Molecular Crystals and Liquid Crystals

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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 Cotter13 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 $\alpha$, etc., were significantly higher than the experimental values.

There have been several computer simulation studies\textsuperscript{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\textsuperscript{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\textsuperscript{13} for different values of the length to breadth ratio $x$. As we shall see, for a value of $x \approx 1.75$, 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 spherocylinders 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\textsuperscript{13} in all our calculations. Assuming that the attractive potential is of the form\textsuperscript{36}

$$u_i = -\mathcal{g}_0 \rho - \mathcal{g}_2 \rho \eta P_2(\cos \theta_i),$$

(1)
where

\[ \eta = \frac{\int_0^{\pi} P_2(\cos \theta) \exp \left\{ \left[ \Lambda(\rho) + \frac{\partial_1 \rho}{kT} \right] \eta P_2(\cos \theta) \right\} \sin \theta d\theta}{\int_0^{\pi} \exp \left\{ \left[ \Lambda(\rho) + \frac{\partial_1 \rho}{kT} \right] \eta P_2(\cos \theta) \right\} \sin \theta d\theta}, \] (2)

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

d = v_0 \rho; \ R = 6(x - 1)^2/\pi(3x - 1); \ q = 2/(3x - 1); \ \partial_0 \text{ and } \partial_2 \text{ are the strengths of the isotropic and the anisotropic parts of the potential, } \rho \text{ is the number density, } v_0 \text{ is the molecular volume and } d \text{ is the packing fraction.}

The pressure \( P \) is given by the relation

\[ P v_0/kT = \pi^* - \frac{1}{2} \frac{d^2}{kT} \left[ \frac{\partial_0}{v_0} + \frac{\partial_2}{v_0} \eta^2 \right] \]

where

\[ \pi^* = d(1 + d + 2/3(1 + q - q^2/2)d^2 + \pi R d/2[1 + (1 + 2q)d/3/(1 - \eta^2)])/(1 - d)^3 \]

The chemical potential \( \mu_c \) is given by

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

\[ + \pi^* - \left( \frac{\partial_0}{v_0} + \frac{\partial_2}{v_0} \eta^2 \right) d/kT \] (5)

For a system of hard spherocylinders, \( \partial_0 = \partial_2 = 0 \). The results of calculations on this system are shown in Table I and will be discussed later. In such a case the coefficient \( \gamma \) defined as

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

is infinity since the order parameter of the system does not directly depend on temperature. (\( \gamma \) is a measure of the relative importance of volume compared to that of temperature in determining the variation of \( \eta \) of the medium near \( T_{N1} \)). 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>
<thead>
<tr>
<th>$x = \frac{1}{2r} + 1$</th>
<th>3.0</th>
<th>2.5</th>
<th>2.0</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Andrew's method</td>
<td>SPT</td>
<td>Andrew's method</td>
<td>SPT</td>
</tr>
<tr>
<td>$T_{\text{N}K}$</td>
<td>409</td>
<td>409</td>
<td>409</td>
<td>409</td>
</tr>
<tr>
<td>$\langle P_2(\cos \theta) \rangle$</td>
<td>0.4718</td>
<td>0.4914</td>
<td>0.4605</td>
<td>0.4799</td>
</tr>
<tr>
<td>$(\nu_0\rho)_{\text{harm}}$</td>
<td>0.6126</td>
<td>0.5588</td>
<td>0.6753</td>
<td>0.6147</td>
</tr>
<tr>
<td>$(\nu_0\rho)_{\text{iso}}$</td>
<td>0.6083</td>
<td>0.5531</td>
<td>0.6726</td>
<td>0.6105</td>
</tr>
<tr>
<td>$\Delta \rho/\rho$</td>
<td>0.0071</td>
<td>0.0104</td>
<td>0.0039</td>
<td>0.0068</td>
</tr>
<tr>
<td>$\alpha_{\text{mea}} \times 10^4/\degree$C</td>
<td>5.855</td>
<td>6.863</td>
<td>4.127</td>
<td>5.343</td>
</tr>
<tr>
<td>$\alpha_{\text{iso}} \times 10^4/\degree$C</td>
<td>4.249</td>
<td>4.421</td>
<td>3.227</td>
<td>3.745</td>
</tr>
<tr>
<td>$\beta_{\text{mea}} \times 10^{12}$cm$^2$/dyne</td>
<td>40.591</td>
<td>64.451</td>
<td>15.520</td>
<td>31.705</td>
</tr>
<tr>
<td>$\beta_{\text{iso}} \times 10^{12}$cm$^2$/dyne</td>
<td>29.455</td>
<td>41.576</td>
<td>12.137</td>
<td>21.850</td>
</tr>
</tbody>
</table>
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, $\delta_0$ and $\delta_2$. $\delta_0$ is the parameter describing the average or isotropic attraction between the centres of mass of the spherocylinders, while $\delta_2$ 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, $\delta_0$ and $\delta_2$ 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 $\delta_0$ and $\delta_2$ 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 $\eta$ 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 $\alpha$, and the isothermal compressibility $\beta$ are shown at $T_{NI}$ for both the N and I phases. Further, the coefficient $\gamma$ 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, $\gamma$ value also increases, first slowly and then very rapidly. The ratio of $\delta_0/\delta_2$ also increases in a similar manner. $C_p$ decreases with $x$, whereas $\alpha$ and $\beta$ 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 $\delta_0$ and $\delta_2$ suitably to get $\gamma = 4$. Further in this case, the second derivatives turn out to be too high13 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 $\gamma \approx 4$. 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 $x$

