CHAPTER VII

EXTENSION OF McMILLAN'S MODEL TO LIQUID CRYSTALS OF DISC-LIKE MOLECULES

7.1 Introduction

As we have discussed in the previous chapter, a number of disc-like molecules are known to exhibit thermotropic mesomorphism. The mesophases so far discovered fall into two distinct categories, the columnar and the nematic. In the columnar (D) type, the discs are stacked one on top of the other, the different columnar stacks forming a two-dimensionally periodic array. Several variants of this structure have been identified - hexagonal, rectangular, tilted, etc. (Fig.1a-e). The nematic phase (N_D), with an orientationally ordered arrangement of the discs and with no long range translational order has been discussed in great detail in the previous chapter. Transitions between columnar and nematic phases have been observed in a few cases (see Tinh et al, 1981; Destrade, 1981a,b). As an example we present in table I, the data for the hexa-n-alkoxybenzoates of triphenylene (HABT). The symbol D_t in table I signifies tilted columns and a face-centered rectangular (FCR) lattice (Figures 1d and 1e), and D_r -

FIGURE 1

(a) Schematic representation of a 'liquid-like stack of disc-shaped molecules(from Levelut, 1980). (b) Hexagonal modification 4 of an upright columnar structure. The filled circle depicts tha,molecular core which is normal to the columnar axis. (c) Rectangular modification D_r of an upright @l ———— structure. @ circular cores are normal to the columnar axes and form a face-centered rectangular lattice, but the asymmetric disposition sf the chains results in a herringbone pattern of ellipses, whose ellipticity is highly exaggerated here for the sake of clarity (Tinh et al, 1981, Destrade et al, 1981

Levelut, 1980). (d) Tilted columnar structure D_t (Tinh et al, 1981 and Destrade et al, 1981). (e) Face-centered rectangular lattice of D_t. The cores are tilted with respect to the columnar axes (Tinh et al, 1981 and Destrade et al, 1981).
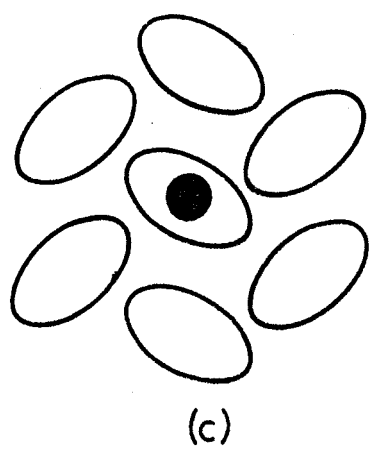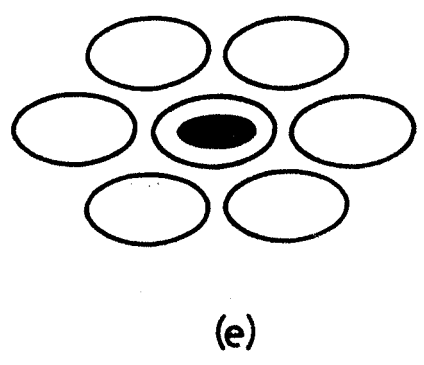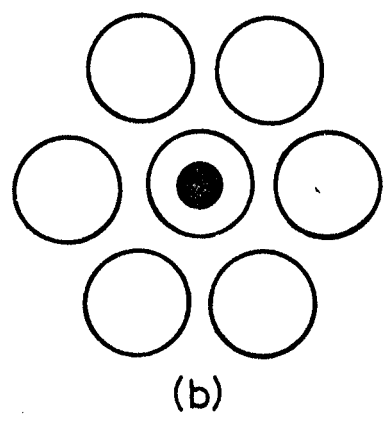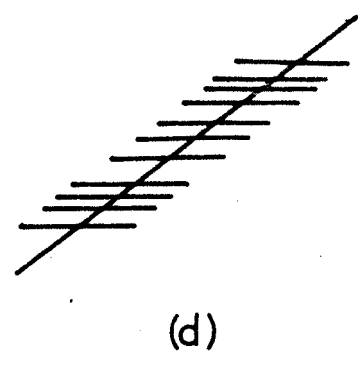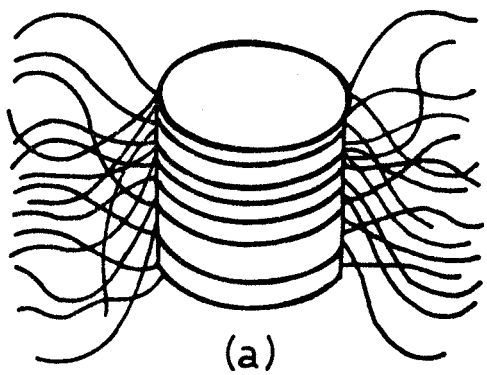
(a)

(d)

(b)

(e)

(c)

TABLE 1

Hexa-n-alkoxybenzoates of triphenylene: Transition temperatures in °C (Tinh et al, 1981 and Destrade et al, 1981)

$R=C_nH_{2n+1}O$	K		D_t		D_x		H_D		I
n = 4	•	257	—		—		•	300	•
5	•	224	—		—		•	298	•
6	•	186	•	193	—		•	274	•
7	•	168	—		—		•	253	•
8	•	152	—		•	168	•	244	•
9	•	154	—		•	183	•	227	•
10	•	142	—		•	191	•	212	•
11	•	145	—		•	179	•	185	•
12	•	146	—		•	174	—		•

upright columns and a rectangular arrangement as in fig. 1c.

