Scaled Particle Theory of a System of Right Circular Cylinders Subjected to an Attractive Potential

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Scaled Particle Theory of a System of Right Circular Cylinders Subjected to an Attractive Potential

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We extend the scaled particle theory of a system of hard right circular cylinders by including a mean field attractive potential of the Maier and Saupe type. The order parameters, internal energy change, density change and the isothermal compressibility of the isotropic phase at the nematic–isotropic transition point are studied for various values of R the radius to height ratio of the cylinders. As in the case of the hard right circular cylinders, there is an approximate symmetry in the phase transition properties between the disc-like and rod-like regions when plotted as functions of the ratio of the larger to smaller dimension of the cylinders.

INTRODUCTION

In a previous paper[1] (hereafter called I) we have applied the scaled particle theory (SPT) to study the phase transition properties of a system of hard right circular cylinders. By varying the radius to height ratio R of the cylinders, we could study the properties of the nematic phase formed either by rod-like molecules ($R < 0.5$) or by disc-like molecules ($R > 0.5$). While nematic liquid crystals of the former type are well known, those of the latter type were found only recently.[2-7] In I we confined our attention to a hard cylindrical system. In the present paper we discuss the effect of superposing an attractive potential of the Maier–Saupe type on such cylindrical molecules.

THEORY

The Gibb's free energy (G_c^*), the pressure (P^*) and the Helmholtz free energy (A_c^*) of a system of hard cylindrical molecules are given by[1]

$$\frac{G_c^*}{NkT} = \langle \ln f (\cos \theta) \rangle + \ln \left(\frac{\rho}{1-d} \right) + \frac{d}{(1-d)}$$
$$+ \frac{Ad(2-d)}{2(1-d)^2} + \frac{Bd^2(3-d)}{3(1-d)^3} \quad (1)$$

$$\frac{P^* v_0}{kT} = \frac{d}{(1-d)} + \frac{Ad^2}{2(1-d)^2} + \frac{2Bd^3}{3(1-d)^3} \quad (2)$$

$$\frac{A_c^*}{NkT} = \langle \ln f (\cos \theta) \rangle - 1 + \ln \left(\frac{\rho}{1-d} \right) + \frac{Ad}{2(1-d)} + \frac{Bd^2}{3(1-d)^2} \quad (3)$$

where the single particle distribution function $f(\cos \theta)$ (θ being the polar angle), the packing fraction (d) and the coefficients A and B have been defined in I.

Following Cotter[8] we subject the molecules to a uniform mean field potential of the form

$$\bar{\Psi} = -\vartheta_0 \rho - \vartheta_2 \rho \langle P_2 \rangle P_2(\cos \theta) \quad (4)$$

where ϑ_0 and ϑ_2 are the strengths of the isotropic and anisotropic interactions. The configurational Gibb's free energy (G_c), the pressure (P) and the Helmholtz free energy (A_c) will now take the form

$$\frac{G_c}{NkT} = \frac{G_c^*}{NkT} - \frac{\vartheta_0 d}{v_0 kT} - \frac{\vartheta_2 d}{v_0 kT} \langle P_2 \rangle^2 \quad (5)$$

$$\frac{P v_0}{kT} = \frac{P^* v_0}{kT} - \frac{1}{2} \frac{\vartheta_0 d^2}{v_0 kT} - \frac{1}{2} \frac{\vartheta_2 d^2}{v_0 kT} \langle P_2 \rangle^2 \quad (6)$$

$$\frac{A_c}{NkT} = \frac{A_c^*}{NkT} - \frac{1}{2} \frac{\vartheta_0 d}{v_0 kT} - \frac{1}{2} \frac{\vartheta_2 d}{v_0 kT} \langle P_2 \rangle^2 \quad (7)$$

The internal energy U of the system is given by

$$\frac{U}{N} = -\frac{1}{2} \vartheta_0 \rho - \frac{1}{2} \vartheta_2 \rho \langle P_2 \rangle^2. \quad (8)$$

