

CHAPTER VI

SCALED PARTICLE THEORY OF A SYSTEM OF RIGHT CIRCULAR CYLINDERS

6.1 Introduction

In chapters IV and V, we have discussed in great detail the importance of the geometrical features of the molecules in determining the properties of nematic liquid crystals.

Disc-shaped molecules have been recently shown (Chandrasekhar et al, 1977) to exhibit a new class of liquid crystalline phases (the discotic phases). Some of these have been found to exhibit a 'fluid' phase with only a long range orientational order, i.e., a discotic nematic phase (Tinh et al, 1979). Indeed the nematic phase exhibited by essentially flat molecules was discovered long ago in the pyrolysis of Coke by Brooks and Taylor (1965). The effect of plate-like molecules on the nematic phase transition was discussed theoretically by Alben (1973). Imihara (1951) has considered phase transition in anisotropic colloidal solutions consisting of disc-like molecules, in an approach similar to that of Onsager (1942, 1949).

As we have discussed in chapter IV, the particle theory as developed by Cotter (1977a,b) gives a good description of the nematic phase of rod-like molecules. In this chapter, we extend the scaled particle theory to the discotic nematic phase. In discussing the thermodynamic properties of the nematic phase made of rod-like molecules, it is conventional that the molecules have a spherocylindrical shape. In order to be able to compare the results on disc-like molecules with those on rod-like molecules, we extend the theory to a system of right circular cylinders. If r is the radius of the cylinder and l its height, the shape-factor $R = r, l$ is > 0.5 for disc-like molecules and < 0.5 for rod-like molecules. We will in the next section, summarize the scaled particle theory of Cotter (1977a) as extended to such a system. The properties of rod-like and disc-like particles have been compared for both a system of hard particles and also for a system superposed with an attractive potential.

6.2 Scaled particle theory

As in chapter IV, we can write the chemical potential of a hard cylindrical molecule oriented in the direction

\hat{n}_1 as

$$\mu_1^{\#} = kT \ln \rho_1 + w_1(\alpha, \lambda); \quad \lambda = \alpha = 1 \quad (1)$$

where $\rho_1 = N_1/V$ is the number density of molecules of 1th type and $w_1(\alpha, \lambda)$ is the work function defined as the reversible work of adding a scaled hard cylindrical molecule of radius αr and height λl , oriented in the direction Ω_1 to the fluid of N cylindrical molecules of radius r and height l . For α and λ which are sufficiently small $w_1(\alpha, \lambda)$ can be written as

$$\exp[-w_1(\alpha, \lambda)/kT] = 1 - \rho \sum_{j=1}^n S_j v_{1j} \quad (2)$$

where $S_j = N_j/n$, n is the number of orientations allowed for the molecule, $\rho = N/V$, v_{1j} is the volume excluded to the centre of a regular cylinder with orientation j by the presence of the scaled cylinder and is given by (Ishihara, 1951)

$$\begin{aligned} v_{1j} = & \pi r^2 l (1 + \alpha^2 \lambda) + \pi r^2 l (\alpha^2 + \lambda) |\cos \theta_{1j}| \\ & + 2\alpha r^3 (\alpha + \alpha^2) |\sin \theta_{1j}| + 2r l^2 (\alpha \lambda + \lambda) |\sin \theta_{1j}| \\ & + 4r^2 l (\alpha + \alpha \lambda) \int_0^{\pi/2} \sqrt{1 - \sin^2 \theta_{1j} \sin^2 \varphi} d\varphi \quad \dots \quad (3) \end{aligned}$$

For large values of α and λ , $w_1(\alpha, \lambda)$ must approach the reversible work of creating a macroscopic cylindrical cavity in the fluid, i.e.,

$$\lim_{\alpha \rightarrow \lambda \rightarrow \infty} W_1(\alpha, \lambda) = n\alpha^2 \lambda r^2 l P^M = \alpha^2 \lambda v_0 P^M \quad (4)$$

where P^M is the pressure of the hard cylinder system and v_0 is the volume of a cylinder. The average work function W is expanded as

$$W = \sum_{i=1}^n S_i W_i(\alpha, \lambda) = C_{00} + C_{10} \alpha + C_{01} \lambda + C_{11} \alpha \lambda + C_{20} \alpha^2 + v_0 P^M \alpha^2 \lambda \quad (5)$$

where

$$C_{ab} = \frac{1}{a!b!} \left[\frac{\partial^a \partial^b W}{\partial \alpha^a \partial \lambda^b} \right]_{\alpha = \lambda = 0}$$

Using equations (2 - 5), we get

$$C_{00}/kT = -\ln(1-d)$$

$$C_{10}/kT = d[2R \langle |\sin \theta_{1j}| \rangle + 4 \langle E(\theta_{1j}) \rangle / \pi] / (1-d)$$

$$C_{01}/kT = d[\langle |\cos \theta_{1j}| \rangle + 2 \langle |\sin \theta_{1j}| \rangle / \pi R] / (1-d)$$

$$C_{11}/kT = d[2 \langle |\sin \theta_{1j}| \rangle / \pi R + \langle E(\theta_{1j}) \rangle / \pi] / (1-d)$$

$$+ d^2 [2R \langle |\sin \theta_{1j}| \rangle + 4 \langle E(\theta_{1j}) \rangle / \pi] \times [\langle |\cos \theta_{1j}| \rangle + 2 \langle |\sin \theta_{1j}| \rangle / \pi R] / (1-d)^2$$

$$C_{20}/kT = d[\langle |\cos \theta_{1j}| \rangle + 2R \langle |\sin \theta_{1j}| \rangle] / (1-d)$$

$$+ d^2 [2R \langle |\sin \theta_{1j}| \rangle + 4 \langle E(\theta_{1j}) \rangle / \pi]^2 / 2(1-d)^2$$

where $R = r/l$, $d = v_0 \rho$, and $E(\theta_{1j}) = \int_0^{\pi/2} \sqrt{1 - \sin^2 \theta_{1j} \sin^2 \varphi} d\varphi$

and $\langle x_{1j} \rangle = \sum_{i=1}^n \sum_{j=1}^n S_i S_j x_{ij}$. By changing over to a continuous distribution with the corresponding distribution

function $F(\cos \theta)$ (θ being the angle between the director and the symmetry axis of the molecule), we can write

$$\langle x_{ij} \rangle = \int_0^1 d(\cos \theta_1) \int_0^1 d(\cos \theta_2) F(\cos \theta_1) F(\cos \theta_2) x_{ij} ,$$

where $F(\cos \theta_1)$ and $F(\cos \theta_2)$ are the single particle distribution functions for the i^{th} and j^{th} type of cylinders. The average work function is now given by.

$$\begin{aligned} w/kT &= -\ln(1-d) + Ad/(1-d) + Bd^2/(1-d)^2 \\ &\quad + v_0 P^E/kT \end{aligned} \quad (6)$$

where

$$\begin{aligned} A &= (4R + 4/\pi R) \langle |\sin \theta_{ij}| \rangle + 8 \langle E(\theta_{ij}) \rangle / \pi + 2 \langle |\cos \theta_{ij}| \rangle , \\ B &= [R \langle |\sin \theta_{ij}| \rangle + 2 \langle E(\theta_{ij}) \rangle / \pi + \langle |\cos \theta_{ij}| \rangle \\ &\quad + 2 \langle |\sin \theta_{ij}| \rangle / \pi R] [2R \langle |\sin \theta_{ij}| \rangle + 4 \langle E(\theta_{ij}) \rangle / \pi] . \end{aligned}$$

In order to be able to develop the mean field theory, we expand $|\sin \theta_{ij}|$, $|\cos \theta_{ij}|$ and $E(\theta_{ij})$ in terms of even Legendre polynomials $[P_{2n}(\cos \theta_{ij})]$. We get

$$\langle |\sin \theta_{ij}| \rangle = \frac{\pi}{4} - \frac{5\pi}{32} \langle P_2 \rangle^2 - \left(\frac{3}{16}\right)^2 \pi \langle P_4 \rangle^2 - \frac{65}{(16)^3} \pi \langle P_6 \rangle^2 - \dots$$

$$\langle |\cos \theta_{ij}| \rangle = \frac{1}{2} + \frac{5}{8} \langle P_2 \rangle^2 - \left(\frac{3}{16}\right) \langle P_4 \rangle^2 + \frac{13}{16\pi R} \langle P_6 \rangle^2 - \dots$$

$$\begin{aligned} \langle E(\theta_{ij}) \rangle &= \frac{\pi^2}{8} + \frac{5\pi^2}{128} \langle P_2 \rangle^2 - \left(\frac{3}{16}\right)^3 \pi^2 \langle P_4 \rangle^2 \\ &\quad + \frac{13}{2} \left(\frac{5\pi}{256}\right)^2 \langle P_6 \rangle^2 - \dots \end{aligned}$$

... (7)

where

$$\langle P_{2n} \rangle = \int_0^1 P_{2n}(\cos \theta) P(\cos \theta) d(\cos \theta) \quad (8)$$

Substituting for $\langle |\sin \theta_{1j}| \rangle$, $\langle \cos \theta_{1j} \rangle$ and $\langle S(\theta_{1j}) \rangle$,

A and B are simplified to

$$A = A_{000} + A_{200} \langle P_2 \rangle^2 + A_{020} \langle P_4 \rangle^2 + A_{002} \langle P_6 \rangle^2,$$

$$\begin{aligned} B = & B_{000} + B_{200} \langle P_2 \rangle^2 + B_{020} \langle P_4 \rangle^2 + B_{002} \langle P_6 \rangle^2 \\ & + B_{220} \langle P_2 \rangle^2 \langle P_4 \rangle^2 + B_{022} \langle P_4 \rangle^2 \langle P_6 \rangle^2 \\ & + B_{202} \langle P_6 \rangle^2 \langle P_2 \rangle^2 + B_{400} \langle P_2 \rangle^4 + B_{040} \langle P_4 \rangle^4 \\ & + B_{004} \langle P_6 \rangle^4 \end{aligned}$$

where

$$A_{000} = (R + 1)(\pi R + 1)/R$$

$$A_{200} = 5(1 - 2R)(\pi R - 2)/16R$$

$$A_{020} = -4(3 + 9\pi R/8)(3 + 8R)/(16)^2 R$$

$$A_{002} = 52(16R - 5)(16 - 5\pi R)/(16)^4 R$$

$$B_{000} = 2\pi(\pi R + 2)(R + 1)^2/16R$$

$$B_{200} = 20\pi(2R^2 + R - 1)(1 - \pi R)/(16)^2 R$$

$$B_{020} = 6\pi[\pi R(-24R^2 - 33R - 9) + (-88R^2 - 121R - 33)]/(16)^3 R$$

$$\begin{aligned}
 B_{002} &= 13\pi(11 - 5\pi R)(16R^2 + 11R - 5)/(16)^4 R \\
 B_{220} &= 30\pi(16R^2 - 2R - 3)(3\pi R + 2)/(16)^4 R \\
 B_{022} &= 156\pi(256R^2 + 16R - 30)(15\pi R - 8)/(16)^7 R \\
 B_{202} &= 520\pi(32R^2 - 26R + 5)(5\pi R - 26)/(16)^6 R \\
 B_{400} &= 50\pi(2R - 1)^2(\pi R - 4)/(16)^3 R \\
 B_{040} &= 216\pi(3\pi R + 16)(8R + 3)^2/(16)^6 R \\
 B_{004} &= 1690\pi(256R^2 - 160R + 25)(5\pi R - 32)/(16)^6 R.
 \end{aligned}$$

The pressure for the hard particle system is obtained from the Gibbs-Duhem equation, viz.,

$$\left[\frac{\partial F^N/kT}{\partial \rho} \right]_{P(\cos \theta)} = 1 + d \left[\frac{\partial d/kT}{\partial d} \right]_{P(\cos \theta)} \quad (9)$$