Levelut (1979) has shown that in the latter case the discs are <u>normal</u> to the columnar axes: thus the 'circular' cores form a FCR lattice but the asymmetrical disposition of the chains results in a herringbone pattern (Fig. 1c). In both D_r and D_t, the columns themselves are 'liquid-like', i.e., there is no long range translational periodicity along the columnar axes. For the n = 11 homologue the lattice parameters have been determined to be a = 32.6 $\overset{o}{A}$ and b = 51.8 $\overset{o}{a}$ (see Tinh et al, 1981 and Destrade et al, 1981a), which represents only a slight departure from true hexagonal symmetry.

It is seen from Table I that the lower members, n =4 and 5, show only the N_D phase. The higher members (with the exception of n = 7) show both the D and N_D phases, the temperature range of the N_D phase decreasing with increasing chain length till at n = 12 the columnar phase transforms directly to the isotropic phase. Broadly, the trend is reminiscent of the behaviour of the S_A-N-I transitions in systems of rod-like molecules. This suggests that one may be able to give a qualitative description of the D-N_D-I transitions by extending McMillan's (1971) mean field model of S_A so that the density wave is now periodic in two

dimensions.   Such an idea had in fact been considered
very briefly by Kats (1978), but no calculations were
presented by him. We undertook a detailed theoretical
study of the problem for the hexagonal and PGR columnar
structures. When our work was nearing completion there
appeared a paper by Feldkamp et al (1981) on essentially
the same theory for the hexagonal case and we were
gratified to find that their conclusions are in exact
agreement with ours. However, our formulation differs
slightly from theirs in some details.

7.2   Theory

We consider a two-dimensional PGR lattice composed
of liquid-like columns, the molecular cores being circular
discs normal to the columnar axes. (Therefore, the
departure from hexagonal symmetry is supposed to be solely
due to the asymmetric disposition of the chains as in
the D_r structure (Fig. 1c) except that for simplicity we
ignore the herringbone pattern.) The PGR lattice can be
described by a superposition of three density waves with
wave vectors (Fig. 2)

$$\vec{A} = 2\pi\left(\frac{\vec{1}}{a} + \frac{\vec{1}}{b}\right) ,$$

$$\vec{B} = 2\pi\left(-\frac{\vec{1}}{a} + \frac{\vec{1}}{b}\right) , \quad \text{and}$$
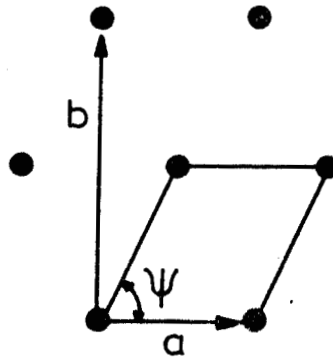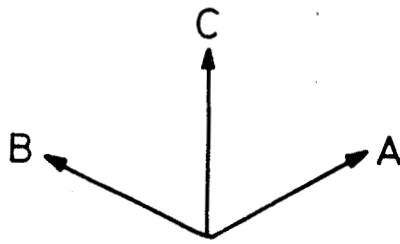
FIG. 2: Two-dimensional face-centered rectangular lattice showing (a) the lattice parameters a and b, and the primitive cell of the direct lattice, (b) the reciprocal lattice vectors $\vec{A}$, B, and $\vec{C}$.

$$\vec{C} = \frac{4\pi \vec{j}}{b} = (\vec{A} + \vec{B})$$

where $\vec{i}$ and $\vec{j}$ are unit vectors along the x and y axes respectively. Since the orientational ordering of the molecules is obviously necessary for the existence of the columnar structure, we need to define order parameters which couple the two types of order. In the smectic A phase of rod-like molecules, the orientational order is normally defined with respect to the director, which also represents the direction of the wave vector of the density wave. On the other hand, in the present case the director is parallel to the columnar axis (z-axis say) whereas the wave vectors $\vec{A}$, $\vec{B}$, $\vec{C}$ are in the orthogonal xy plane. Therefore, we couple each density wave to the appropriate component of the orientational order parameter along $\vec{A}$, $\vec{B}$ or $\vec{C}$, rather than to the component along z. Retaining only the leading terms in the Fourier expansion of the density waves, the single particle potential in the mean field approximation is assumed to be of the form

$$V_1(\vec{r}, \theta, \varphi) = -V_0[-\eta_1 P_2(\sin\theta\cos\varphi) - \eta_2 P_2(\sin\theta\sin\varphi)$$
$$- 2\alpha_1\sigma_1 \, P_2(\sin\theta\cos\varphi)\cos\vec{C}\cdot\vec{r}$$
$$- 2\alpha_2\sigma_2\{P_2(\sin\theta\cos(\psi+\varphi))\cos\vec{A}\cdot\vec{r}$$
$$+ P_2(\sin\theta\cos(\psi-\varphi))\cos\vec{B}\cdot\vec{r}\}]$$