The normalized single particle distribution function $f(\cos \theta)$ which minimizes the configurational Helmholtz free energy [Eq. (7)] is now given by

$$
f(\cos\theta) = \frac{\exp[-U_2(d)\langle P_2\rangle P_2(\cos\theta) - U_4(d)\langle P_4\rangle P_4(\cos\theta) - U_6(d)\langle P_6\rangle P_6(\cos\theta)]}{\displaystyle\int_0^1 \exp[-U_2(d)\langle P_2\rangle P_2(\cos\theta) - U_4(d)\langle P_4\rangle P_4(\cos\theta) - U_6(d)\langle P_6\rangle P_6(\cos\theta)]d(\cos\theta)} \quad (9)
$$

where

$$
U_2(d) = \frac{dA_{200}}{1-d} + \frac{2d^2}{3(1-d)^2}[B_{200} + B_{220}\langle P_4\rangle^2 + B_{202}\langle P_6\rangle^2
$$

$$
+ 2B_{400}\langle P_2\rangle^2] - \frac{\vartheta_2\rho}{kT}
$$

$$
U_4(d) = \frac{dA_{020}}{1-d} + \frac{2d^2}{3(1-d)^2}[B_{020} + B_{220}\langle P_2\rangle^2 + B_{022}\langle P_6\rangle^2
$$

$$
+ 2B_{040}\langle P_4\rangle^2]
$$

$$
U_6(d) = \frac{dA_{002}}{1-d} + \frac{2d^2}{3(1-d)^2}[B_{002} + B_{202}\langle P_2\rangle^2 + B_{022}\langle P_4\rangle^2
$$

$$
+ 2B_{004}\langle P_6\rangle^2] \quad (10)
$$

and

$$
\langle P_{2n}\rangle = \int_0^1 P_{2n}(\cos\theta)f(\cos\theta)d(\cos\theta) \quad (11)
$$

where the angle-dependent terms of the excluded volume of the cylinders have been expanded up to $P_6(\cos\theta)$ and the B coefficients have been defined in I.

For the sake of completeness we give the expressions for the internal energy change $\Delta U/Nk$ at T_{NI} and the isothermal compressibility β of the isotropic phase:

$$
\frac{\Delta U}{Nk} = -\frac{1}{2}\frac{\vartheta_0}{v_0 k}(d_{\text{nem}} - d_{\text{iso}}) - \frac{1}{2}\frac{\vartheta_2}{v_0 k}d_{\text{nem}}\langle P_2\rangle^2 \quad (12)
$$

$$
\beta = -\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]
$$

$$
= \frac{v_0}{d_{\text{iso}}kT}\left[\frac{1}{(1-d_{\text{iso}})^2} + \frac{A_{000}d_{\text{iso}}}{(1-d_{\text{iso}})^3} + \frac{2B_{000}d_{\text{iso}}^2}{(1-d_{\text{iso}})^4}\right]^{-1} \quad (13)
$$

RESULTS AND DISCUSSION

As we have noted in our earlier paper,[1] Alben[9,10] 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[9] 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 theory has three parameters, viz., R, ϑ_0 and ϑ_2. We assume that $T_{NI} = 600°K$ which appears to be a reasonable value for disc-like mesogens.[2,3] This will essentially determine the value of ϑ_2. For a given value of R, we also fix d_{nem} at T_{NI} to determine the value of ϑ_0.

The calculations are made by assuming some value of $\vartheta_2/v_0 k$ to start with, and the self-consistent long range order parameters $\langle P_{2n} \rangle$ are evaluated by using Eqs. (9–11). The pressure is then obtained by using Eq. (6). It is equated to the atmospheric pressure to get the value of $\vartheta_0/v_0 k$. Equating the pressure of the nematic phase to that of the isotropic phase (obtained by using Eq. (6) with $\langle P_{2n} \rangle = 0$), d_{iso} is calculated. Equation (5) is now used to calculate the Gibb's free energy of both the nematic and isotropic phases. The assumed value of $\vartheta_2/v_0 k$ is adjusted by an iterative procedure to equalize the Gibb's 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. (12)] at T_{NI} and β of the isotropic phase [Eq. (13)] can now be calculated.