The above equation is solved with the relation (6), to get

$$P^N v_0/kT = d/(1-d) + Ad^2/2(1-d)^2 + 2Bd^3/(1-d)^3 \quad (10)$$

Equations (1), (6) and (10) can be combined to give the chemical potential μ^N ,

$$\begin{aligned}
 \frac{\mu^N}{kT} &= \int \frac{\mu_1^N}{kT} P(\cos \theta_1) d(\cos \theta_1) \\
 &= \langle \ln r(\cos \theta_1) \rangle + \ln \left[\frac{\rho}{1-d} \right] + \frac{d}{1-d} + \frac{Ad(2-d)}{2(1-d)^2} + \frac{Bd^2(3-d)}{3(1-d)^3} \\
 &\quad \dots(11)
 \end{aligned}$$

hence the Helmholtz free energy of the hard cylinder system is

$$\begin{aligned} \Lambda_c^{\#}/NkT &= \mu^{\#}/kT - P^{\#}v_0/dkT \\ &= \langle \ln P(\cos \theta_1) \rangle - 1 + \ln[P/(1-d)] \\ &\quad + Ad/2(1-d) + Bd^2/3(1-d)^2. \end{aligned} \quad (12)$$

We assume that the molecule is moving with a uniform mean field potential defined as

$$\bar{\Psi}_1 = -\psi_0\rho - \psi_2\rho \langle P_2 \rangle P_2(\cos \theta_1). \quad (13)$$

By including this attractive potential as in the last two chapters, we get the following expressions for total configurational Gibbs free energy, pressure, Helmholtz free energy and the internal energy:

$$\frac{G_c}{NkT} = \frac{G_0^{\#}}{NkT} - \frac{\psi_0 d}{v_0 kT} - \frac{\psi_2 d}{v_0 kT} \langle P_2 \rangle^2, \quad (14)$$

$$\frac{Pv_0}{kT} = \frac{P^{\#}v_0}{kT} - \frac{1}{2} \frac{\psi_0 d^2}{v_0 kT} - \frac{1}{2} \frac{\psi_2 d^2}{v_0 kT} \langle P_2 \rangle^2, \quad (15)$$

$$\frac{\Lambda_c}{NkT} = \frac{\Lambda_0^{\#}}{NkT} - \frac{1}{2} \frac{\psi_0 d}{v_0 kT} - \frac{1}{2} \frac{\psi_2 d}{v_0 kT} \langle P_2 \rangle^2, \quad (16)$$

$$\frac{U}{N} = -\frac{1}{2} \psi_0 \rho - \frac{1}{2} \psi_2 \rho \langle P_2 \rangle^2. \quad (17)$$

where $G_0^{\#}$, $P^{\#}$ and $\Lambda_0^{\#}$ are the Gibbs free energy, the pressure and the Helmholtz free energy of the purely hard

molecule system and are obtained respectively from equations (11), (10) and (12). Substituting these in equations (14-16), we get

$$\frac{G_c}{NkT} = \langle \ln F(\cos \theta_1) \rangle + \ln\left[\frac{\rho}{1-d}\right] + \frac{d}{(1-d)} + \frac{Ad(2-d)}{2(1-d)^2} + \frac{Bd^2(3-d)}{3(1-d)^3} - \frac{U_0\rho}{kT} - \frac{U_2\rho}{kT} \langle P_2 \rangle^2, \quad (18)$$

$$\frac{Pv_0}{kT} = \frac{d}{(1-d)} + \frac{Ad^2}{2(1-d)^2} + \frac{2Bd^3}{3(1-d)^3} - \frac{U_0d^2}{2v_0kT} - \frac{U_2d^2}{2v_0kT} \langle P_2 \rangle^2 \quad \dots \quad (19)$$

and

$$\begin{aligned} \frac{A_c}{NkT} &= \frac{G_c}{NkT} - \frac{Pv_0}{kT} \\ &= \langle \ln F(\cos \theta_1) \rangle - 1 + \ln\left[\frac{\rho}{1-d}\right] + \frac{Ad}{2(1-d)} \\ &\quad + \frac{Bd^2}{3(1-d)^2} - \frac{1}{2} \frac{U_0\rho}{kT} - \frac{1}{2} \frac{U_2\rho}{kT} \langle P_2 \rangle^2. \end{aligned} \quad (20)$$

The normalized single particle distribution function $F(\cos \theta)$ which minimises the Helmholtz free energy (eq. 21) is given by

$$F(\cos \theta) = \frac{\exp[-U_2(d) \langle P_2 \rangle P_2(\cos \theta) - U_4(d) \langle P_4 \rangle P_4(\cos \theta) - U_6(d) \langle P_6 \rangle P_6(\cos \theta)]}{\int_0^1 \exp[-U_2(d) \langle P_2 \rangle P_2(\cos \theta) - U_4(d) \langle P_4 \rangle P_4(\cos \theta) - U_6(d) \langle P_6 \rangle P_6(\cos \theta)] d(\cos \theta)} \quad (21)$$

where

$$\begin{aligned}
 U_2(d) &= \frac{dA_{200}}{1-d} + \frac{2d^2}{3(1-d)^2} [B_{200} + B_{220} \langle P_4 \rangle^2 + B_{202} \langle P_6 \rangle^2 \\
 &\quad + 2B_{400} \langle P_2 \rangle^2] - \frac{v_2 p}{kT} \\
 U_4(d) &= \frac{dA_{020}}{1-d} + \frac{2d^2}{3(1-d)^2} [B_{020} + B_{220} \langle P_2 \rangle^2 + B_{022} \langle P_6 \rangle^2 \\
 &\quad + 2B_{040} \langle P_4 \rangle^2] \\
 U_6(d) &= \frac{dA_{002}}{1-d} + \frac{2d^2}{3(1-d)^2} [B_{002} + B_{202} \langle P_2 \rangle^2 + B_{022} \langle P_4 \rangle^2 \\
 &\quad + 2B_{004} \langle P_6 \rangle^2]
 \end{aligned}
 \quad \dots (22)$$

For the sake of completeness we give the expressions for the entropy change $\Delta S/Nk$ at T_{HI} for the purely hard cylinders :

$$\frac{\Delta S}{Nk} = \frac{Pv_0}{kT} \left[\frac{d_{nem} - d_{iso}}{d_{nem} d_{iso}} \right]. \quad (23)$$

Including the attractive potential, the internal energy change at T_{HI} is given by

$$\frac{\Delta U}{Nk} = -\frac{1}{2} \frac{v_0}{v_0 k} (d_{nem} - d_{iso}) - \frac{1}{2} \frac{v_2}{v_0 k} d_{nem} \langle P_2 \rangle^2. \quad (24)$$

For both cases, the isothermal compressibility β of the isotropic phase is given by

$$\begin{aligned}
 \beta &= -\frac{1}{V} \left[\frac{\partial V}{\partial P} \right]_T = \frac{v_0}{d_{iso} kT} \left[\frac{\partial P v_0 / kT}{\partial d_{iso}} \right]_T^{-1} \\
 &= \frac{v_0}{d_{iso} kT} \left[\frac{1}{(1-d_{iso})^2} + \frac{A_{000} d_{iso}}{(1-d_{iso})^3} + \frac{2B_{000} d_{iso}^2}{(1-d_{iso})^4} \right]^{-1}. \quad (25)
 \end{aligned}$$

6.3 RESULTS AND DISCUSSION

As we have mentioned already, Alben (1973a,b) has used a lattice model to discuss the nematic-isotropic phase transition in a system of rectangular plates. In a single component system, if the plates are not very much like square plates (i.e., they have a biaxial nature), Alben (1973a) also found a biaxial nematic phase, separating a positive uniaxial nematic in which the longest axes of the plates tend to be parallel and a negative uniaxial nematic in which the flat faces of the plates tend to be parallel. However, in the system of cylinders that we have studied, the particles have uniaxial symmetry and as such we can only get a positive uniaxial nematic in the rod-like region ($R < 0.5$) and a negative uniaxial nematic in the disc-like region ($R > 0.5$).

The properties of the ensemble are completely determined by the shape factor R , the packing fraction d and the NI transition temperature T_{NI} . In equations (7), $|\sin \theta|$, $|\cos \theta|$ and $E(\theta)$ have been expanded in terms of even Legendre polynomials. It is necessary to truncate the series in order to make calculations. We have plotted the three functions of θ by retaining terms up to the second, fourth and sixth order Legendre polynomials in figures 1a-1c.

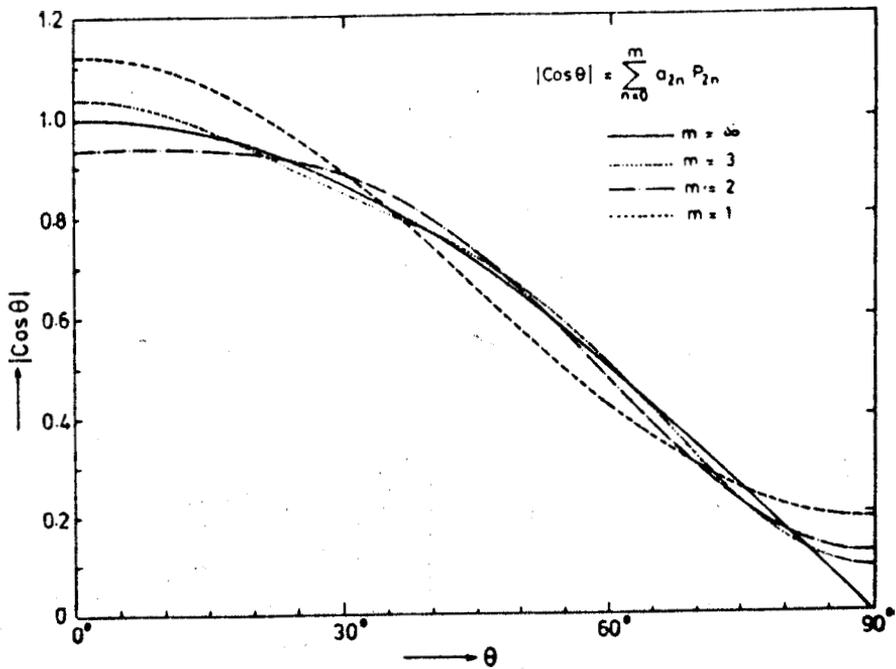
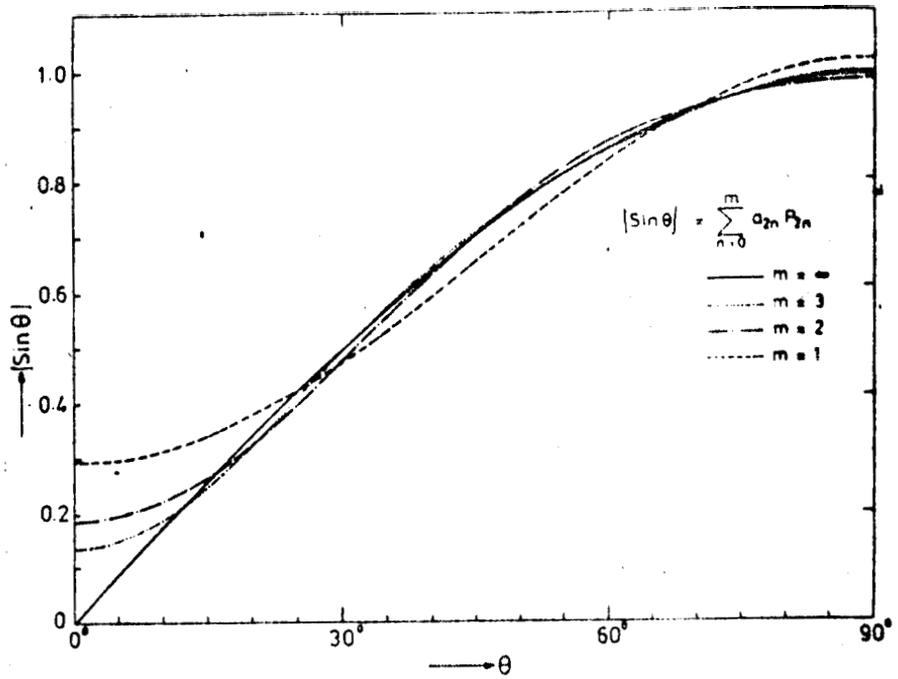


FIG. 1a: Comparison between $|\cos \theta|$ and the values obtained by retaining terms up to different even Legendre polynomials in the expansion of $|\cos \theta|$.



