_i/kT \rangle = \sum_{i=1}^{m} \frac{\mu_i}{kT} f(\Omega_i)d\Omega_i$$

$$= \ln\left[\frac{d}{(1-d)}\right] + \langle \ln f(\Omega_i)\rangle + \frac{Ad}{1 - \omega\rho} \tag{15}$$

where

$$A = \frac{14 + 21(x-1) + 6(x-1)^2 \frac{4}{\pi}\sum_i \sum_k \sin\theta_{ik} f(\Omega_i) f(\Omega_k)}{(3x-1)}$$

For the sake of simplicity, we expand $\sin\theta_{ik}$ in terms of Legendre polynomials. Retaining terms up to $P_2(\cos\theta_{ik})$ only and ignoring correlations between the i and k molecules in the mean field theory, we can write[13]

$$\sin\theta_{ik} \simeq \frac{\pi}{4} - \frac{5\pi}{32} P_2(\cos\theta_i)P_2(\cos\theta_k)$$

The pressure is given by[35]

$$\frac{P^*V}{NkT} = 1 - \frac{1}{\rho}\int_0^{\rho} \frac{\partial}{\partial\rho'}\left[\sum_{i=1}^{m}(f(\Omega_i)\ln a_i^{-1})\right]d\rho'$$

$$= -\frac{1}{d}\ln(1-d) + \frac{Ad}{1-\omega\rho} - \frac{A}{d}\int_0^d \frac{ydy}{1-(\omega/v_0)y}. \tag{16}$$

The Helmholtz free energy

$$\frac{A_c^*}{NkT} = \frac{G_c^*}{NkT} - \frac{P^*V}{NkT} = \ln d - \frac{(1-d)}{d}\ln(1-d) + \langle \ln f(\Omega)\rangle$$

$$+ \frac{A}{d}\int_0^d \frac{ydy}{1 - \frac{\omega}{v_0}y} \tag{17}$$

ω can be expected to depend on the density[35] and is assumed to be of the form $\omega = \sum_{n=0}^{\infty} \omega_n \rho^n$.

For the close packed solid,

$$\omega_{\text{solid}} = \frac{1}{\rho_0} = 2\sqrt{3}v_0 = 2v_0\frac{(x - 1 + \sqrt{2/3})}{[\pi(x - \frac{1}{3})]}. \tag{18}$$

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

$$\left(\frac{P^*V}{NKT}\right)_{\text{iso}} = -\frac{1}{d}\ln(1 - d) + \frac{A_0 d}{1 + \omega\rho} - \frac{A_0}{d}\int_0^d \frac{y\,dy}{1 - \omega/v_0 y}, \tag{19}$$

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/NkT of the isotropic phase of spherocylinders are not in good agreement with the computer calculations[29–32] for $x = 2$ and 3. 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, $n = 0, 1, \ldots, 6$, we proceed as follows:

$$\omega_{\text{solid}} = \sum_{n=0}^{6} \omega_n \rho_0^n \tag{20}$$

where ω_{solid} and ρ_0 are given by the relation (18). The pressure relation (19) is expanded in powers of ρ and the first eight virial coefficients (i.e., B_1, B_2, B_3, B_4, ..., B_8) are obtained in terms of ω_n:

$$B_1 = 1$$

$$B_2 = (1 + A_0)/2$$
$$= (3x^2 + 6x - 1)/(3x - 1) \text{ which is an exact value}[39]$$

$$v_0 B_3 = (v_0 + 2A_0\omega_0)/3$$

$$v_0^2 B_4 = (v_0^2 + 3A_0\omega_1 + 3A_0\omega_0^2)/4$$

$$v_0^3 B_5 = (v_0^3 + 4A_0\omega_2 + 8A_0\omega_0\omega_1 + 4A_0\omega_0^3)/5$$

$$v_0^4 B_6 = (v_0^4 + 5A_0\omega_3 + 10A_0\omega_0\omega_2 + 15A_0\omega_0^2\omega_1 + 5A_0\omega_1^2 + 5A_0\omega_0^4)/6$$

$$v_0^5 B_7 = (v_0^5 + 6A_0\omega_4 + 12A_0\omega_0\omega_3 + 12A_0\omega_1\omega_2 + 18A_0\omega_0^2\omega_2 + 18A_0\omega_0\omega_1^2 + 24A_0\omega_0^3\omega_1 + 6A_0\omega_0^5)/7$$

$$v_0^6 B_8 = (v_0^6 + 7A_0\omega_5 + 14A_0\omega_1\omega_3 + 14A_0\omega_0\omega_4 + 21A_0\omega_0^2\omega_3 + 7A_0\omega_2^2 + 42A_0\omega_0\omega_1\omega_2 + 7A_0\omega_1^3 + 28A_0\omega_0^3\omega_2 + 42A_0\omega_0^2\omega_1^2 + 35A_0\omega_0^4\omega_1 + 7A_0\omega_0^6)/8.$$