<table>
<thead>
<tr>
<th>$x = \frac{1}{2r} + 1$</th>
<th>2.45</th>
<th>2.20</th>
<th>2.0</th>
<th>1.80</th>
<th>1.75</th>
<th>1.50</th>
<th>1.2</th>
<th>1.0</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>0.5012</td>
<td>0.4821</td>
<td>0.4688</td>
<td>0.4574</td>
<td>0.4548</td>
<td>0.4442</td>
<td>0.4363</td>
<td>0.4345</td>
<td>0.36</td>
</tr>
<tr>
<td>$\eta_{norm}$</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>$\eta_{iso}$</td>
<td>0.61364</td>
<td>0.61475</td>
<td>0.61557</td>
<td>0.61632</td>
<td>0.61650</td>
<td>0.61733</td>
<td>0.61815</td>
<td>0.61840</td>
<td></td>
</tr>
<tr>
<td>$\gamma_{iso}$</td>
<td>24.1518</td>
<td>14.791</td>
<td>7.324</td>
<td>4.337</td>
<td>3.853</td>
<td>2.216</td>
<td>1.227</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>$\gamma_{norm}$</td>
<td>254.452</td>
<td>15.402</td>
<td>7.561</td>
<td>4.440</td>
<td>3.938</td>
<td>3.244</td>
<td>1.230</td>
<td>1.00</td>
<td>4</td>
</tr>
<tr>
<td>$\Delta U/NkT$</td>
<td>0.5024</td>
<td>0.5046</td>
<td>0.5056</td>
<td>0.5079</td>
<td>0.5084</td>
<td>0.5135</td>
<td>0.5200</td>
<td>0.5224</td>
<td>0.17</td>
</tr>
<tr>
<td>$(C_p/Nk)_{norm}$</td>
<td>7.112</td>
<td>7.991</td>
<td>8.942</td>
<td>10.092</td>
<td>10.406</td>
<td>12.067</td>
<td>13.917</td>
<td>14.495</td>
<td>72.9 (at $T_e - 1$)</td>
</tr>
<tr>
<td>$(C_p/Nk)_{iso}$</td>
<td>5.540</td>
<td>5.256</td>
<td>5.031</td>
<td>4.813</td>
<td>4.760</td>
<td>4.510</td>
<td>4.276</td>
<td>4.210</td>
<td></td>
</tr>
<tr>
<td>$(C_v/Nk)_{norm}$</td>
<td>0.0014</td>
<td>0.2932</td>
<td>0.9524</td>
<td>2.041</td>
<td>2.380</td>
<td>4.425</td>
<td>7.098</td>
<td>8.006</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{iso} \times 10^4$/K</td>
<td>2.846</td>
<td>2.846</td>
<td>2.847</td>
<td>2.849</td>
<td>2.850</td>
<td>2.853</td>
<td>2.853</td>
<td>2.857</td>
<td>2.859</td>
</tr>
<tr>
<td>$\beta_{norm} \times 10^{12}$ cm$^2$/dyne</td>
<td>19.926</td>
<td>20.102</td>
<td>20.257</td>
<td>20.448</td>
<td>20.504</td>
<td>20.843</td>
<td>21.327</td>
<td>21.502</td>
<td>82.3 (at $T_e - 1$)</td>
</tr>
</tbody>
</table>
TABLE III
Equation of state in the isotropic phase