From our calculations on a system of hard right circular cylinders in I, 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. In the present calculations including the attractive potential, we 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 1a and 1b 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}. We recall that there is a discontinuity in transition properties near $R \simeq 0.5$ for a system of *hard* cylindrical molecules,[1] since the aniso-
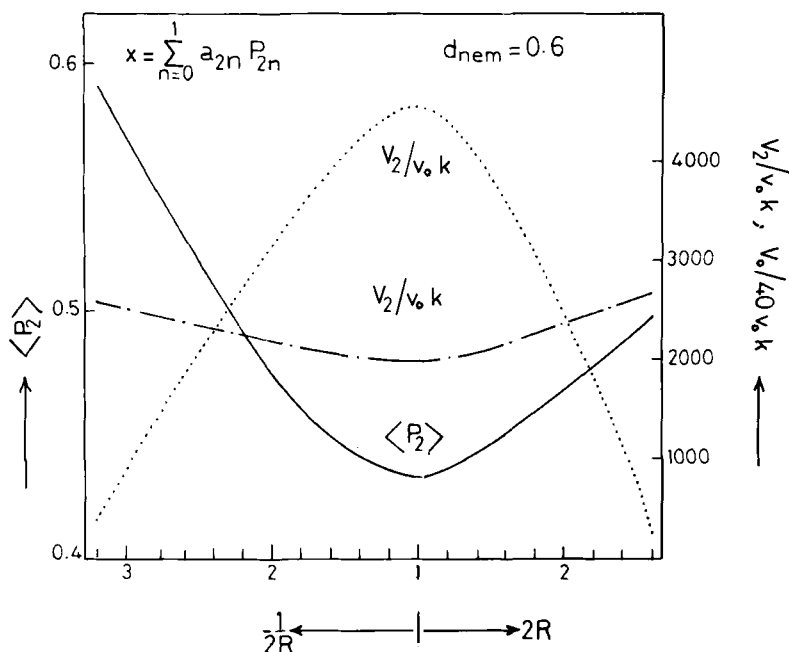
FIGURE 1a   Variation of $\langle P_2 \rangle$, $\vartheta_2/v_0 k$, and $\vartheta_0/v_0 k$ with the shape anisotropy obtained by retaining terms up to $P_2 (\cos \theta)$ only in the expansions of angle dependent terms and with $d_{nem} = 0.6$.

tropic part of the potential is zero for $R = 0.5$ when $\vartheta_2 = 0$. 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 ($\vartheta_2 \neq \vartheta_0 \neq 0$) and fixing 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 $P_2 (\cos \theta)$.