where V_o determines T_{NI}, α_2 is an interaction strength related to density waves along $\vec{A}$ and $\vec{B}$ and α_1 that along $\vec{C}$, $\psi = \tan^{-1}(b/a)$, θ and φ are the polar angles, $\vec{r}$ is the position vector, and P_2 is the Legendre polynomial of order two. Since the molecular core is assumed to be circularly symmetric, we get

$$\alpha_1 = 2\exp[-(2\pi r_o/b)^2]$$

$$\alpha_2 = 2\exp[-\{\pi r_o (a^2 + b^2)^{1/2}/ab\}^2]$$

where r_o is the range of the intermolecular attractive potential.

In general there are four order parameters, η_2 and η_1 the orientational order parameters measured along the x and y axes, and σ_2 and σ_1 the order parameters coupling the orientational and translational orders along the $\vec{A}$ (or $\vec{B}$) and $\vec{C}$ directions respectively. We have chosen to define the order parameters in such a way that they vary from 0 fin the disordered system to $+1$ in the perfectly ordered system. We then have

$$\eta_1 = \langle -2P_2(\sin\theta\cos\varphi)\rangle$$

$$\eta_2 = \langle -2P_2(\sin\theta\sin\varphi)\rangle$$

$$\sigma_1 = \langle -2P_2(\sin\theta\cos\varphi)\cos\vec{C}\cdot\vec{r}\rangle \tag{1}$$

$$\sigma_2 = \langle -\{P_2(\sin\theta\cos(\psi+\varphi))\cos\vec{A}\cdot\vec{r} + P_2(\sin\theta\cos(\psi-\varphi))\cos\vec{B}\cdot\vec{r}\}\rangle .$$

where the angular brackets represent a statistical average, and the normalised single partition distribution function

$$f_1(\vec{r}, \Theta, \varphi) = \frac{\exp\{-V_1(\vec{r}, \Theta, \varphi)/kT\}}{\int d\vec{r} \int_0^1 d(\cos\Theta) \int_0^{2\pi} d\varphi \ \exp\{-V_1(\vec{r},\Theta,\varphi)/kT\}} \qquad (2)$$

where $\int d\vec{r}$ is over the primitive cell.

The molar internal energy of the oriented system can now be written as

$$\frac{\Delta U}{NkT} = -\frac{V_o}{2kT}\left\{\frac{1}{2}\eta_1^2 + \frac{1}{2}\eta_2^2 + \alpha_1\sigma_1^2 + 2\alpha_2\sigma_2^2\right\} \qquad (3)$$

where N is the Avogadro number, the entropy as

$$\frac{\Delta S}{Nk} = -\int\int_0^1\int^{2\pi} f(\vec{r}, \Theta, \varphi)\ln f(\vec{r}, \Theta, \varphi)d(\cos\Theta)d\varphi \ d\vec{r}$$

$$= -\frac{V_o}{kT}\left(\frac{\eta_1^2}{2} + \frac{\eta_2^2}{2} + \alpha_1\sigma_1^2 + 2\alpha_2\sigma_2^2\right)$$

$$+ \ln\frac{1}{\pi ab}\int_0^1\int_0^{2\pi}\int \exp\{-V_1(\vec{r},\Theta,\varphi)/kT\}d(\cos\Theta)d\varphi \ d\vec{r}$$

$$\qquad \qquad \cdots \ (4)$$

and hence the molar free energy as

$$\frac{\Delta F}{NkT} = \frac{\Delta U - T\Delta S}{NkT} = \frac{V_o}{2kT}\left(\frac{\eta_1^2}{2} + \frac{\eta_2^2}{2} + \alpha_1\sigma_1^2 + 2\alpha_2\sigma_2^2\right)$$

$$- \ln\frac{1}{\pi ab}\int_0^1\int_0^{2\pi}\int \exp\{-V_1(\vec{r},\Theta,\varphi)/kT\}\ d(\cos\Theta)d\varphi \ d\vec{r}$$

$$\qquad \qquad \cdots \ (5)$$

The distribution function $f_1(\vec{r}, \theta, \varphi)$ (eq.2) minimizes the above free energy expression.

There are four possible solutions to the equations:

1) $\eta_1 \neq \eta_2 \neq 0$, $\sigma_1 \neq \sigma_2 \neq 0$ biaxial rectangular columnar phase

2) $\eta_1 \neq \eta_2 \neq 0$, $\sigma_1 \neq 0$, $\sigma_2 = 0$ biaxial smectic phase

3) $\eta_1 = \eta_2 \neq 0$, $\sigma_1 = \sigma_2 = 0$ uniaxial nematic phase

4) $\eta_1 = \eta_2 = \sigma_1 = \sigma_2 = 0$ isotropic phase.