(i) $P_{v_0}/kT$ for $x = 3$

<table>
<thead>
<tr>
<th>$d$</th>
<th>Computer simulation(^a)</th>
<th>Martha-Cotter(^b)</th>
<th>Present calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.54</td>
<td>12.6 ± 0.2</td>
<td>15.56</td>
<td>12.69</td>
</tr>
<tr>
<td>0.50</td>
<td>9.0 ± 0.2</td>
<td>10.56</td>
<td>9.04</td>
</tr>
<tr>
<td>0.45</td>
<td>5.85 ± 0.07</td>
<td>6.6</td>
<td>5.94</td>
</tr>
<tr>
<td>0.40</td>
<td>3.84 ± 0.04</td>
<td>4.17</td>
<td>3.89</td>
</tr>
<tr>
<td>0.35</td>
<td>2.51 ± 0.04</td>
<td>2.63</td>
<td>2.53</td>
</tr>
<tr>
<td>0.30</td>
<td>1.62 ± 0.04</td>
<td>1.65</td>
<td>1.62</td>
</tr>
</tbody>
</table>

(ii) $PV/nkT$ for $x = 2$

<table>
<thead>
<tr>
<th>$d$</th>
<th>Computer simulation(^a)</th>
<th>Martha-Cotter(^b)</th>
<th>Present calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3351</td>
<td>5.53 ± 0.14</td>
<td>5.70</td>
<td>5.55</td>
</tr>
<tr>
<td>0.3879</td>
<td>7.57 ± 0.26</td>
<td>7.88</td>
<td>7.53</td>
</tr>
<tr>
<td>0.4460</td>
<td>10.74 ± 0.24</td>
<td>11.53</td>
<td>10.75</td>
</tr>
<tr>
<td>0.5096</td>
<td>16.80 ± 0.90</td>
<td>18.12</td>
<td>16.35</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$Z^c$</th>
<th>Computer simulation(^a)</th>
<th>SPT(^d)</th>
<th>Present calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>1.36</td>
<td>1.36</td>
<td>1.36</td>
</tr>
<tr>
<td>0.20</td>
<td>1.89</td>
<td>1.89</td>
<td>1.89</td>
</tr>
<tr>
<td>0.30</td>
<td>2.68</td>
<td>2.70</td>
<td>2.68</td>
</tr>
<tr>
<td>0.40</td>
<td>3.90</td>
<td>3.97</td>
<td>3.90</td>
</tr>
<tr>
<td>0.50</td>
<td>5.83</td>
<td>6.04</td>
<td>5.84</td>
</tr>
<tr>
<td>0.55</td>
<td>7.23</td>
<td>7.55</td>
<td>7.24</td>
</tr>
<tr>
<td>0.60</td>
<td>9.06</td>
<td>9.57</td>
<td>9.10</td>
</tr>
<tr>
<td>0.625</td>
<td>10.18</td>
<td>10.82</td>
<td>10.25</td>
</tr>
<tr>
<td>0.65</td>
<td>11.48</td>
<td>12.28</td>
<td>11.60</td>
</tr>
<tr>
<td>0.67</td>
<td>12.66</td>
<td>13.62</td>
<td>12.83</td>
</tr>
<tr>
<td>0.68</td>
<td>13.32</td>
<td>14.36</td>
<td>13.52</td>
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<tr>
<td>0.69</td>
<td>14.01</td>
<td>15.15</td>
<td>14.26</td>
</tr>
<tr>
<td>0.70</td>
<td>14.75</td>
<td>15.99</td>
<td>15.05</td>
</tr>
</tbody>
</table>

\(^a\) Computer simulation values from Ref. 29 for $x = 3$, Ref. 33 for $x = 2$, and Ref. 44 for $x = 1$.