The last 6 equations along with Eq. (20) are solved for ω_n, $n = 0, 1, \ldots, 6$ 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[35] (see Table III). Nazbeda[40] has proposed the following (essentially empirical) analytical expression for calculating the virial coefficients of a fluid of hard spherocylinders.

$$B_n = (4n^2 - 13n + 13)\alpha + (-2n^2 + 11n - 14)\alpha^2 + (3n - n^2 - 1) \quad (21)$$

where $\alpha = x(x + 1)/(3x - 1)$. The first 6 virial coefficients given by the above equation are in very good agreement with Monte Carlo calculations[33] for $x \leq 3$. Furthermore, the expression can be utilised to calculate the virial coefficients for any arbitrary value of $x \leq 3$.

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

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

Let us denote the activity of a component i by a_i,[13]

$$a_i = \frac{\rho_i}{\langle\langle \exp\{-\Psi_i(r_1, \ldots, r_N)/kT\}\rangle\rangle}$$

where $\Psi_i(r_1, \ldots, r_N)$ is the total potential energy of the molecules of the type i located at r_i with all other molecules. $\langle\langle\ \rangle\rangle$ denotes the ensemble average over the $(N - 1)$ particle system 2, 3, ..., N, *and* an averaging over r_1 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 u_i given by Eq. (1). If a_i^* is the activity of the component i with the attractive potential turned off, then

$$\frac{\rho_i}{a_i} = \langle\langle \exp\{-\Psi_i/kT\}\rangle\rangle = \frac{\rho_i}{a_i^*} \exp\{-u_i/kT\}.$$

Therefore

$$a_i = a_i^* \exp\{+u_i/kT\}.$$

Following the procedure of Ref. 13, the configurational Gibbs free energy is given by

$$\frac{G_c(N_1, \ldots, N_m)}{NkT} = \sum_{i=1}^{m} f(\Omega_i) \ln a_i$$

$$= \sum_{i=1}^{m} f(\Omega_i) \ln a_i^* - \frac{\vartheta_0 \rho}{kT} - \frac{\vartheta_2 \rho \eta^2}{kT}.$$

The expressions for pressure P and the Helmholtz free energy A_c can now be written. Taking the limit of continuous orientations with the corresponding distribution function denoted by $F(\Omega)$, the thermodynamic quantities take the following form

$$\frac{G_c}{NkT} = \frac{G_c^*}{NkT} - \frac{\vartheta_0 \rho}{kT} - \frac{\vartheta_2 \rho}{kT} \eta^2 \tag{22}$$

where

$$\frac{G_c^*}{NkT} = \int F(\Omega_i) \ln a_i^* d\Omega.$$

The internal energy of the system is given by

$$\frac{U}{N} = -\tfrac{1}{2}\vartheta_0 \rho - \tfrac{1}{2}\vartheta_2 \rho \eta^2. \tag{23}$$

The pressure is given by

$$P = P^* - \tfrac{1}{2}\vartheta_0 \rho^2 - \tfrac{1}{2}\vartheta_2 \rho^2 \eta^2, \tag{24}$$

Substituting for G_c^* and P^* from the relations (15) and (16), we can obtain the configurational Gibbs free energy and the pressure relation. The Helmholtz free energy is given by

$$\frac{A_c}{NkT} = \ln\left(\frac{d}{1-d}\right) + \frac{\ln(1-d)}{d} + \langle \ln F(\Omega_1) \rangle + \frac{A}{d} \int_0^d \frac{y dy}{1 - \sum_{n=0}^{6} \frac{\omega_n y^{n+1}}{v_0^{n+1}}}$$

$$- \frac{1}{2} \frac{\vartheta_0 \rho}{kT} - \frac{1}{2} \frac{\vartheta_2 \rho}{kT} \eta^2. \tag{25}$$