BIG. 1b: Comparison between $|\sin \theta|$ and the values obtained by retaining terms up to different even Legendre polynomials in the expansion of $|\sin \theta|$.

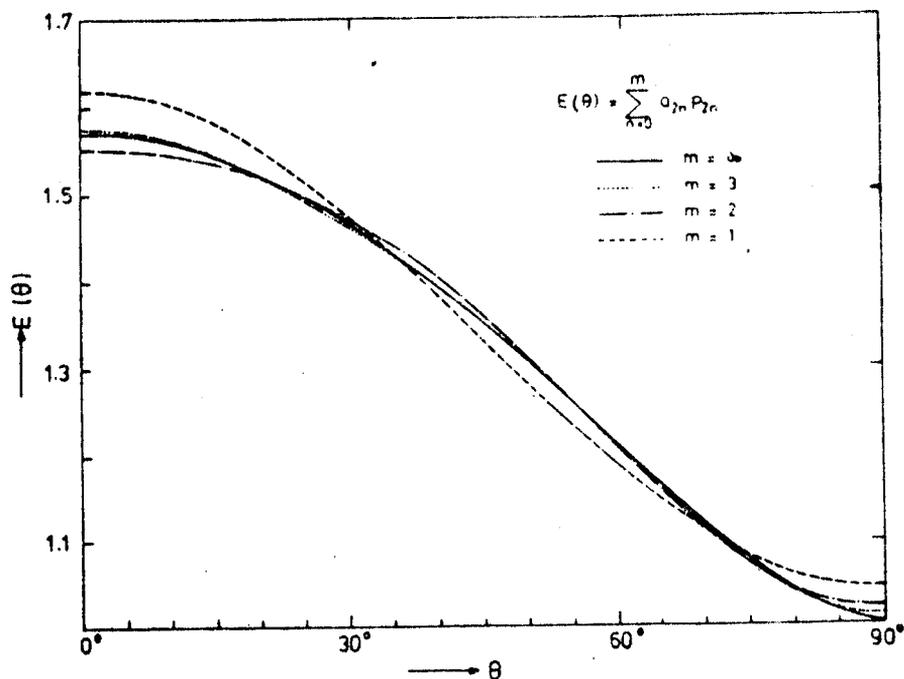


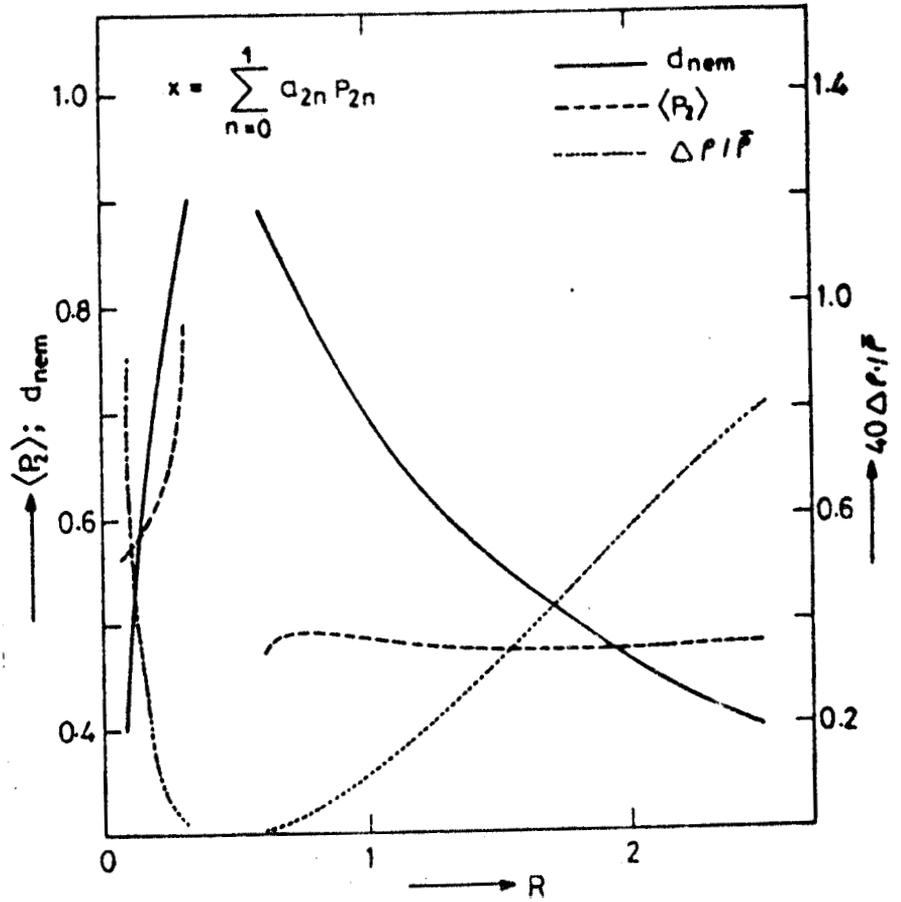
FIG. 1c: Comparison between $E(\theta)$ and the values obtained by retaining terms up to different even Legendre polynomials in the expansion of $E(\theta)$.

It is clear from the figures that the errors are reduced by including higher order terms. Retaining terms up to $P_6(\cos \theta)$ only, the error in $E(\theta)$ is *putts* small over the entire range of values of θ (Fig. 1c), while the error for $|\cos \theta|$ still remains noticeable for large angles (Fig. b). As we had seen in the last two chapters, the inclusion of higher order terms in $|\sin \theta|$ expansion does not affect the qualitative behaviour of the transition properties of a system of spherocylinders. On the other hand, from the present calculations on a system of cylinders, we shall see that the $P_4(\cos \theta)$ term is essential to get a qualitatively correct trend in the results. We have made calculations by retaining terms up to $P_2(\cos \theta)$, $P_4(\cos \theta)$ and $P_6(\cos \theta)$ respectively in the expansions (7) for a hard particle system. When the attractive potential fa also included, the calculations are made by retaining terms up to $P_2(\cos \theta)$ and $P_6(\cos \theta)$ in the expansions (7).

(a) Results for a system of hard cylinders

For the purely hard molecule system ($v_2 = v_0 = 0$), we made the calculations as follows. For a given value of R , assuming some reasonable value of d_{nem} , we can use eqn. (8) along with equations (21) and (22) to get consistent values of $\langle P_{2n} \rangle$. The integrals have been evaluated on a DEC-10

computer by using a 16-points Gaussian quadrature scheme and the consistent values of $\langle P_{2n} \rangle$ have been obtained by adopting a least squares fitting procedure. The pressure can then be calculated using equation (10). Setting $\langle P_{2n} \rangle = 0$, the same equation can then be used to calculate the packing fraction of the isotropic phase (d_{iso}) by equating the pressure to that of the nematic phase. Equation (11) can now be used to calculate the chemical potentials of the phases. d_{nem} is now adjusted by an iterative procedure to make the chemical potentials of the two phases equal. The calculations are repeated for a range of values of R between $R = 0.08$ (rod-like molecules) and $R = 3.0$ (disc-like molecules). The data are used to calculate $\Delta\rho/\bar{\rho}$ (which is the relative density change at NI transition, $\bar{\rho} = (\rho_{nem} + \rho_{iso})/2$), the isothermal compressibility β of the isotropic phase and the entropy change $\Delta S/Nk$ at NI transition. Retaining, in the first instance, only the first two terms in eq.(7) the calculated values of $\langle P_2 \rangle$, d_{nem} and $\Delta\rho/\bar{\rho}$ at the NI transition point as functions of R are shown in fig. 2. We see that a 'rod-like' region ($R < 0.5$) gets very much compressed in the figure compared to the 'disc-like' region ($R > 0.5$). Hence for a better comparison between the two regions, we have plotted the properties as functions of $2R$ for $R > 0.5$ and



F10.2: Variation of $\langle P_2 \rangle$, d_{nem} and $\Delta \rho / \bar{\rho}$ as functions of R obtained by retaining terms up to $P_2(\cos \theta)$ in the expansions of angle dependent terms.

$1/2R$ for $R < 0.5$ in figure 3. Figures 3a-3c correspond to calculations made by retaining terms up to $P_2(\cos \theta)$, $P_4(\cos \theta)$ and $P_6(\cos \theta)$ respectively as described above. The entropy change $\Delta S/Nk$ (eq. 23), Pv_0/kT and the isothermal compressibility β (eq. 24) of the isotropic phase at the NI transition point are shown in figures 4a-4c.

When the expansion is restricted to terms up to $P_2(\cos \theta)$, it is seen from equation (22) and from the definition of A and B that there is no anisotropic phase for $R = 0.5$ (as was noticed by Ishihara (1951)). But by including higher order terms, we get the anisotropic phase for the entire range of values of R. Though $U_2(d) = 0$ for $R = 0.5$, $U_4(d)$ and $U_6(d)$ still contribute to the stability of the nematic phase. From fig. 3a, it is seen that as I-shape anisotropy decreases, i.e., as the value of R approaches 0.5 from either side, d_{nem} at the NI transition increases monotonically. However, the closest packed density for a system of right circular cylinders is $\pi/2\sqrt{3} \approx 0.91$. We have not shown the results for the range $0.31 < R < 0.6$ in fig. 3a, since the calculated value of d_{nem} exceed 0.91 in this range. This unphysical result is removed by including the higher order terms as is seen in figures 3b and 3c, and d_{nem} at NI point is a maximum for $R \approx 0.47$. It means that less anisotropic particles exhibit the nematic phase at greater packing

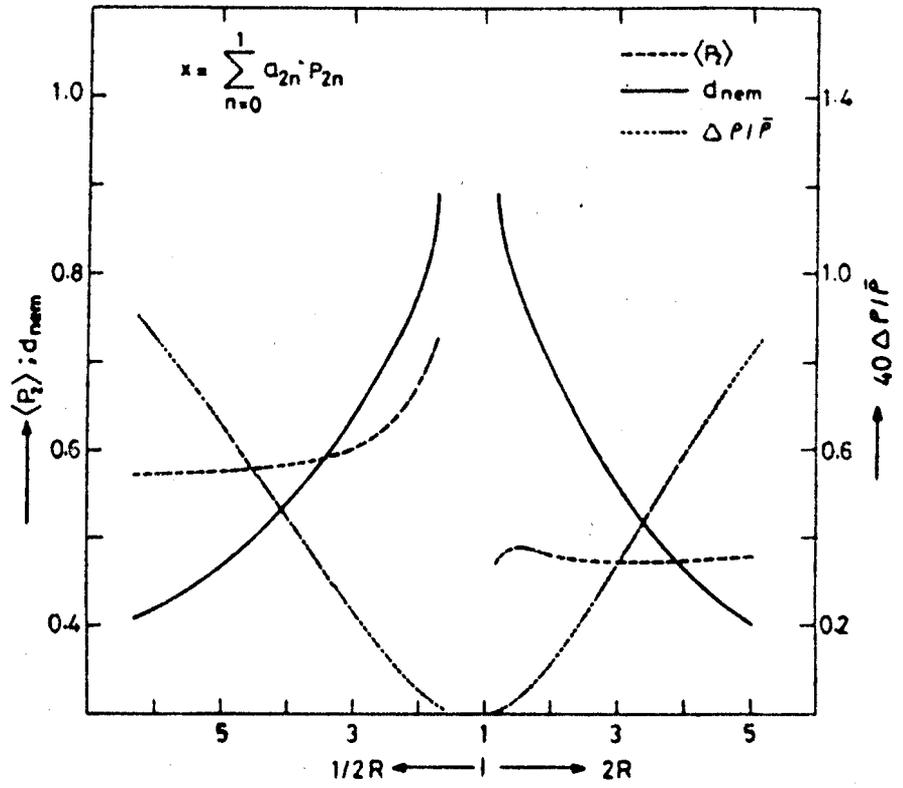


FIG. 3a: Variation of $\langle P_2 \rangle$, d_{nem} and $\Delta P/\bar{P}$ obtained by retaining terms up to $P_2(\cos \theta)$ in the expansions of angle dependent term and plotted as functions of $2R$ (for $R > 0.5$) and $1/2R$ (for $R < 0.5$).