\(^b\) Ref. 13.

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

\(^d\) 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.
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

\[
Q_N(N_1 \cdots N_m, V, T) = (N_1! \cdots N_m!)^{-1} \int \cdots \int d^3r_1 \cdots d^3r_N \frac{d^3\Omega_1 \cdots d^3\Omega_N}{\exp\left\{ -U_N(r_1 \cdots r_N; \Omega_1 \cdots \Omega_N)/kT \right\}} \tag{7}
\]

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 \( \Omega_i \) is given by

\[
\mu_i = -\frac{\partial \ln Q_N}{\partial N_i} = \ln(f(\Omega_i)\rho) - \ln a_i^{-1}(\rho, T) \tag{8}
\]

where \( \rho = N/V \) is the number density, \( f(\Omega_i) = \frac{N_i}{N} \), 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

\[
a_i^{-1} = \frac{1}{Z_N} \int \cdots \int \prod_{\alpha=1}^{N} d^3r_\alpha \int d^3r_{N+1} \int \cdots \int \prod_{\alpha=1}^{N} d\Omega_\alpha \\
\exp\left\{ -\frac{1}{kT} \sum_{\alpha=1}^{N} U_{N+1,\alpha}(r_{N+1,\alpha}; \Omega_\alpha) \right\} \exp\left\{ -U_N(r_1 \cdots r_N; \Omega_1 \cdots \Omega_N)/kT \right\} \tag{9}
\]

where

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

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 \( \Omega_i \) represents its angular coordinates, and \( \sum_{\alpha=1}^{N} U_{N+1,\alpha}(r_{N+1,\alpha}; \Omega_\alpha) \) its energy. Assuming that the equilibrium structure is unaffected by the introduction of the new
particle, we can write

\[ 4\pi V a_1^{-1} = \int d^3r_{N+1} \exp \left\{ -\frac{1}{kT} \sum_{z} U_{N+1,z}(r_{N+1}, r_z; \Omega_1, \Omega_2) \right\} \]  \tag{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, \( U_{N+1,z} \) is \( \infty \) 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. Adopting Andrews method\textsuperscript{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

\[ (1 - v_0 \rho) = 1 - (4/3\pi r^3 + \pi r^2 l)\rho \]  \tag{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 \( a_1^{-1} \) 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

\[ v_{\text{add}}^{ik} = 8\pi r^2 l + \frac{32}{3} \pi r^3 + 4rl^2 \sin \theta_{ik} - (4/3\pi r^3 + \pi r^2 l) \]  \tag{12}  

where \( \theta_{ik} \) 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 \( v_{\text{add}}^{ik} \) is the \( N_k \)th power of the probability that one of them lies outside \( v_{\text{add}}^{ik} \). Assuming that the available free volume is independent of the species, we may write for large values of \( N_k \)

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

where \( (V - \sum_{k=1}^{m} N_k \omega) \) is the "free" volume available to the molecules. \( \omega \) 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 \( \omega \) 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

\[ \prod_{k=1}^{m} P_k = \exp \left( -\sum_{k=1}^{m} \frac{v_{\text{add}}^{ik} N_k}{V - N_k \omega} \right) = \exp \left( -\rho \frac{\sum_{k=1}^{m} v_{\text{add}}^{ik} f(\Omega_k)}{1 - \omega \rho} \right). \]
Hence we can write
\[ a_i^{-1} = (1 - v_0 \rho) \exp \left( -\frac{\rho \sum_{k=1}^{m} f(\Omega_k) v_{i,k}^{\text{add}}}{1 - \omega \rho} \right) \]  

(14)