The free energy corresponding to the different solutions can be evaluated to determine the phase diagram as a function of the α coefficients for a given value of the axial ratio b/a.

When $b/a = \sqrt{3}$, $\Psi = 60°$, and we have a hexagonal lattice. It then follows that $\alpha_1 = \alpha_2$ and the solutions take the simpler form

1) $\eta_1 = \eta_2 \neq 0$, $\sigma_1 = \sigma_2 \neq 0$ uniaxial hexagonal columnar phase

2) $\eta_1 = \eta_2 \neq 0$, $\sigma_1 = \sigma_2 = 0$ uniaxial nematic phase

3) $\eta_1 = \eta_2 = \sigma_1 = \sigma_2 = 0$ isotropic phase.

7.3   Calculations and results

The consistency conditions (eq. 1) were solved by using PDP-11 and DEC-10 computers. The numerical integrations

were performed in double precision by using the Guassian quadrature technique with 12 (or sometimes 16) quadrature points.

For $b/a = \sqrt{3}$, the phase diagram is shown in fig.3. This is exactly identical to the one presented by Feldkamp et al (1981) for hexagonal case. As pointed out by these authors, the hexagonal-nematic transition is always first order, unlike the S_A-N transition which is predicted to become second order for $\alpha < 0.70$.

For $b/a \neq \sqrt{3}$, we get two types of rectangular columnar lattices depending upon whether $b/a < \sqrt{3}$ or $> \sqrt{3}$.

For $b/a = 1.6$ and 1.5, we present the phase diagrams along with the transition entropies in figures 4 and 5 respectively. The transition entropies close to the triple points are not calculated. The nature of the phase diagram is very much similar to that for the hexagonal lattice (fig.3) and leads to a first order transition between the biaxial rectangular columnar phase and the uniaxial nematic phase. It is seen that the temperature range of the nematic phase decreases with increasing α_1 and for values of α_1 higher than some value, say α_0, the columnar phase transforms directly to the isotropic phase. If, as in McMillan's
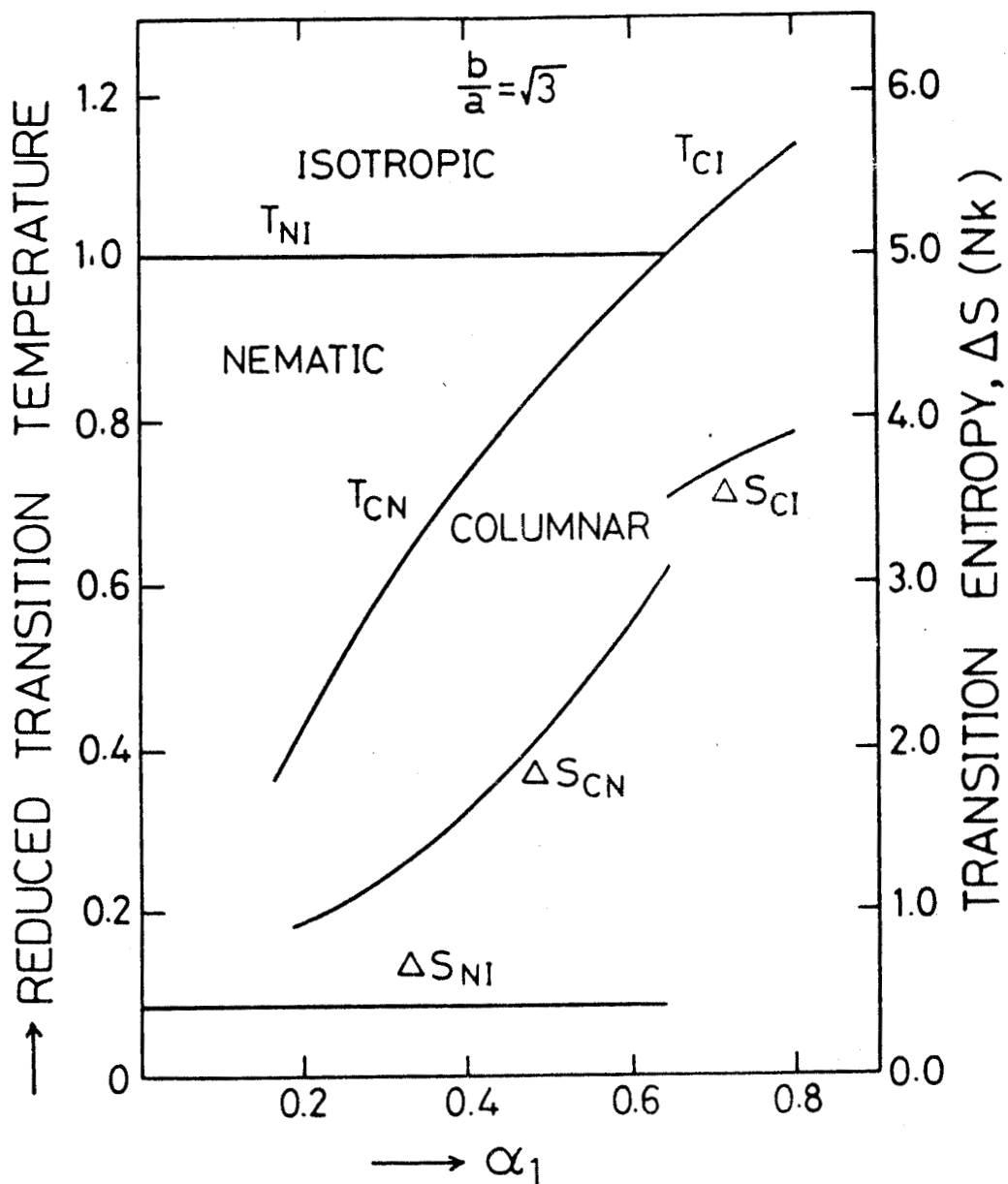
FIG.3: Theoretical diagram for $b/a = \sqrt{3}$, showing the hexa-gonal, nematic and isotropic phase boundaries and the corresponding transition entropies. All the transitions are of first order.