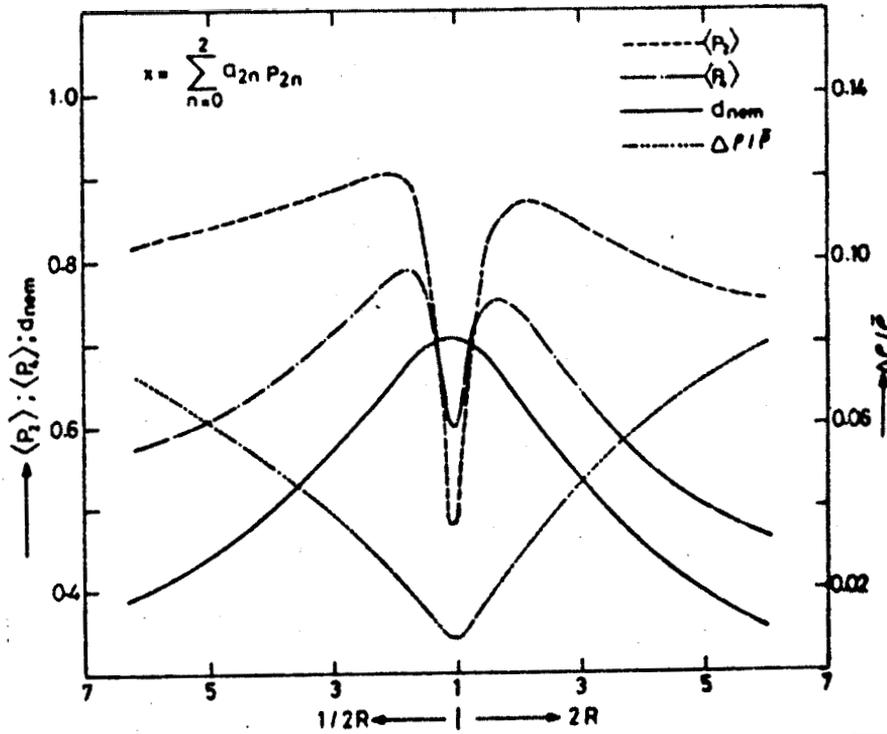


FIG.3b: Variation of $\langle P_2 \rangle$, $\langle P_4 \rangle$, d_{nem} and $\Delta P/\bar{P}$ obtained by retaining terms up to $P_4(\cos \theta)$ in the expansions of angle dependant terms.

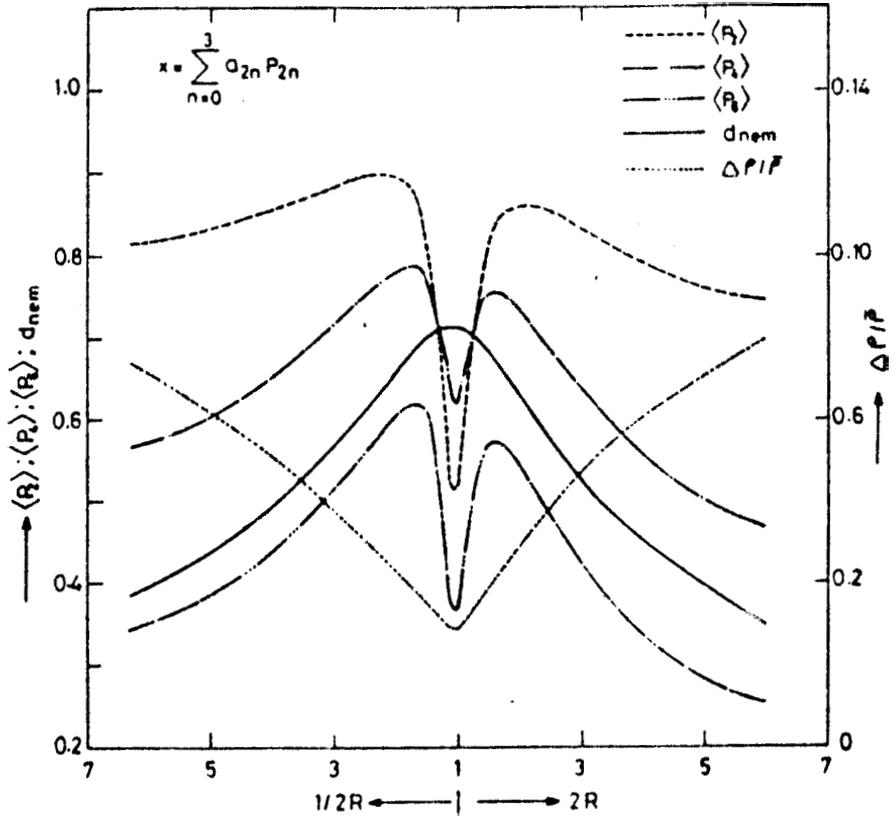


FIG.3c: Variations of $\langle P_2 \rangle$, $\langle P_4 \rangle$, $\langle P_6 \rangle$, d_{nem} and $\Delta P/\bar{P}$ obtained by retaining terms up to $P_6(\cos \theta)$ in the expansions of angle dependent terms.

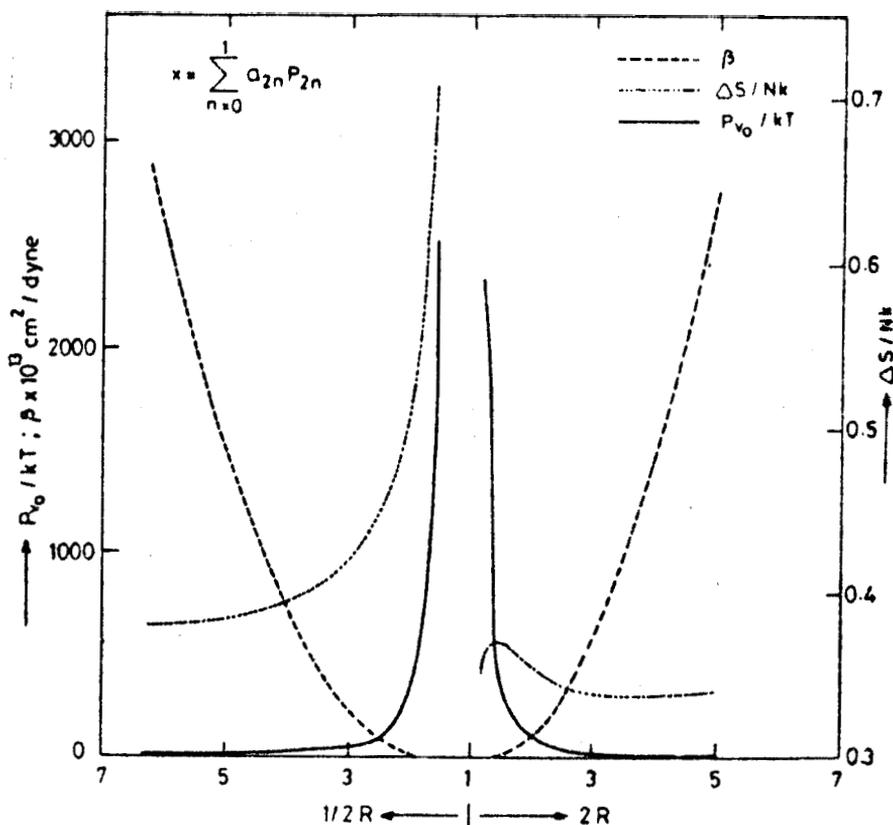


FIG.4a: $\Delta S/Nk$, P_{v_0}/kT and β obtained by retaining terms up to $P_2(\cos \epsilon_3)$ in the expansions of angle dependent terms.

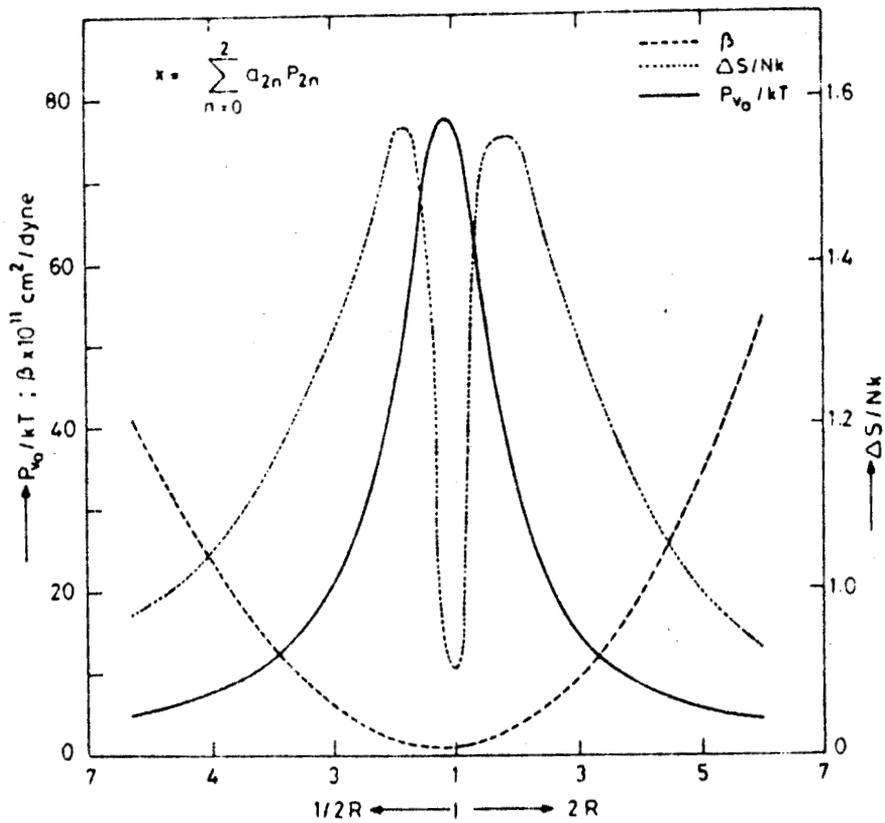


FIG.4b: $\Delta S/Nk$, P_{v_0}/kT and β obtained by retaining terms up to $P_4(\cos \theta)$ in the expansions of angle dependent terms.

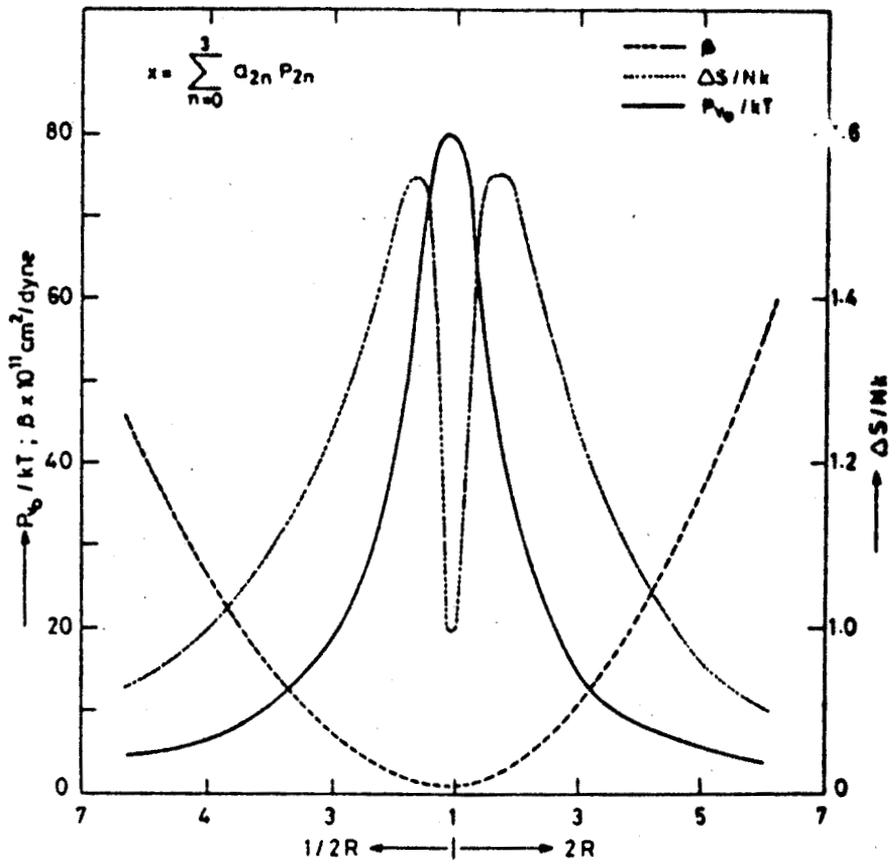


FIG.4c: $\Delta S/Nk$, Pv_0/kT and β obtained by retaining terms up to $P_6(\cos \theta)$ in the expansions of angle dependent terms.