Using the relations (8) and (14), the Gibbs free energy of the hard spherocylinder system can be written as
\[ \frac{G^*_e}{N k T} = \frac{\mu_i}{k T} = \sum_{i=1}^{m} \frac{\mu_i}{k T} f(\Omega_i) d\Omega_i \]
\[ = \ln \left[ \frac{d}{(1 - d)} \right] + \langle \ln f(\Omega_i) \rangle + \frac{A d}{1 - \omega \rho} \]  

(15)

where
\[ A = \frac{14 + 21(x - 1) + 6(x - 1)^2}{(3x - 1)} \]

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
\[ \sin \theta_{ik} \approx \frac{\pi}{4} - \frac{5\pi}{32} P_2(\cos \theta_i) P_2(\cos \theta_k) \]

The pressure is given by
\[ \frac{P^* V}{N k T} = 1 - \frac{1}{\rho} \int_{0}^{\rho} \frac{\partial}{\partial \rho} \left[ \sum_{i=1}^{m} (f(\Omega_i) \ln a_i^{-1}) \right] d\rho' \]
\[ = -\frac{1}{d} \ln(1 - d) + \frac{A d}{1 - \omega \rho} - \frac{A}{d} \int_{0}^{d} \frac{ydy}{1 - (\omega / v_0) y}. \]  

(16)

The Helmholtz free energy
\[ \frac{A^*_e}{N k T} = \frac{G^*_e}{N k T} - \frac{P^* V}{N k T} = \ln d - \frac{(1 - d)}{d} \ln(1 - d) + \langle \ln f(\Omega) \rangle \]
\[ + \frac{A}{d} \int_{0}^{d} \frac{ydy}{1 - (\omega / v_0) y} \]  

(17)

\( \omega \) can be expected to depend on the density and is assumed to be of the form \( \omega = \sum_{n=0}^{\infty} \omega_n \rho^n \).
ANDREWS METHOD FOR N-I TRANSITION

For the close packed solid,

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

$\omega_{\text{solid}}$ is the high density limit. To calculate the low density limit of $\omega$, the pressure relation in the isotropic phase, viz.,

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

where $A_0 = (6x^2 + 9x - 1)/(3x - 1)$ is expanded in powers of $\rho$. 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 for $x = 2$ and $3$. Hence we took the higher order terms in the expansion of $\omega$ and found that 7 terms of the $\omega$ expansion are sufficient to give reasonable agreement with the computer calculations. To calculate the coefficients $\omega_n, n = 0, 1, \ldots, 6$, we proceed as follows:

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

where $\omega_{\text{solid}}$ and $\rho_0$ are given by the relation (18). The pressure relation (19) is expanded in powers of $\rho$ and the first eight virial coefficients (i.e., $B_1, B_2, B_3, B_4, \ldots, B_8$) are obtained in terms of $\omega_n$:

$$B_1 = 1$$

$$B_2 = (1 + A_0)/2$$

$$= (3x^2 + 6x - 1)/(3x - 1)$$ which is an exact value

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

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

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

$$v_0^4 B_6 = (v_0^4 + 5A_0 \omega_3 + 10A_0 \omega_0 \omega_2 + 15A_0 \omega_0^2 \omega_1 + 5A_0 \omega_0^3 + 5A_0 \omega_0^4)/6$$

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

$$v_0^6 B_8 = (v_0^6 + 7A_0 \omega_5 + 14A_0 \omega_1 \omega_3 + 14A_0 \omega_0 \omega_4 + 21A_0 \omega_0 \omega_0 \omega_2 + 7A_0 \omega_0^2 \omega_1 + 28A_0 \omega_0 \omega_0 \omega_0^2 + 42A_0 \omega_0 \omega_0^2 \omega_1 + 7A_0 \omega_0 \omega_0 \omega_0^3 + 28A_0 \omega_0 \omega_0 \omega_0^3 \omega_2 + + 42A_0 \omega_0 \omega_0 \omega_0^3 \omega_1 + 35A_0 \omega_0 \omega_0 \omega_0^3 \omega_1 + 7A_0 \omega_0 \omega_0^6)/8.$$
The last 6 equations along with Eq. (20) are solved for $\omega_n$, $n = 0, 1, \ldots, 6$ 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 ($^3^5$) (see Table III). Nazbeda ($^4^0$) has proposed the following (essentially empirical) analytical expression for calculating the virial coefficients of a fluid of hard spherocylinders.