FIG.4: Theoretical diagram for $\frac{b}{a} = 1.6$, showing the rectangular columnar, nematic and isotropic phase boundaries and the corresponding transition entropies. All the transitions are of first order.
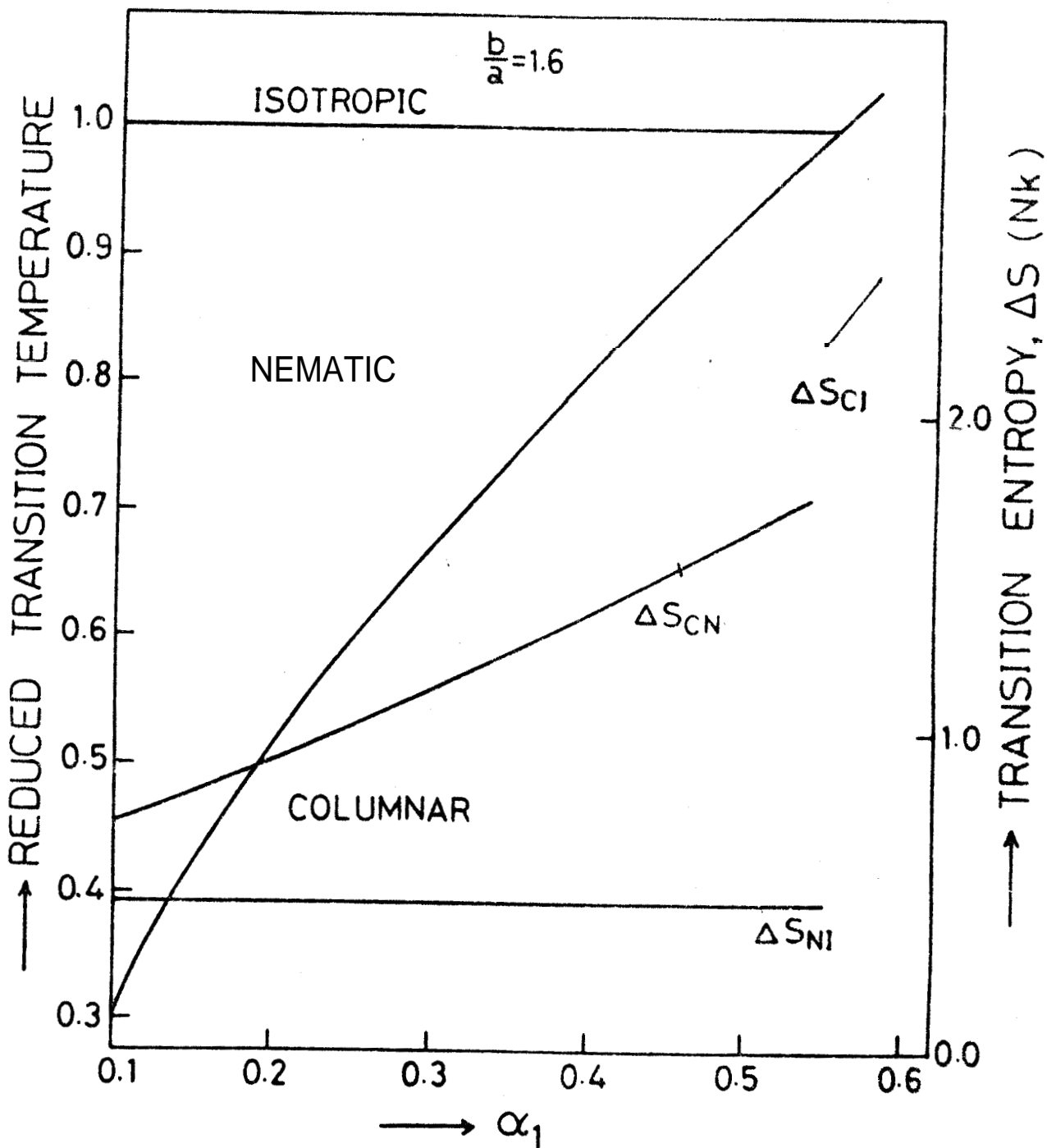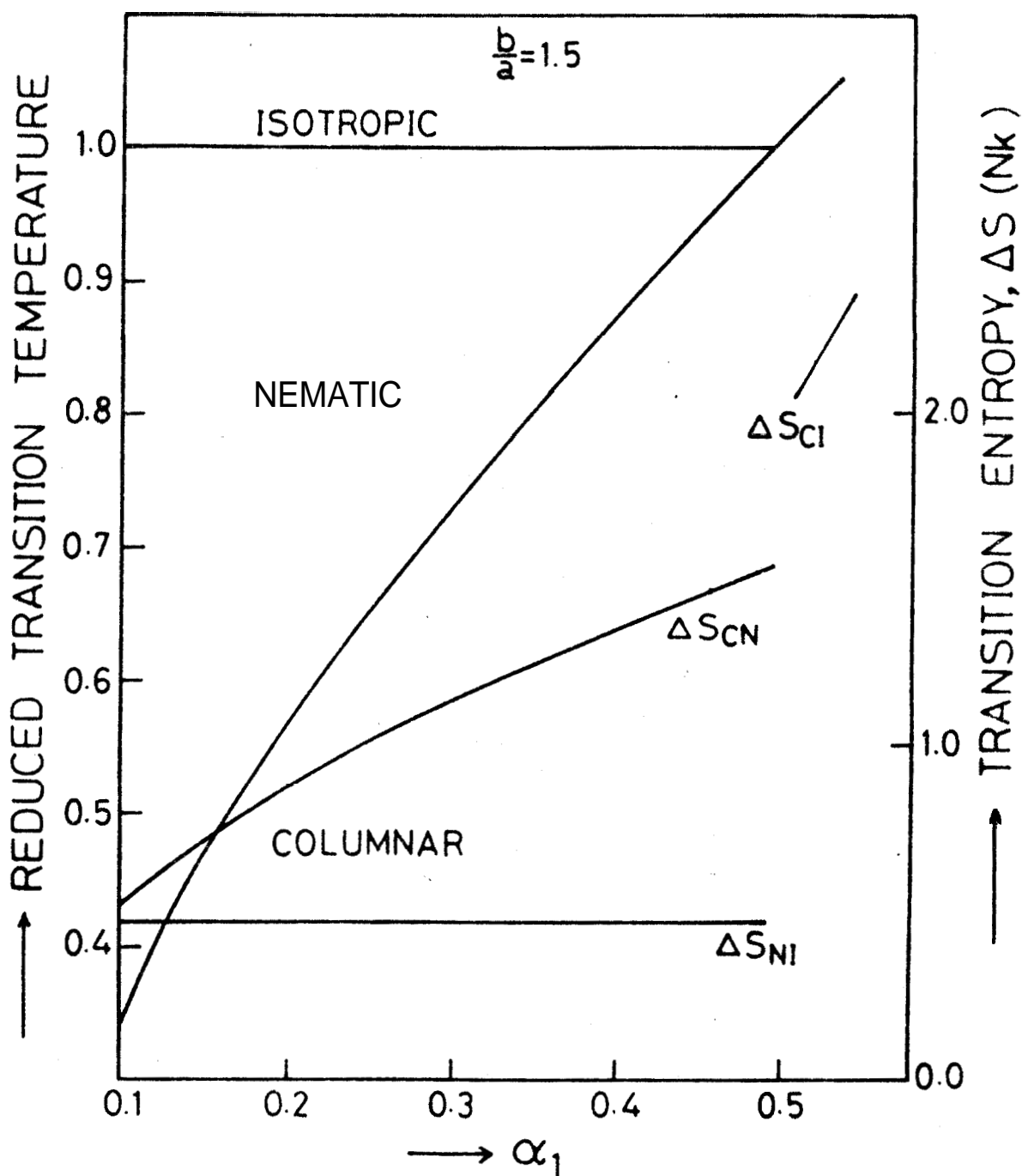