fractions. The density change $\Delta\rho/\bar{\rho}$ at the NI transition decreases relatively rapidly as the anisotropy of the molecule is decreased. Retaining terms only up to $P_2(\cos \theta)$ in the expansion, $\Delta\rho/\bar{\rho}$ approaches zero. Including terms up to $P_4(\cos \theta)$ (fig. 3b) and $P_6(\cos \theta)$ (fig. 3c), $\Delta\rho/\bar{\rho}$ attains a minimum value $\simeq 0.008$ $R \simeq 0.47$. Retaining terms only up to $P_2(\cos \theta)$, we found that $\langle P_2 \rangle$ decreases as the shape-anisotropy increases for the 'rod-like' region. This trend is opposite to that for hard-spherocylinders (see chapters IV and V). On the other hand in the 'disc-like' region the value of $\langle P_2 \rangle$ at NI transition appears to be essentially independent of R (fig. 3a). However, this is an artifact of the approximation, since inclusion of higher order terms lead to a symmetric trend in the two sides (figures 3b, 3c). $\langle P_{2n} \rangle$ increases as the anisotropy decreases, attains a maximum and has a sharp dip as we approach $R = 0.5$ taking a minimum value for $R \simeq 0.47$. As seen in the same figures, $\langle P_4 \rangle$ has higher values than $\langle P_2 \rangle$ in a small range of values of $2R$ around $2R = 1$. As $2R$ approaches the value $\simeq 1.0$, $U_2(d)$ becomes smaller and smaller. Hence to get the NI transition, $\langle P_2 \rangle$ has to larger and larger values around $2R \simeq 1.6$ (see eq.22). Further since $U_2(d)=0$ at $R=0.5$, the transition is mostly determined

by $U_4(d)$. Hence in the region close to $2R = 1.0$, $\langle P_4 \rangle$ exceeds the value of $\langle P_2 \rangle$. The maximum value of $\langle P_{2n} \rangle$ in the 'rod-like' region is somewhat larger than that in the 'disc-like' region. From figures 3a-3c, selecting the value of R such that $(2R)_{\text{disc-like}} = (1/2R)_{\text{rod-like}}$ we found that $\langle P_{2n} \rangle$, d_{nem} and $\Delta\rho/\bar{\rho}$ for rod-like molecules are somewhat larger than those of the disc-like molecules. Further the product of $(2R)_{\text{disc-like}} \times (1/2R)_{\text{rod-like}}$ having the same value of d_{nem} at the NI transition is seen to be $\simeq 0.8$.

The trends in other properties of the nematic phase are also changed somewhat as a consequence of introducing higher order terms. The entropy change $\Delta S/Nk$ at NI transition point increases as the shape anisotropy decreases, attains a maximum and decreases sharply attaining a minimum value $\simeq 0.98$ for $R \simeq 0.47$ (figures 4b and 4c). Experimentally Destradé et al (1979) found that $\Delta S/Nk \simeq 0.06$ for $R \simeq 4$ (see table I). The calculated value is an order of magnitude larger. Pv_0/kf increases as R approaches 0.5 from either side and reaches a maximum $\simeq 80$ for $R \simeq 0.47$. Assuming that the pressure is held constant, NI transition temperature increases as the anisotropy increases. Further the isothermal compressibility β of the isotropic phase decreases as R decreases to 0.5 from either side and attains

Table 1

The nematic-isotropic transition temperatures (T_{NI}) of different hexa-alkoxybenzoates of triphenylene

R	T_{NI} °C
C_4H_9O	> 300
$C_5H_{11}O$	298
$C_6H_{13}O$	274
$C_7H_{15}O$	253
$C_8H_{17}O$	244
$C_9H_{19}O$	227
$C_{10}H_{21}O$	212
$C_{11}H_{23}O$	185 and $\Delta S/Nk = 0.054$ kcal mol ⁻¹

a minimum $\simeq 0.1 \times 10^{-10}$ cm²/dyne at $R \simeq 0.47$.

(b) Results after including the attractive potential

The theory has three parameters, viz., R , v_0 and v_2 . We assume that $T_{NI} = 600^\circ\text{K}$ which appears to be a reasonable value for disc-like mesogens (see table I). This will essentially determine the value of v_2 . For a given value of R , we also fix d_{nem} at T_{NI} to determine the value of v_0 .

The calculations are made by assuming some value of $v_2/v_0 k$ to start with, and the self-consistent long range order parameters $\langle P_{2n} \rangle$ are evaluated by using equation (8). The pressure is then obtained by using equation (19). It is equated to the atmospheric pressure to get the value of $v_0/v_0 k$. Equating the pressure of the nematic phase to that of the isotropic phase (obtained by using equation (20) with $\langle P_{2n} \rangle = 0$), d_{iso} is calculated. Equation (18) is now used to calculate the Gibbs free energy of both the nematic and isotropic phases. The assumed value of $v_2/v_0 k$ is adjusted by an iterative procedure to equalize the Gibbs free energy of both the phases. Calculations have been repeated for different values of R . The relative density change $\Delta\rho/\bar{\rho}$, where $\bar{\rho}$ is the average value of the densities of the nematic and isotropic phases, the internal energy change $\Delta U/NkT$ (eq. 24) at T_{NI} and β of the isotropic phase (eq. 25) can now be calculated.

From our calculations on a system of hard right circular cylinders, it is clear that the angle-dependent terms of the excluded volume have to be expanded at least up to $P_4(\cos \theta)$ to get qualitatively correct results. Including the attractive potential, we now compare the results with the angle dependent terms expanded up to $P_6(\cos \theta)$ with those in which they are restricted to $P_2(\cos \theta)$.

Figures 5a and 5b exhibit various transition properties when the expansion is restricted to $P_2(\cos \theta)$ and d_{nem} is assumed to be 0.6 at T_{NI} . recall that there is a discontinuity in transition properties near $R \approx 0.5$ for a system of hard cylindrical molecules, since the anisotropic part of the potential is zero for $R = 0.5$ when $\psi_2 = 0$ (see fig. 3a). Further in this case as R approaches 0.5 from either side, the packing fraction tends to exceed the closest packed density. But by including the attractive potential ($\psi_2 \neq \psi_0 \neq 0$) and d_{nem} to a value less than the value of the closest packed density, all the transition properties vary smoothly around $R = 0.5$ even when the expansion is restricted to $P_2(\cos \theta)$. (see table II)

From figure 5a, we see that the anisotropic energy parameter ψ_2/v_0k takes a maximum value for $R = 0.5$ and

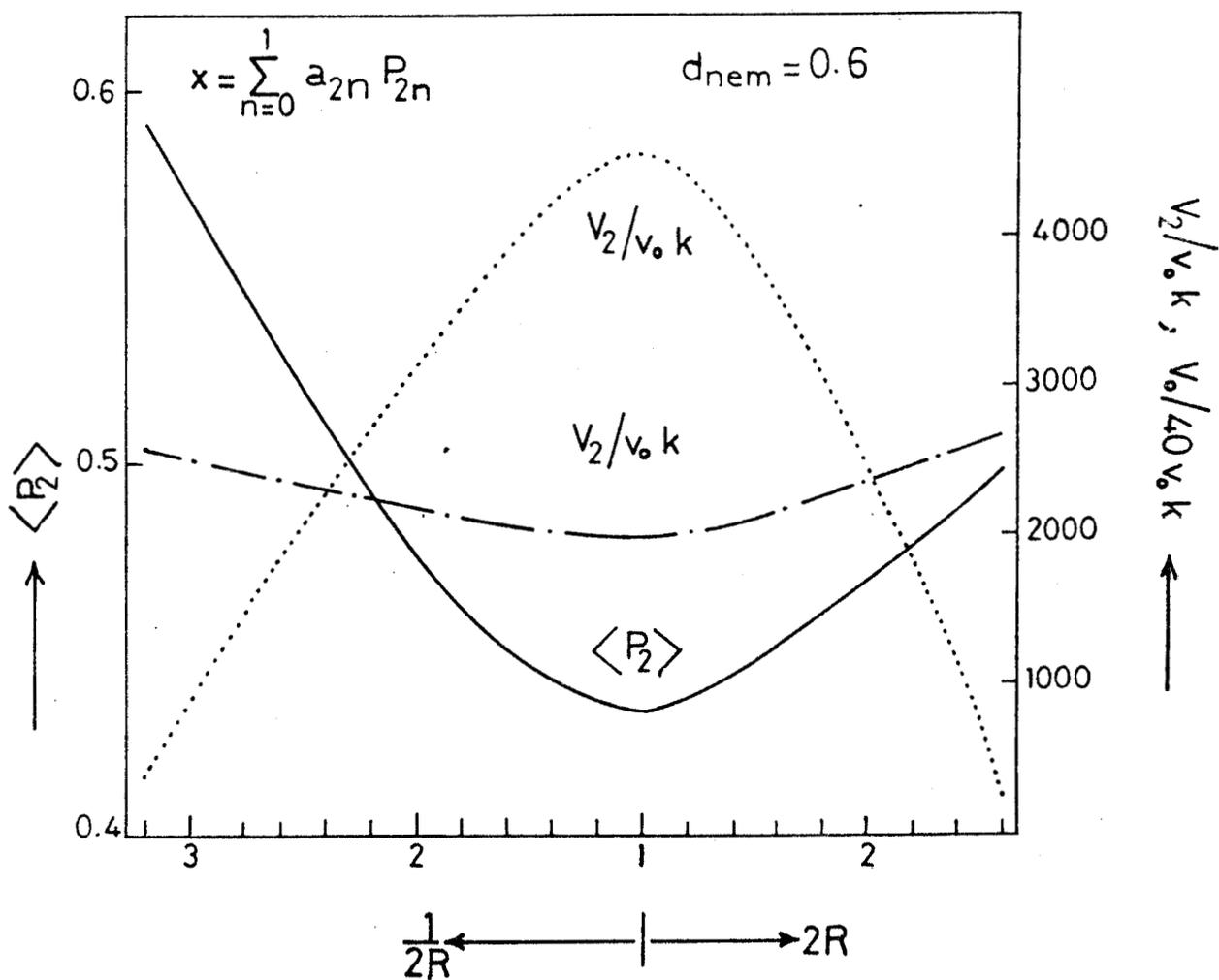


FIG.5a: $\langle P_2 \rangle$, $V_2/v_0 k$ and $V_0/v_0 k$ obtained by including an attractive potential and retaining terms up to $P_2(\cos \theta)$ in the expansions of angle dependent terms and fixing $d_{nem} = 0.6$.