From Figure 1a, we see that the anisotropic energy parameter $\vartheta_2/v_0 k$ takes a maximum value for $R = 0.5$ and decreases on either side as the shape anisotropy increases. It drops to zero for $1/2R \simeq 3.2$ in the rod-like region and for $2R \simeq 2.6$ in the disc-like region. In these calculations T_{NI} was kept constant and $\vartheta_2/v_0 k$ allowed to vary. The NI transition is essentially determined by the term $\vartheta_2/v_0 kT$. Hence if the calculations are made by fixing $\vartheta_2/v_0 k$, the variation in T_{NI} as a function of R will be opposite to that of $\vartheta_2/v_0 k$, i.e., T_{NI} will have a minimum value at $R = 0.5$ and increase on either side as the shape anisotropy increases. The order parameter $\langle P_2 \rangle$ also takes a minimum value at
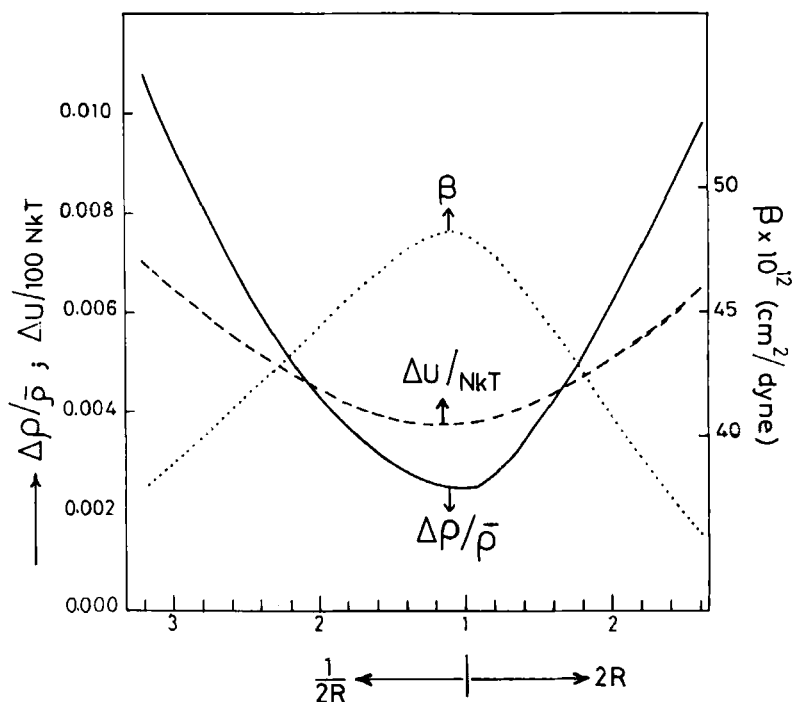
FIGURE 1b   Variation of $\Delta\rho/\bar\rho$, $\Delta U/NkT$ and β with the shape anisotropy, obtained by retaining the terms up to P_2 (cos θ) only and with $d_{nem} = 0.6$.

$R = 0.5$ and increases on either side as the shape anisotropy increases. This trend is in agreement with the experimental results for rod-like molecules and with the theoretical trend got by Cotter[8] and us[11] for spherocylinders. The other properties like ϑ_0/v_0k, $\Delta\rho/\bar\rho$ and $\Delta U/NkT$ behave in a manner similar to that of $\langle P_2\rangle$. The isothermal compressibility β of the isotropic phase behaves in a manner similar to that of ϑ_2/v_0k (see Figure 1b). This trend is exactly opposite to that found for the hard particle system.[1] All these properties, viz., ϑ_2/v_0k, ϑ_0/v_0k, $\langle P_2\rangle$, $\Delta\rho/\bar\rho$, $\Delta U/NkT$ and β at T_{NI} are almost symmetrical about $R \simeq 0.5$ when they are plotted as functions of the ratio of the larger to smaller dimension of the cylinders.