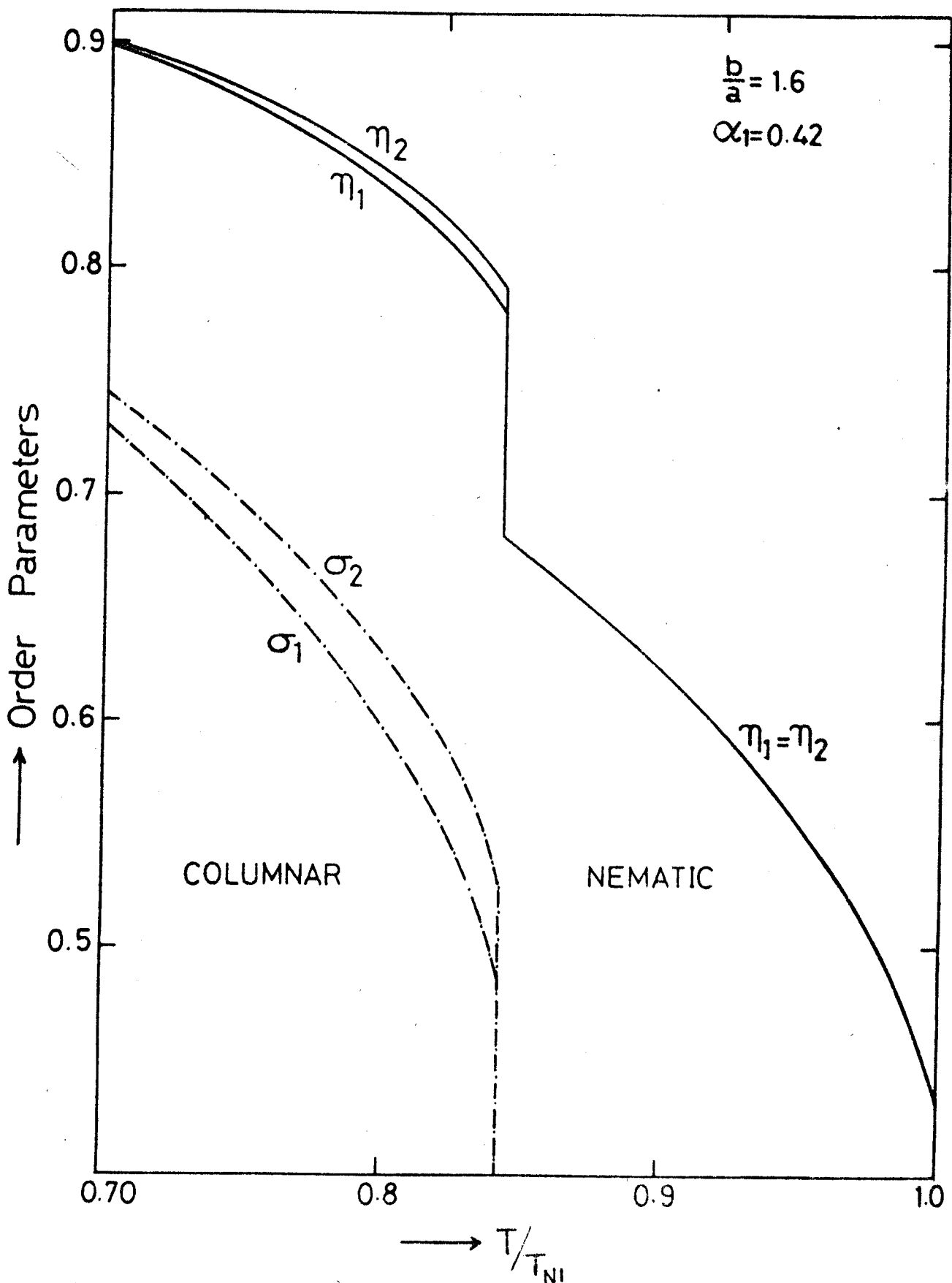
FIG.5: Theoretical diagram for $\frac{b}{a} = 1.5$ showing the rectangular columnar, nematic and isotropic phase boundaries and the corresponding transition entropies. All the transitions are of first order.