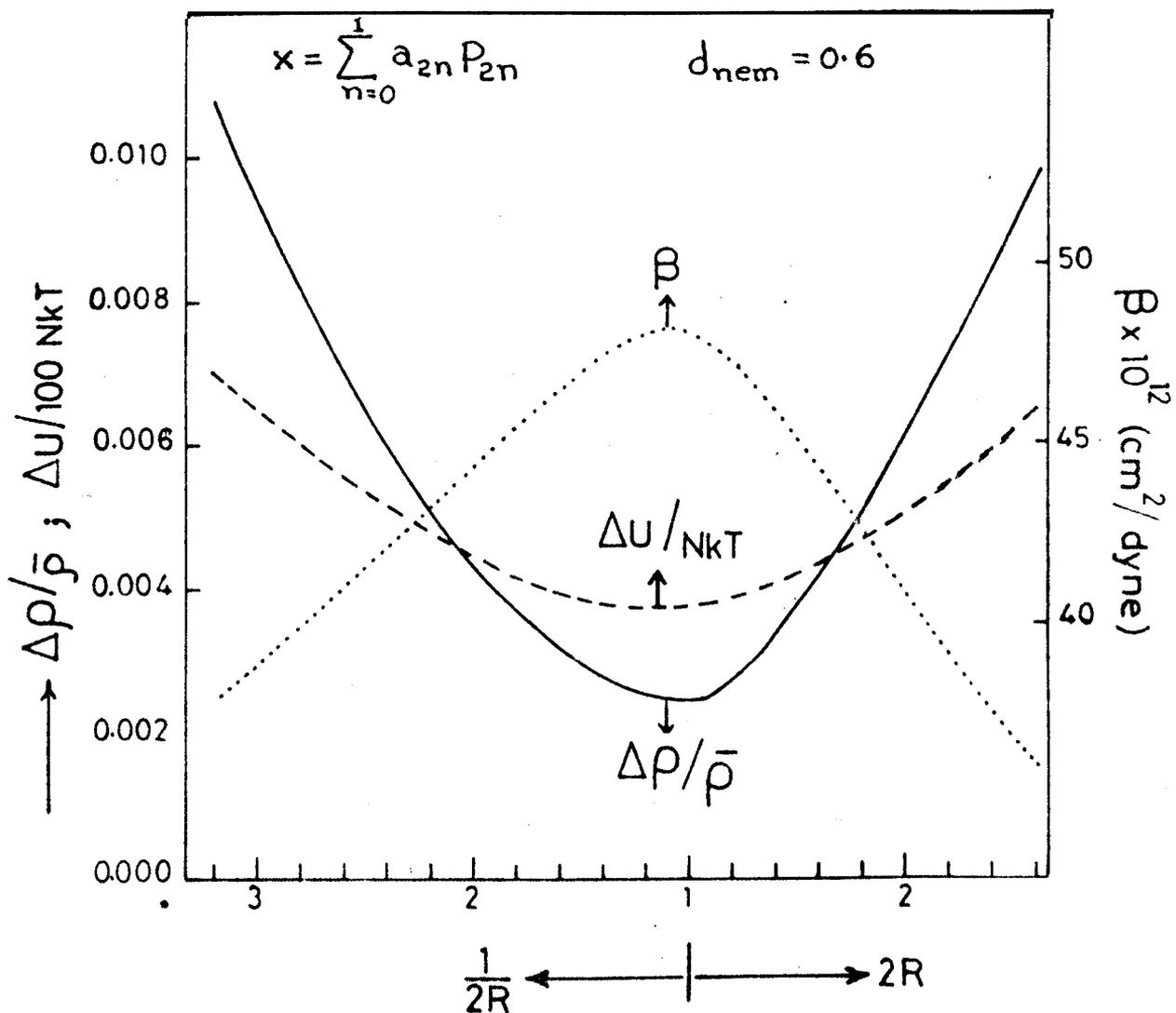


FIG.5b. $\Delta\rho/\bar{\rho}$, $\Delta U/NkT$ and β obtained by including an attractive potential and retaining terms up to $P_2(\cos \theta)$ in the expansions of angle dependent terms and fixing $d_{nem} = 0.6$.

TABLE II

Results for $R \approx 0.5$. $x(\cos \theta) = \sum_{n=0}^m a_{2n} P_{2n}(\cos \theta)$

	$v_2/v_0 k$	$v_0/v_0 k$	$\langle P_2 \rangle$	$\langle P_4 \rangle$	$\langle P_6 \rangle$	$\Delta p/\bar{p}$	$\Delta U/kT$
$m = 1$	0.0	0.0	Calculations near $R \approx 0.5$ are not possible since $d_{nem} > d_{close\ packed}$				
$m = 2$	0.0	0.0	0.483	0.598	-	0.0082	0.925
$m = 3$	0.0	0.0	0.515	0.620	0.367	0.0087	1.008
$m = 1$ $d_{nem} = 0.6$	4547.15	80365.38	0.434	-	-	0.0025	0.376
$m = 3$ $d_{nem} = 0.6$	3570.22	72833.76	0.832	0.629	0.413	0.0026	1.858
$m = 3$ $d_{nem} = 0.4$	7030.90	23573.03	0.667	0.337	0.138	0.098	0.978

By including terms up to $P_6(\cos \theta)$ in the expansions

(larger dimension/smaller dimension) of the cylinders.

about $R \approx 0.5$ when they are plotted as functions of the ratio

$\langle P_2 \rangle$, $\Delta \epsilon / \rho$, $\Delta U / kT$ and β at T_{HI} are almost symmetrical

FIG. 4a). All these properties, viz., $\beta / \Delta \epsilon$, $\Delta U / kT$,

opposite to that found for the hard particle system (see

to that of $\beta / \Delta \epsilon$ (see FIG. 5b). This trend is exactly

bilily β of the isotropic phase behaves in a manner similar

a manner similar to that of $\langle P_2 \rangle$. The isotropic compress-

other properties like $\beta / \Delta \epsilon$, $\Delta \epsilon / \rho$ and $\Delta U / kT$ behave in

trend for spherocylinders (see chapter IV and V). The

results for rod-like molecules and with the theoretical

increases. This trend is in agreement with the experimental

$R = 0.5$ and increases on either side as the shape anisotropy

The order parameter $\langle P_2 \rangle$ also takes a minimum value at

and increase on either side as the shape anisotropy increases.

of $\beta / \Delta \epsilon$, i.e., T_{HI} will have a minimum value at $R = 0.5$

variation in T_{HI} as function of R will be opposite to that

Hence if the calculations are made by fixing $\beta / \Delta \epsilon$, the

T_{HI} transition is essentially determined by the term $\beta / \Delta \epsilon$.

T_{HI} was kept constant and $\beta / \Delta \epsilon$ allowed to vary. The

for $2R \approx 2.6$ in the disc-like region. In these calculations

It drops to zero for $1/2R \approx 3.2$ in the rod-like region and

decreases on either side as the shape anisotropy increases.

of angle dependent terms, we repeated the calculations for various values of R by taking $d_{\text{nem}} = 0.6$ at T_{NI} . The results obtained for different transition properties are shown in figures 6a and 6b. Comparing these with the results shown in fig. 5a and 5b, we find that the inclusion of higher order terms leads to an increase in the strength of the NI transition, i.e., $\langle P_2 \rangle$, $\Delta\rho/\rho$ and $\Delta U/NkT$ increase substantially at T_{NI} . Both the energy parameters v_0 and v_2 decrease. Except for this quantitative difference, the qualitative behaviour of all the properties remain essentially similar.. Unlike in the hard particle system, $\langle P_6 \rangle$ is less than $\langle P_4 \rangle$ which itself is less than $\langle P_2 \rangle$ for all values of R . By including the higher order terms, the range of values of R for which the calculations yield positive values of v_0 and v_2 for the given T_{NI} and d_{nem} gets somewhat reduced; $1/2R \simeq 2.6$ to $2R \simeq 2.2$. However, the variation of β changes considerably compared to that in fig. 5b. For disc-like molecules β increases with decrease in the shape anisotropy. For rod-like molecules, as the shape anisotropy increases, β first decreases slightly and then increases (fig. 6b).

In order to study the effect of the packing density on the phase transition properties, we have also made calculations by fixing $d_{\text{nem}} = 0.4$ at T_{NI} and by taking terms up

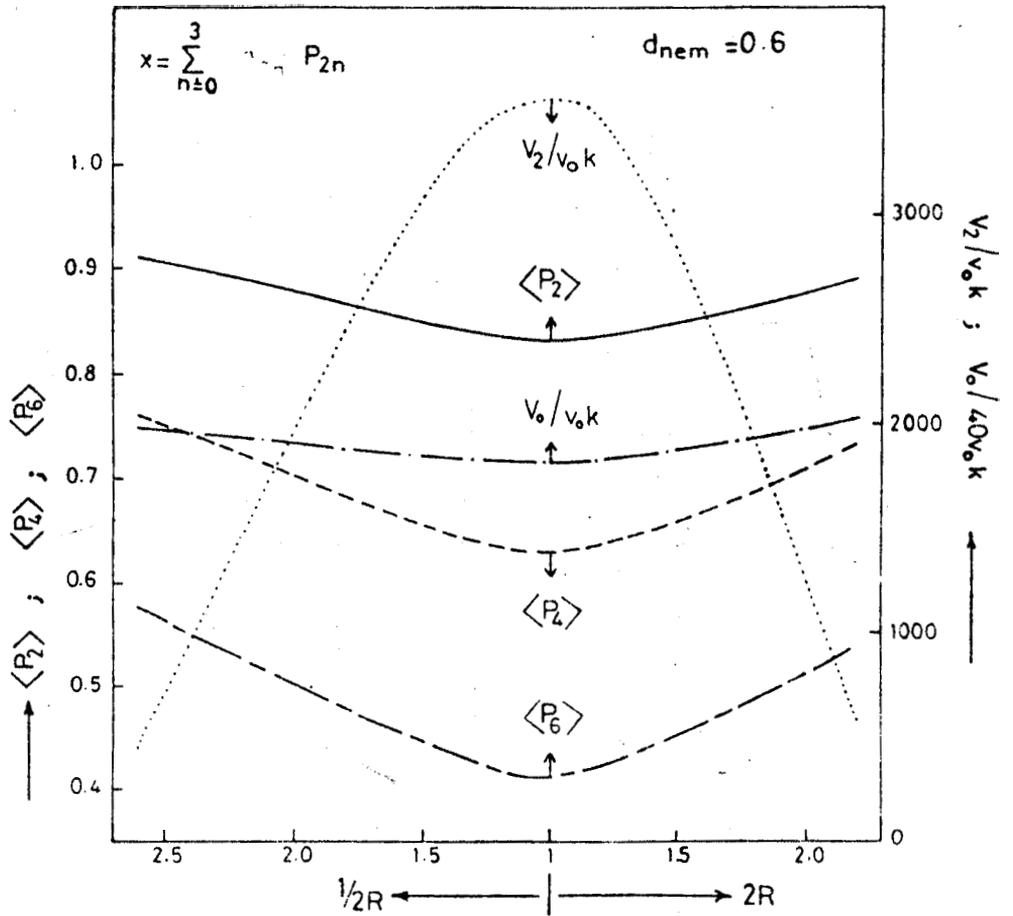


FIG.6a: $\langle P_2 \rangle$, $\langle P_4 \rangle$, $\langle P_6 \rangle$, $v_0/v_0 k$ and $v_2/v_0 k$ obtained by including an attractive potential and retaining terms up to $P_6(\cos \theta)$ in the expansions of angle dependent terms and fixing $d_{nem} = 0.6$.