$$B_n = (4n^2 - 13n + 13)x + (-2n^2 + 11n - 14)x^2 + (3n - n^2 - 1)$$  \hspace{1cm} (21)

where $x = x(x + 1)/(3x - 1)$. The first 6 virial coefficients given by the above equation are in very good agreement with Monte Carlo calculations ($^3^3$) 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 $a_i$, ($^1^3$)

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

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. $\langle \rangle$ 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

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

Therefore

$$a_i = a_i^* \exp\{+u_i/kT\}.$$
Following the procedure of Ref. 13, the configurational Gibbs free energy is given by

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

\[
= \sum_{i=1}^{m} f(\Omega_i) \ln a_i^* - \frac{\delta_0 \rho}{kT} - \frac{\delta_2 \rho \eta^2}{kT}.
\]

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

\[
\frac{G_c}{NkT} = \frac{G_c^*}{NkT} - \frac{\delta_0 \rho}{kT} - \frac{\delta_2 \rho \eta^2}{kT}
\]

where

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

The internal energy of the system is given by

\[
\frac{U}{N} = -\frac{1}{2} \frac{\delta_0 \rho}{kT} - \frac{1}{2} \frac{\delta_2 \rho \eta^2}{kT}.
\]

The pressure is given by

\[
P = \frac{U}{N} = \frac{P^*}{N} - \frac{1}{2} \frac{\delta_0 \rho}{kT} - \frac{1}{2} \frac{\delta_2 \rho \eta^2}{kT}.
\]

Substituting for \(G_c^*\) and \(P^*\) from the relations (15) and (16), we can obtain

The Helmholtz free energy is given by

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

\[
- \frac{1}{2} \frac{\delta_0 \rho}{kT} - \frac{1}{2} \frac{\delta_2 \rho \eta^2}{kT}.
\]

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

\[
F(\Omega) = \frac{\exp \left[ \left( \frac{\delta_2 \rho}{kT} + \frac{15}{2d(3x-1)} \right) \int_0^d \frac{ydy}{1 - \sum_{n=0}^{d} \frac{\omega_n y^{n+1}}{v_0^{n+1}}} \right] \eta P_2(\Omega) d\Omega}{\int \exp \left[ \left( \frac{\delta_2 \rho}{kT} + \frac{15}{2d(3x-1)} \right) \int_0^d \frac{ydy}{1 - \sum_{n=0}^{d} \frac{\omega_n y^{n+1}}{v_0^{n+1}}} \right] \eta P_2(\Omega) d\Omega}
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<td>49.366</td>
<td>48.845</td>
<td>44.145</td>
<td>31.985</td>
<td>82.3 (at $T_c - 1$)</td>
</tr>
<tr>
<td>$\beta_{iso} \times 10^{12} \mathrm{cm^2/dyne}$</td>
<td>41.977</td>
<td>41.377</td>
<td>41.524</td>
<td>41.546</td>
<td>41.592</td>
<td>41.446</td>
<td>31.618</td>
<td></td>
</tr>
</tbody>
</table>
(Eq. 22) can be calculated in both the phases. The assumed value of $9z/v_0 k$

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, $\gamma \approx 4$ for $x = 2.075$, which is a reason-

able improvement over $x = 1.75$ of SPT. Further, it is obvious from Table

IV that the new theoretical values of the second derivatives, viz., $C_v$, $C_p$, $\alpha$ and

$\beta$ are considerable improvements over those of SPT. In fact they come quite

close to the experimental data. However, the volume change at the transition, $\Delta \rho/\rho$ and the heat of transition $\Delta U$, still remain somewhat larger

than the experimental values. The latter result is a consequence of using the

mean field approximation. 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 reason-

able 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. How-

ever, 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 ex-

perimental 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. 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 sym-

metric 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 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 and Luckhurst et al who used a suitable extension of the Maier–Saupe model. Very recently Gelbart and Barbo 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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References

34. P. A. Monson and M. Rigby, (private communication).