By including terms up to P_6 (cos θ) in the expansions of angle dependent terms, we repeated the calculations for various values of R by taking $d_{nem} = 0.6$ at T_{NI}. The results obtained for different transition properties are shown in Figures 2a and 2b. Comparing these with the results shown in Figures 1a and 1b, we find that the inclusion of higher order terms leads to an increase in the strength of the NI transition, i.e.,
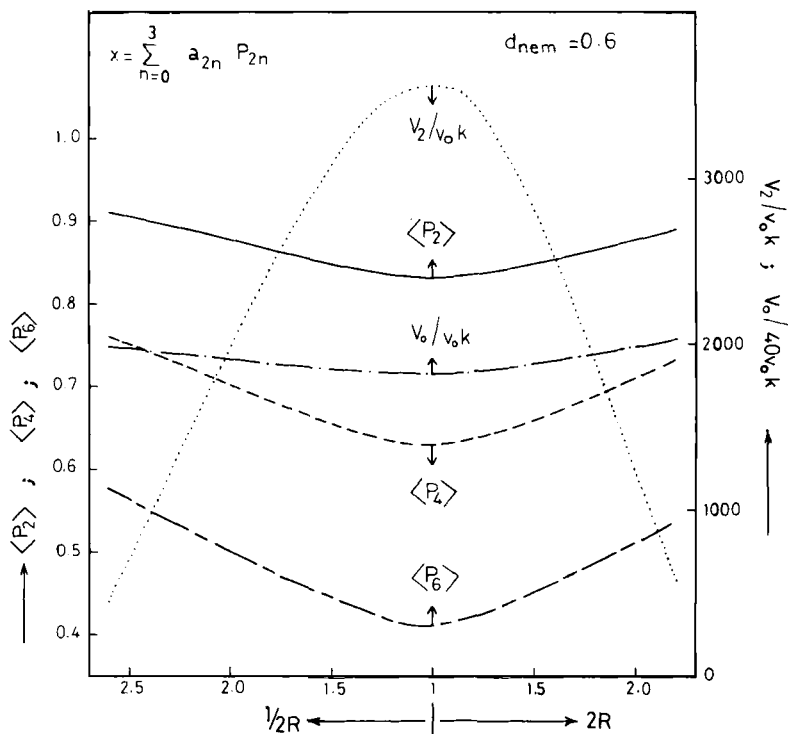
FIGURE 2a Variation of $\langle P_2 \rangle$, $\langle P_4 \rangle$, $\langle P_6 \rangle$, $\vartheta_2/v_0 k$ and $\vartheta_0/v_0 k$ with the shape anisotropy, obtained by retaining terms up to P_6 (cos θ) in the expansion and with $d_{nem} = 0.6$.

$\langle P_2 \rangle$, $\Delta\rho/\bar{\rho}$ and $\Delta U/NkT$ increase substantially at T_{NI}. Both the energy parameters ϑ_0 and ϑ_2 decrease. Except for this quantitative difference, the qualitative behavior of most of the properties remain essentially unaltered. Unlike in the hard particle system,[1] $\langle P_6 \rangle$ 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 value of ϑ_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 Figure 1b. 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 (Figure 2b).

In order to study the effect of the packing density on the phase transition properties, we have also made calculations by fixing $d_{nem} = 0.4$ at T_{NI} and by taking terms up to P_6 (cos θ) in the expansion of the angle dependent terms. The results obtained for various properties are
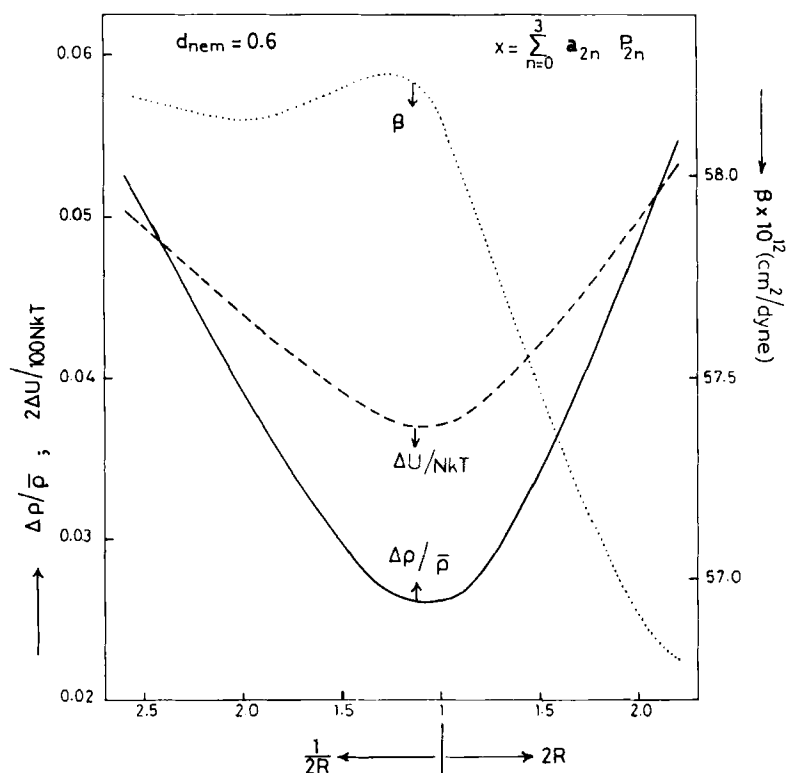
FIGURE 2b   Variation of $\Delta\rho/\bar{\rho}$, $\Delta U/NkT$ and β with the shape anisotropy obtained by retaining terms up to P_6 (cos θ) in the expansion and with $d_{nem} = 0.6$.