The normalized distribution function $F(\Omega)$ which minimises this Helmholtz free energy is given by

$$F(\Omega) = \frac{\exp\left[\left\{\frac{\vartheta_2 \rho}{kT} + \frac{15}{2d} \frac{(x-1)^2}{(3x-1)} \int_0^d \frac{y dy}{1 - \sum_{n=0}^{6} \omega_n y^{n+1}/v_0^{n+1}}\right\} \eta P_2(\Omega)\right]}{\int \exp\left[\left\{\frac{\vartheta_2 \rho}{kT} + \frac{15}{2d} \frac{(x-1)^2}{(3x-1)} \int_0^d \frac{y dy}{1 - \sum_{n=0}^{6} \omega_n y^{n+1}/v_0^{n+1}}\right\} \eta P_2(\Omega)\right] d\Omega} \tag{26}$$

TABLE IV

Results of Andrew's model for different values of x

$x = \frac{1}{2r} + 1$	2.90	2.5	2.075	2.05	2.0	1.5	1.0	Experimental value
ϑ_0/ϑ_2	589.46	62.72	30.79	29.86	28.15	18.02	15.99	
ϑ_2/kv_0	92.09	833.23	1610.60	1655.12	1743.53	2552.15	2998.85	
$T^{\circ}_{NI}K$	409	409	409	409	409	409	409	409
η	0.4915	0.4713	0.4549	0.4541	0.4524	0.4397	0.4332	0.36
$(v_0\rho)_{nem}$	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
$(v_0\rho)_{iso}$	0.61329	0.61483	0.61617	0.61624	0.61639	0.61767	0.61875	
$\Delta\rho/\rho$	0.01088	0.0084	0.0062	0.0061	0.0058	0.0038	0.0021	0.0035
γ_{nem}	107.26	9.933	4.022	3.850	3.533	1.632	1.000	4
γ_{iso}	102.607	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	0.500	0.17
$(C_P/Nk)_{nem}$	16.984	20.487	21.475	21.461	21.414	20.074	17.882	72.9 (at $T_c - 1$)
$(C_P/Nk)_{iso}$	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 $T_c - 1$)
$\alpha_{iso} \times 10^4/^{\circ}K$	6.288	5.997	5.734	5.720	5.690	5.335	4.259	
$\beta_{nem} \times 10^{12}\,cm^2/dyne$	61.102	55.146	49.634	49.366	48.845	44.145	31.985	82.3 (at $T_c - 1$)
$\beta_{iso} \times 10^{12}\,cm^2/dyne$	41.977	41.377	41.524	41.546	41.592	41.446	31.618	

TABLE IV

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$T_{NI}^{\circ}K$	409	409	409	409	409	409	409	409
η	0.4915	0.4713	0.4549	0.4541	0.4524	0.4397	0.4332	0.36
$(v_0\rho)_{nem}$	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
$(v_0\rho)_{iso}$	0.61329	0.61483	0.61617	0.61624	0.61639	0.61767	0.61875	
$\Delta\rho/\rho$	0.01088	0.0084	0.0062	0.0061	0.0058	0.0038	0.0021	0.0035
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$\beta_{iso} \times 10^{12}\,cm^2/dyne$	41.977	41.377	41.524	41.546	41.592	41.446	31.618	

(Eq. 22) can be calculated in both the phases. The assumed value of $\vartheta_2/v_0 k$ is adjusted by an iterative procedure till the Gibbs free energy in the two phases become equal. The other parameters like C_p, etc., are then calculated as usual. Table IV lists the results for different values of x.

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 these based on SPT could only be made up to $x = 2.45$ (Table II). The trends of different physical quantities as functions of x are similar to those given by SPT (Table II). But in the case of the Andrews model, $\gamma \simeq 4$ for $x = 2.075$, 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.[41–43] However, the volume change at the transition, $\Delta\rho/\rho$ and the heat of transition ΔU, still remain somewhat larger than the experimental values. The latter result is a consequence of using the mean field approximation.[8,13] Short-range order effects in the medium have to be taken into account to correct for the discrepancies.

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 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_c 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.[45] We have made some calculations in which the models presented in the present paper have been extended to take into account short-range order effects. The results will be discussed elsewhere.

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[46,47] showed that such deviations can account for the lowering of order parameter at T_c. This result has been confirmed by more recent calculations due to Straley[48] and Luckhurst *et al*[49] who used a suitable extension of the Maier–Saupe model. Very recently Gelbart and Barboy[50] 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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