theory, α is interpreted to be a measure of the chain length these results are in qualitative accord with the observed trends for HABT (table I). We have also studied the temperature variation of order parameters η_1, η_2, σ_1 and σ_2 in columnar and nematic phases. For this purpose we selected that value of α for which the range of nematic phase is the same for both values of b/a ratio. The results are shown in figures 6 and 7. When the value of b/a decreases from $\sqrt{3}$ to 1.5, we observe the following behaviour in the transition properties:

a   The value of α_0 decreases from 0.64 to 0.495, i.e., the range of values of α over which the nematic phase exists will be reduced as one decreases the value of b/a (Figures 4 and 5).

b   The value of ΔS_{CI} at the triple point decreases.

c $\eta_2 > \eta_1$; $\sigma_2 > \sigma_1$ and $\eta_2 - \eta_1$ and $\sigma_2 - \sigma_1$ increase as b/a decreases from $\sqrt{3}$ (see figures 6 and 7), i.e., larger the asymmetry of the lattice, stronger is the biaxial order of the rectangular columnar phase.

If b/a is slightly greater than $\sqrt{3}$ say equal to 1.85 (see fig. 8), the phase diagram is again rather similar to that for the hexagonal lattice. However as

FIG.6: Variation of long range order parameters η_1, η_2, σ_1 and σ_2 of the biaxial rectangular columnar and the uniaxial nematic phases as functions of T/T_{NI} for $b/a = 1.6$ and $\alpha_1 = 0.42$.