plotted in Figures 3a and 3b. In comparison with the results on the more closely packed system (Figures 2), the range of possible values of R gets wider; from $1/2R \simeq 7.4$ for rod-like molecules to $2R \simeq 6.6$ for disc-like molecules (Figure 3a). Further the values of $\langle P_{2n} \rangle$, $\Delta U/NkT$ and $\vartheta_0/v_0 k$ decrease whereas $\Delta\rho/\bar{\rho}$ and $\vartheta_2/v_0 k$ 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 $R \simeq 0.5$ (Figure 3b). The value of β itself goes up by a factor of ~15. At $R \simeq 0.5$, β takes a maximum value and decreases on either side as the shape aniso-tropy increases and takes a minimum value at $1/2R \simeq 2.4$ for rod-like molecules and at $2R \simeq 2.4$ for disc-like molecules. As the shape aniso-tropy increases further, the value of β increases again.
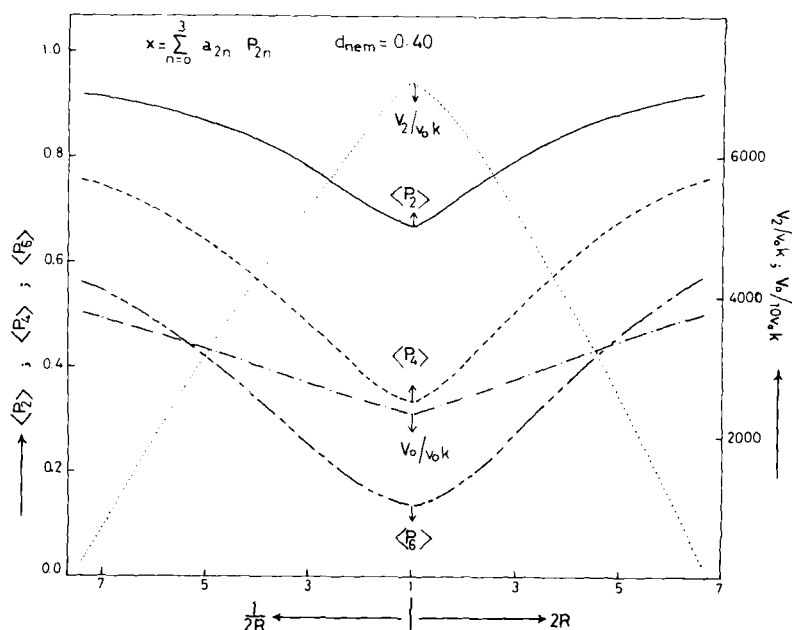
FIGURE 3a   Variation of $\langle P_2 \rangle$, $\langle P_4 \rangle$, $\langle P_6 \rangle$, $\vartheta_2/v_0 k$ and $\vartheta_0/v_0 k$ with the shape anisotropy, obtained by retaining terms up to $P_6 (\cos \theta)$ in the expansion and with $d_{nem} = 0.4$.