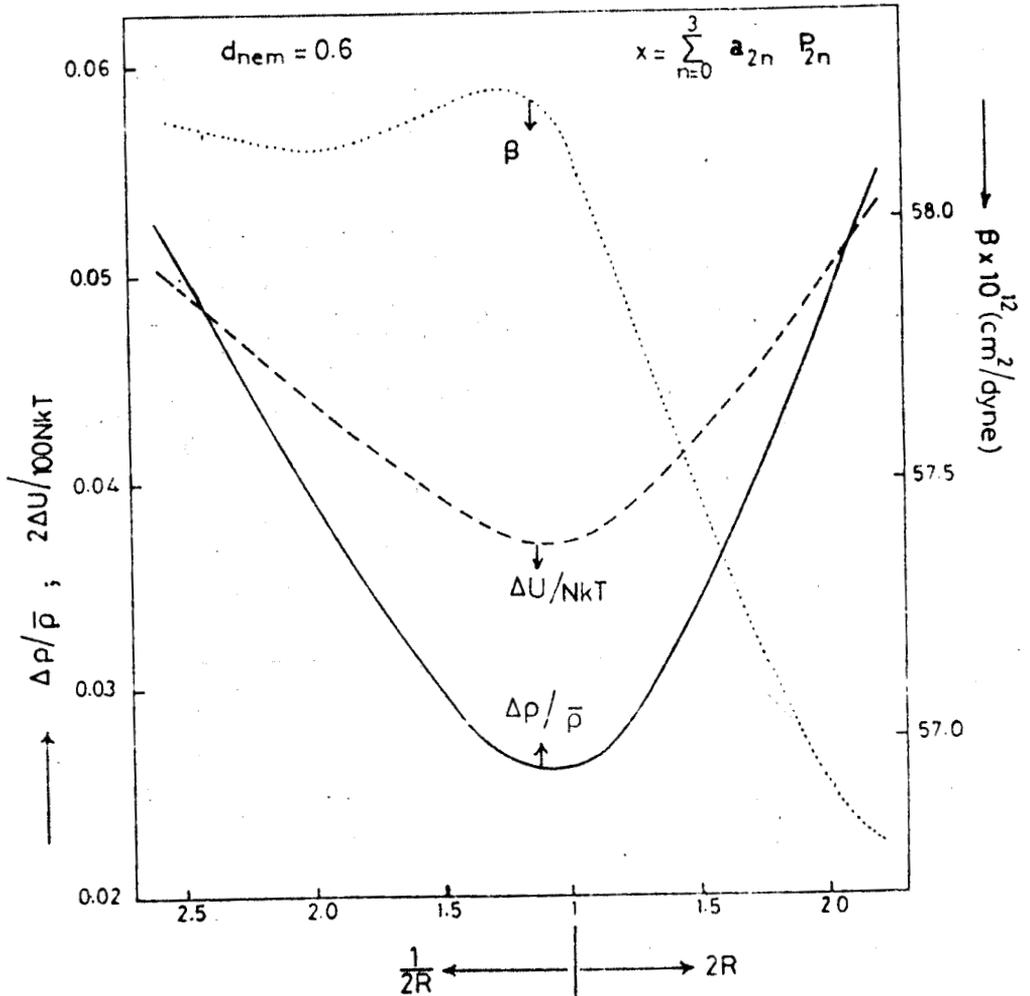


FIG.6b: $\Delta\rho/\bar{\rho}$, $\Delta U/NkT$ and β obtained by including an attractive potential and retaining term up to $P_6(\cos \theta)$ in the expansions of angle dependent terms and fixing $d_{nem} = 0.6$.

to $P_6(\cos \theta)$ in the expansion of the angle dependent terms. The results obtained for various properties are plotted in figures 7a and 7b. In comparison with the results on the more closely packed system (figure 6), the range of possible values of R gets wider, from $1/2R \approx 7.4$ for rod-like molecules to $2R \approx 6.6$ for disc-like molecules (Fig. 7a). Further the values of $\langle P_{2n} \rangle$, $\Delta U/NkT$ and $v_0/v_0 k$ decrease whereas $\Delta \rho/\rho$ and $v_2/v_0 k$ increase. The variation of β as a function of R is very much affected by the decrease in the value of d_{nem} , becoming almost symmetrical about $R \approx 0.5$ (Fig. 7b). The value of β itself goes up by a factor of ~ 15 . At $R \approx 0.5$, β takes a maximum value and decreases on either side as the shape anisotropy increases and takes a minimum value at $\frac{1}{2R} \approx 2.4$ for rod-like molecules and at $2R \approx 2.4$ for disc-like molecules. As the shape anisotropy increases further, the value of β increases again.

In conclusion, our calculations demonstrate that the phase transition properties of nematic liquid crystals of disc-like molecules are essentially analogous to those of rod-like molecules. The transition properties are functions of the ratio (larger dimension/smaller dimension) of the cylinders. Inclusion of higher order terms at least up to $P_4(\cos \theta)$ in the expansions of angle dependent terms is

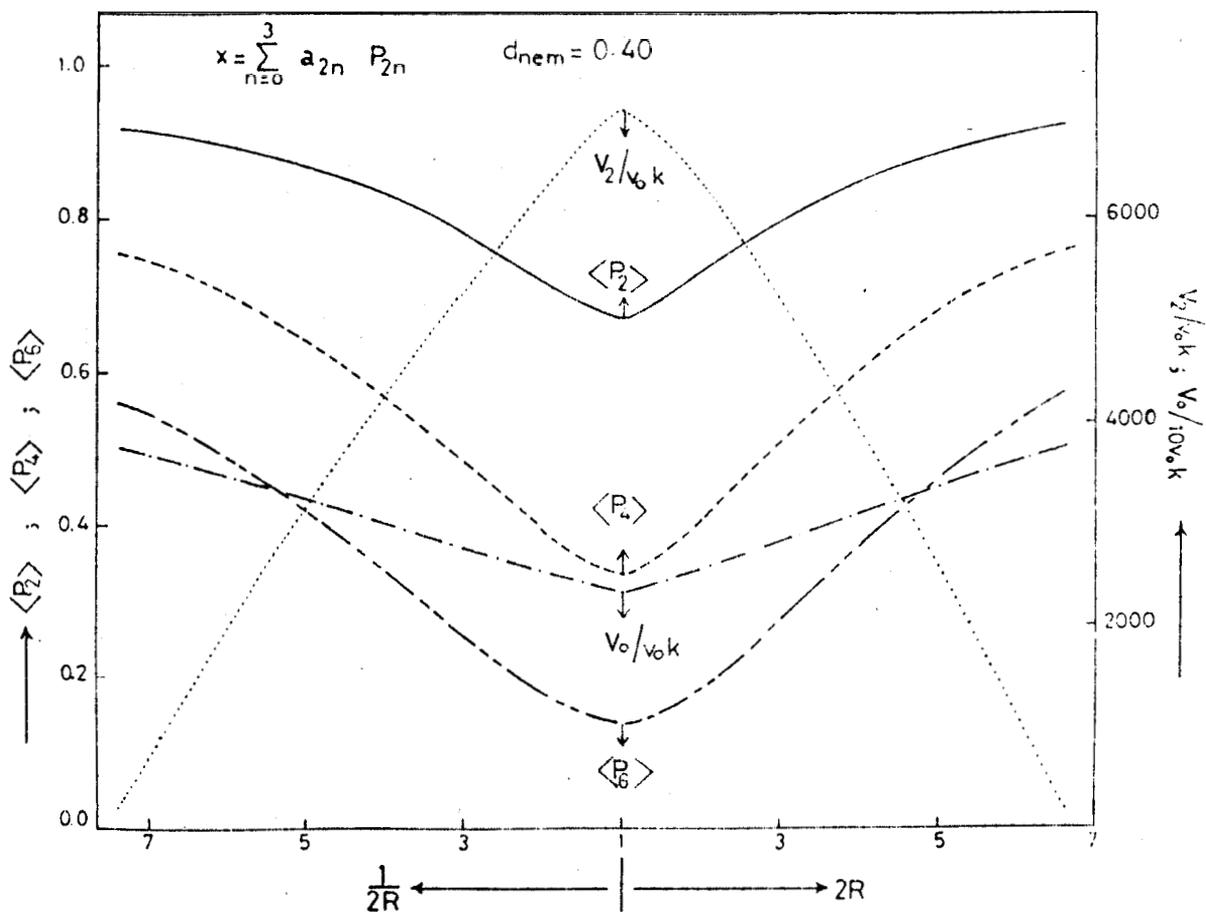


FIG. 7a: $\langle P_2 \rangle$, $\langle P_4 \rangle$, $\langle P_6 \rangle$ ■ v_0/v_0k and v_2/v_0k obtained by including an attractive potential and retaining terms up to $P_6(\cos \theta)$ in the expansions of angle dependant terms and fixing $d_{nem} = 0.6$.

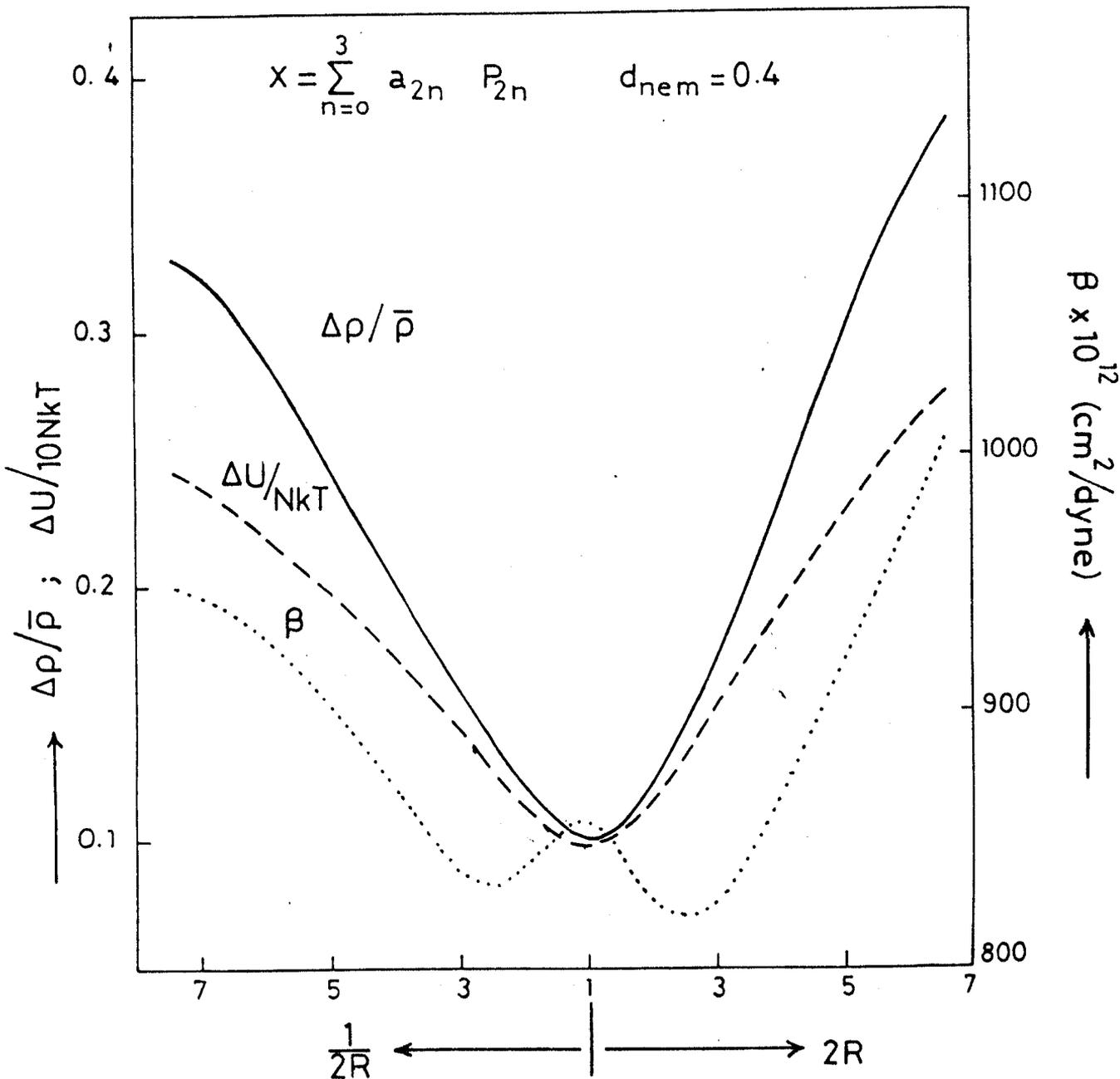


FIG. 7b: $\Delta\rho/\bar{\rho}$, $\Delta U/NkT$ and β obtained by including an attractive potential and retaining terms up to $P_6(\cos \theta)$ in the expansions of angle dependent terms and fixing $d_{nem} = 0.4$.

necessary to get qualitatively correct results, for the system of hard cylinders. However this is not so much important when the system is superposed with an attractive potential, but it does effect the compressibility of the system.