COMPARISON WITH EXPERIMENTAL RESULTS

A few homologous series of single component disc-like molecules, viz., hexa-n-alkanoyloxy truxenes,[6] hexa-n-alkoxybenzoates of truxene[7] and of triphenylene[3] have been found to exhibit the nematic phase. The nature of the nematic phase was confirmed by Levelut et al.[12] from mobility and X-ray diffraction studies. They also measured the magnetic susceptibility in the case of two hexa-n-alkoxybenzoates of triphenylene (sixth and eleventh members of the series). The magnetic anisotropy is negative in the nematic phase as is to be expected for such flat molecules. Further they observed a jump in the value of magnetic anisotropy at T_{NI} confirming that the transition is of first order.

The heat of transition $\Delta U/NkT$ is known only for the eleventh member of the series and is ~ 0.054 kcal mole^{-1}. The calculated value of $\Delta U/NkT$ is larger by an order of magnitude. The mean field approximation is known to over-estimate the value of $\Delta U/NkT$. The experi-
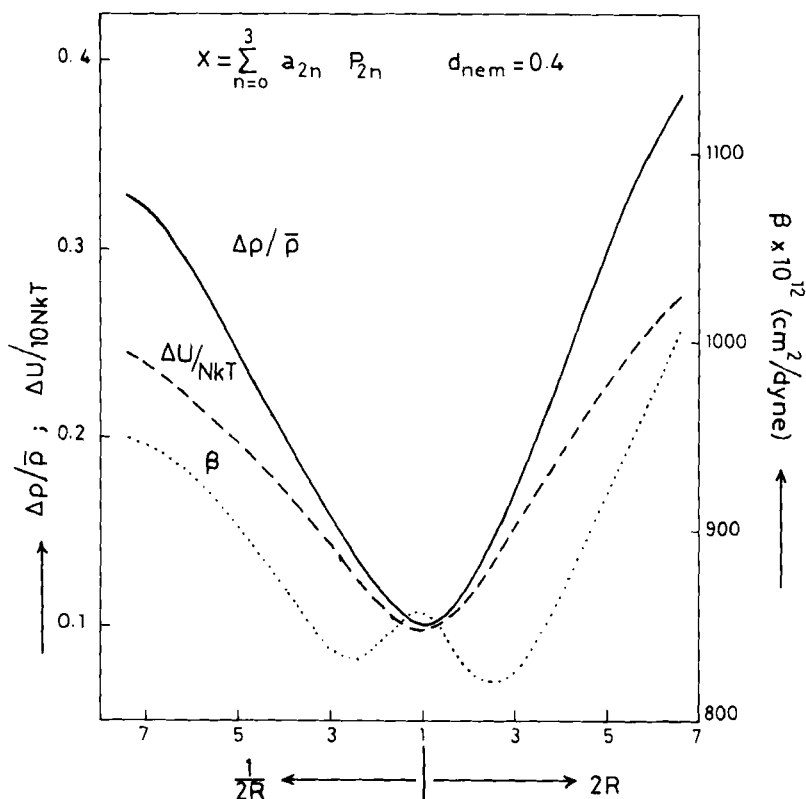
FIGURE 3b   Variation of $\Delta\rho/\bar{\rho}$, $\Delta U/NkT$ and β with the shape anisotropy obtained by retaining terms up to P_6 (cos θ) in the expansion and with $d_{nem} = 0.4$.

mental value of T_{NI} decreases as the chain length increases.[3] 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 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[13] has shown, the chain statistics plays an important role in determining the behavior 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. 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_{NI} ranges from 185°C–298°C which is in a sufficiently high range to explain the decrease of trend of T_{NI} with increasing chain length.

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 of the larger to smaller dimension of the cylinders. The higher order terms in the expansions of angle dependent functions are not as important as in the case of the hard particle system, but they do affect the compressibility of the system.

Acknowledgment

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