6.4 Comparison with experimental results

As we have already mentioned in the introduction, the nematic phase exhibited by essentially flat molecules was discovered long ago in the pyrolysis of coke by Brooks and Taylor (1965). A few homologous series of single component disc-like molecules, viz., hexa-*n*-alkoxyloxy truxene, hexa-alkoxybenzoates of truxene and of triphenylene have been found to exhibit the nematic phase (see Destradé et al, 1979, 1980; Tinh et al, 1981). The chemical formulae of hexa-alkoxybenzoates of triphenylene, hexa-*n*-alkanoates of truxene and the proposed arrangement of the disc-like molecules in the nematic phase are shown in figures 8a, 8c and 8b respectively. The nature of the nematic phase was confirmed by Levelut et al (1981) from mobility and X-ray diffraction studies. They also measured the magnetic susceptibility for the sixth and the eleventh members of the series. The magnetic anisotropy is negative in the nematic phase as is to be expected for such flat molecules (see fig.8b). They also observed a jump in the value of magnetic anisotropy at T_{NI} indicating that the transition is of first order.

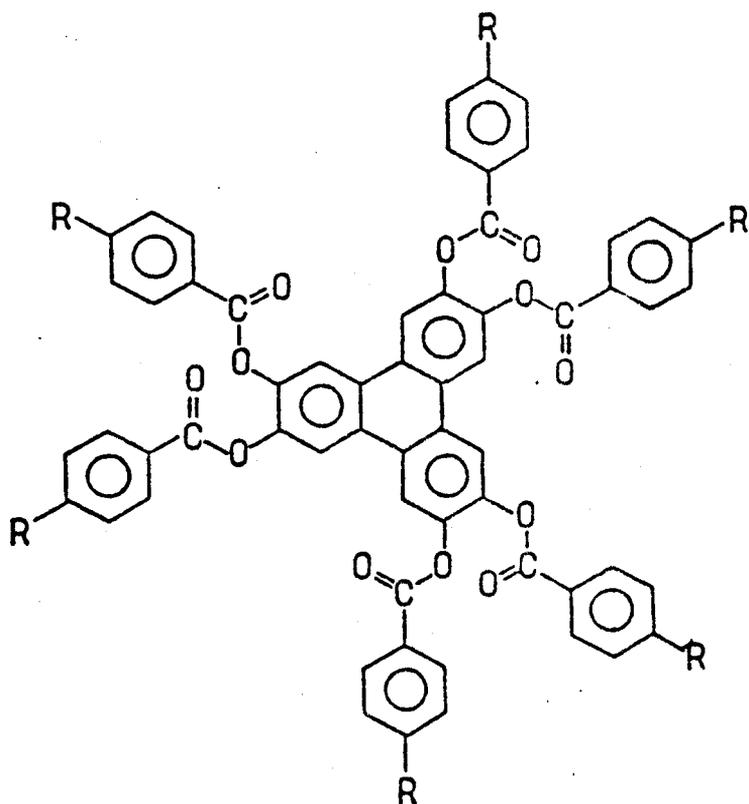


FIG.8a: Chemical formula of hexa-alkoxybenzoates of triphenylene

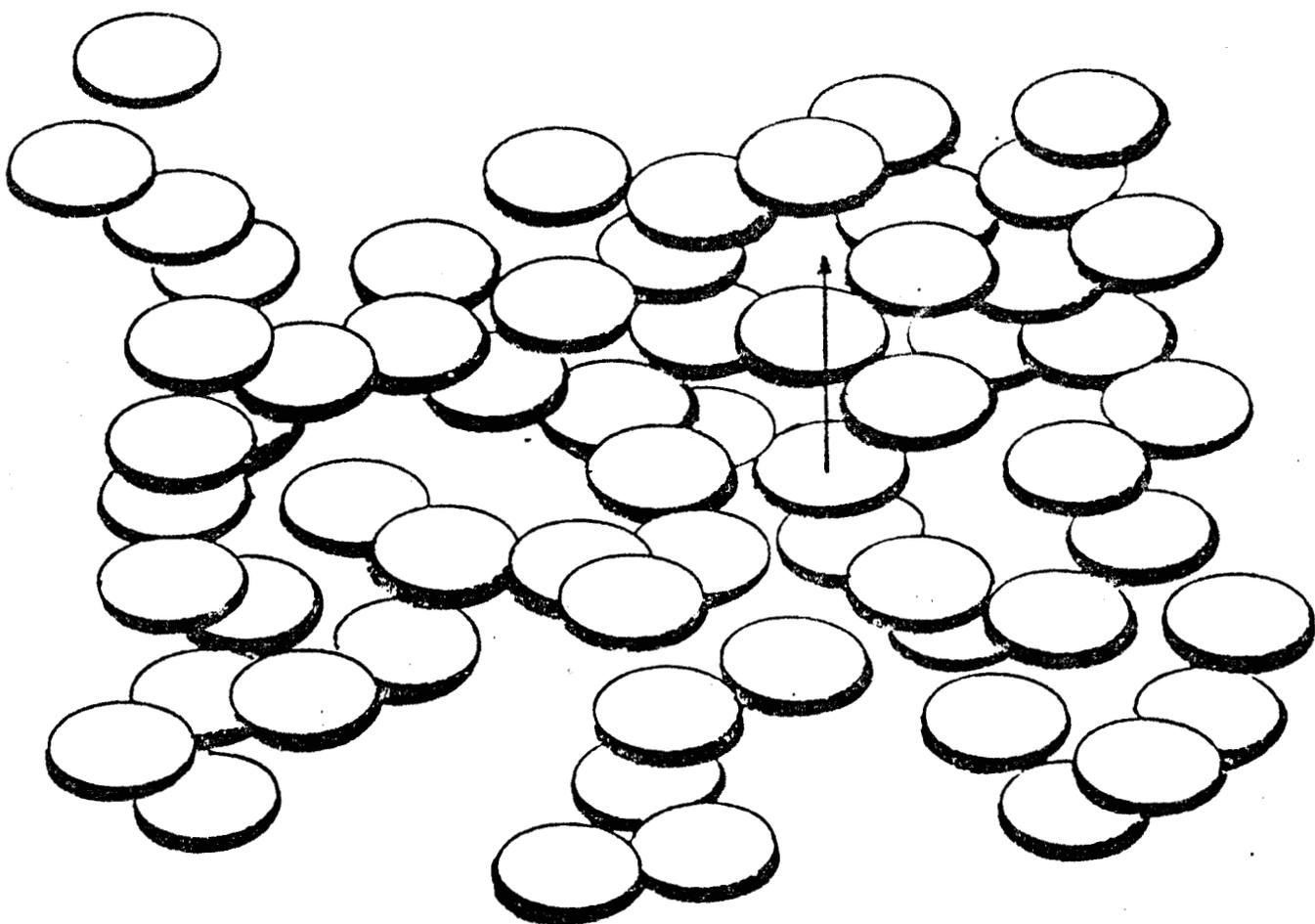


FIG.8B: Structure of a discotic nematic phase.

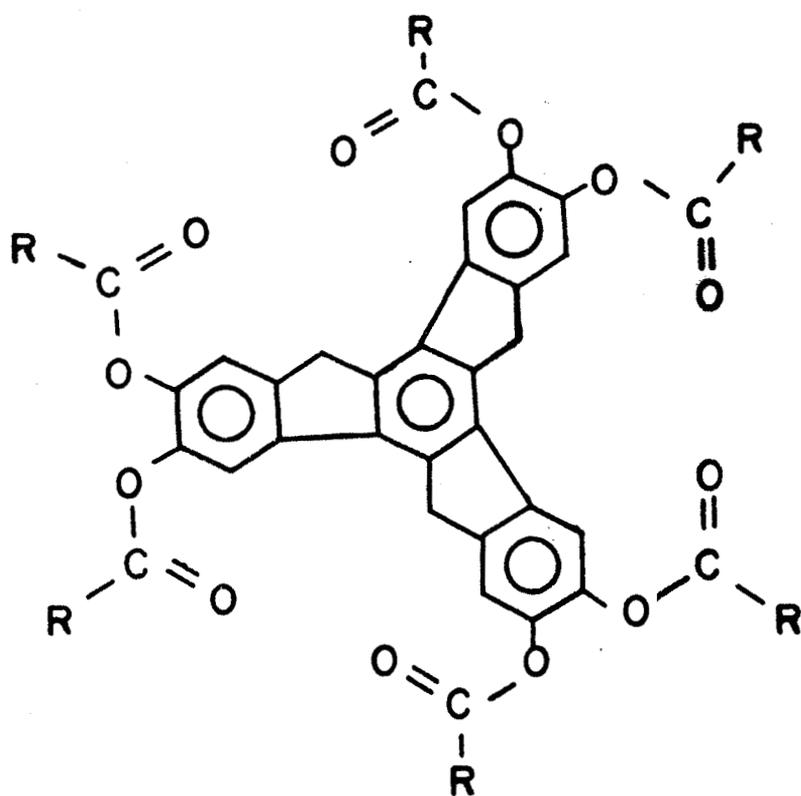


FIG. 8c: Chemical formula of hexa-n-alkanoates of truxene

The nematic-isotropic transition temperature obtained for the series are tabulated in table I. The heat of transition is known only for the eleventh member of the series. Our calculated value of ΔU is larger by an order of magnitude. The experimental values of T_{NI} decreases as the chain length increases. At first, this may appear to contradict the calculated trend in which T_{NI} increases as the molecular size increases. However in developing the theory, we have assumed the molecule to be a rigid cylinder. But as we can see from fig. 8a, the real molecules have six chains around the periphery with a lot of free space between them and the chains can take different conformations. Hence the chain statistics has to be taken into account in the development of the theory. For rod-like molecules, as Marcelja (1974) has shown, chain statistics plays an important role in determining the behaviour of T_{NI} . For instance he showed that for a homologous series with relatively low transition temperatures, T_{NI} increases with molecular size, while for series with relatively high transition temperatures, T_{NI} decreases as the molecular size increases. For example, for p-p'-di-n-alkyl-azoxybenzenes, T_{NI} ranges from 25°C to 75°C and increases as n increases whereas for p-p'-di-n-alkoxy-azoxybenzenes, T_{NI} ranges from 175°C to 100°C and decreases

as n increases. In the first case, because of the relatively low temperature, the chains are rigid and increasing their lengths increases the average anisotropic interactions between the molecules. In the second case, chains are rather flexible because of the high temperatures and the larger chains which are more flexible decrease the average anisotropic interactions. For hexa-alkoxybenzoates which exhibit the discotic nematic phase, T_{HI} ranges from 185°C to 298°C which is in a sufficiently high range to explain the decreasing trend of T_{HI} with increasing chain length.

Recently Flapper and Vertogen (1981) made calculations on nematics made of disc-like and oblong molecules. To study the system of hard cylinders, they have used the equation of state of a system of hard spheres as given by Carnahan and Starling with the modified definition of $d = \rho \langle v_{\text{excl}} \rangle$, where $\langle v_{\text{excl}} \rangle$ is the average value of excluded volume of two cylinders (eq. 3). Terms only up to $P_2(\cos \theta)$ are retained in the expansion of v_{excl} . The discontinuity in the properties that exists in this case is removed by an approximate expression for v_{excl} . Calculations are made by using both the actual and the approximate expressions for v_{excl} . In both the cases they found that $\langle P_2 \rangle$ and $\Delta\rho/\bar{\rho}$ decrease as $x (= \frac{1}{2R})$ decreases to

a value close to 1. X starts increasing as the value of x is decreased further and d_{nem} behaves exactly in the opposite manner. The qualitative behaviour of $\Delta\rho/\bar{\rho}$ and d_{nem} as functions of x are analogous to our results. The trend of our calculated value of $\langle P_2 \rangle$ depends on the number of terms retained in the expression of V_{excl} . By including an attractive potential, they made calculations for $x = \sqrt{\pi}/2$ by adjusting ν_0 and ν_2 to get $T = 409^\circ\text{K}$ and $\gamma = 4.0$ at T_{NI} . The other properties at T_{NI} are found to be $\langle P_2 \rangle = 0.535$, $d_{\text{nem}} = 0.478$, $\Delta\rho/\bar{\rho} = 0.0465$ and $\Delta S/Nk = 0.973$. For the same value of x by fixing $T_{\text{NI}} = 600^\circ\text{K}$ and $d_{\text{nem}} = 0.6$ at T_{NI} , we get $\langle P_2 \rangle = 0.43$, $\Delta\rho/\bar{\rho} = 0.0024$ and $\Delta S/Nk = 0.34$, i.e., a considerably weaker transition.

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