FIG.7: Variation of long range order parameters η_1, η_2, σ_1 and σ_2 of the biaxial rectangular columnar and the uniaxial nematic phases as functions of T/T_{NI} for b/a = 1.5 and α_1 = 0.38.
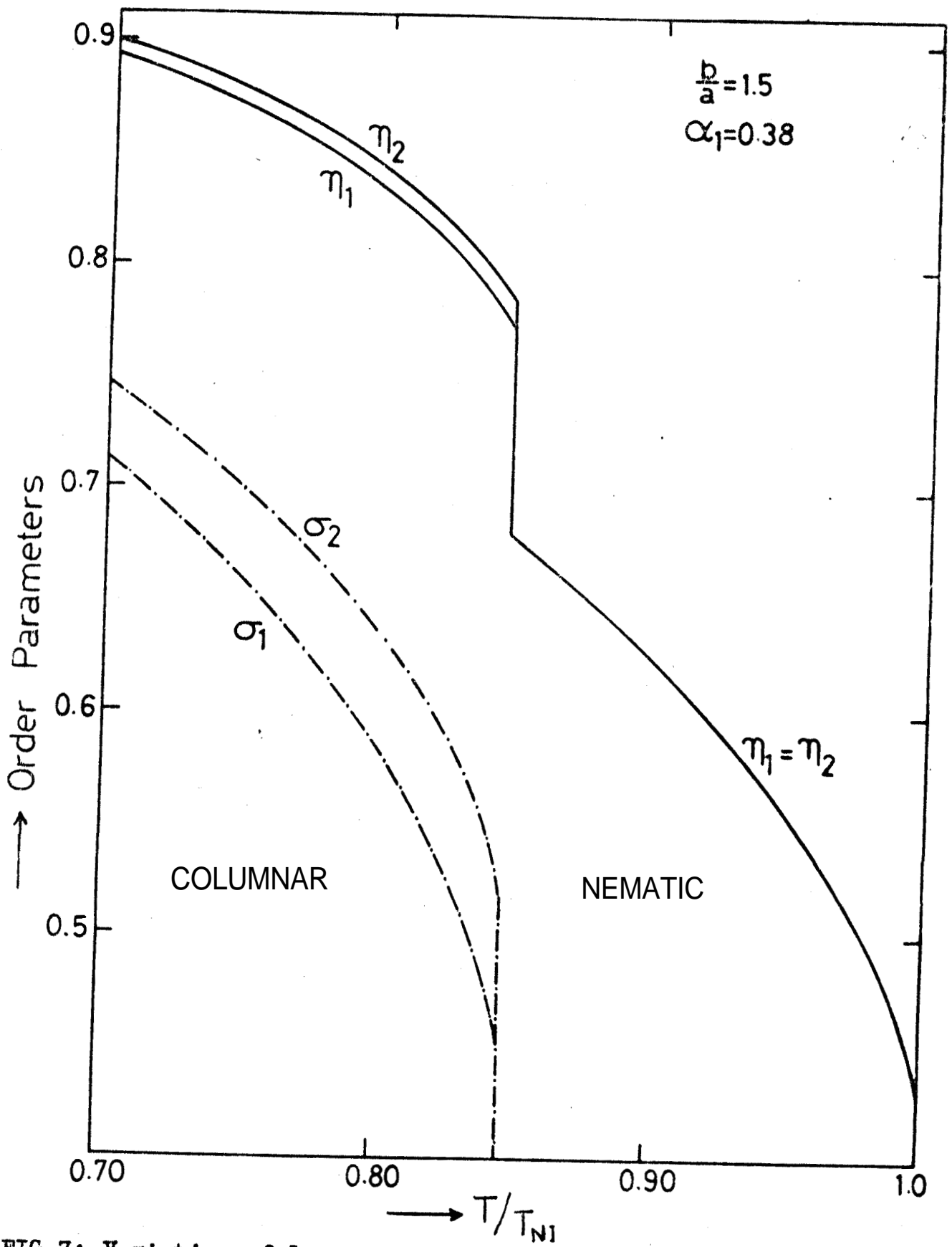
FIG.8: Theoretical diagram for b/a = 1.85 showing rectangular columnar, nematic and isotropic phase boundaries and the corresponding transition entropies. All the transitions are of first order.

the asymmetry of the lattice is increased, we get
solutions corresponding to a smectic phase also. Fig. 9
presents the phase diagram as well as the transition
entropies for $b/a = 1.95$ ($\psi = 62°51'$). In this case,
for values of $\alpha_1 < 0.52$, the rectangular columnar phase
transforms to a smectic A phase (with the layer normal
along $\vec{d}$) which in turn undergoes a second order transi-
tion to the nematic phase at a higher temperature. Both
the columnar and smectic phase are weakly biaxial (see
fig. 10). The columnar phase goes over to the nematic
phase for $0.52 < \alpha_1 < 0.7$, and to the isotropic phase for
$\alpha_1 > 0.70$.

The temperature variation of order parameter in diffe-
rent phases are shown in figures 10 to 12. As we increase
b/a from $\sqrt{3}$ to 1.95, we observe the following trends in
the transition properties.

a   The value of α_0 increases from 0.64 to 0.70 (see
     figures 8 and 9).

b   For $b/a = 1.95$, if $\alpha_1 < 0.27$, ΔS_{CS} is less than
     ΔS_{NI} and for larger values of α, ΔS_{CS} exceeds
     ΔS_{NI} (figures 8 and 9).

c $\eta_1 > \eta_2$, $\sigma_1 > \sigma_2$ and $\eta_1 - \eta_2$ and $\sigma_1 - \sigma_2$ now
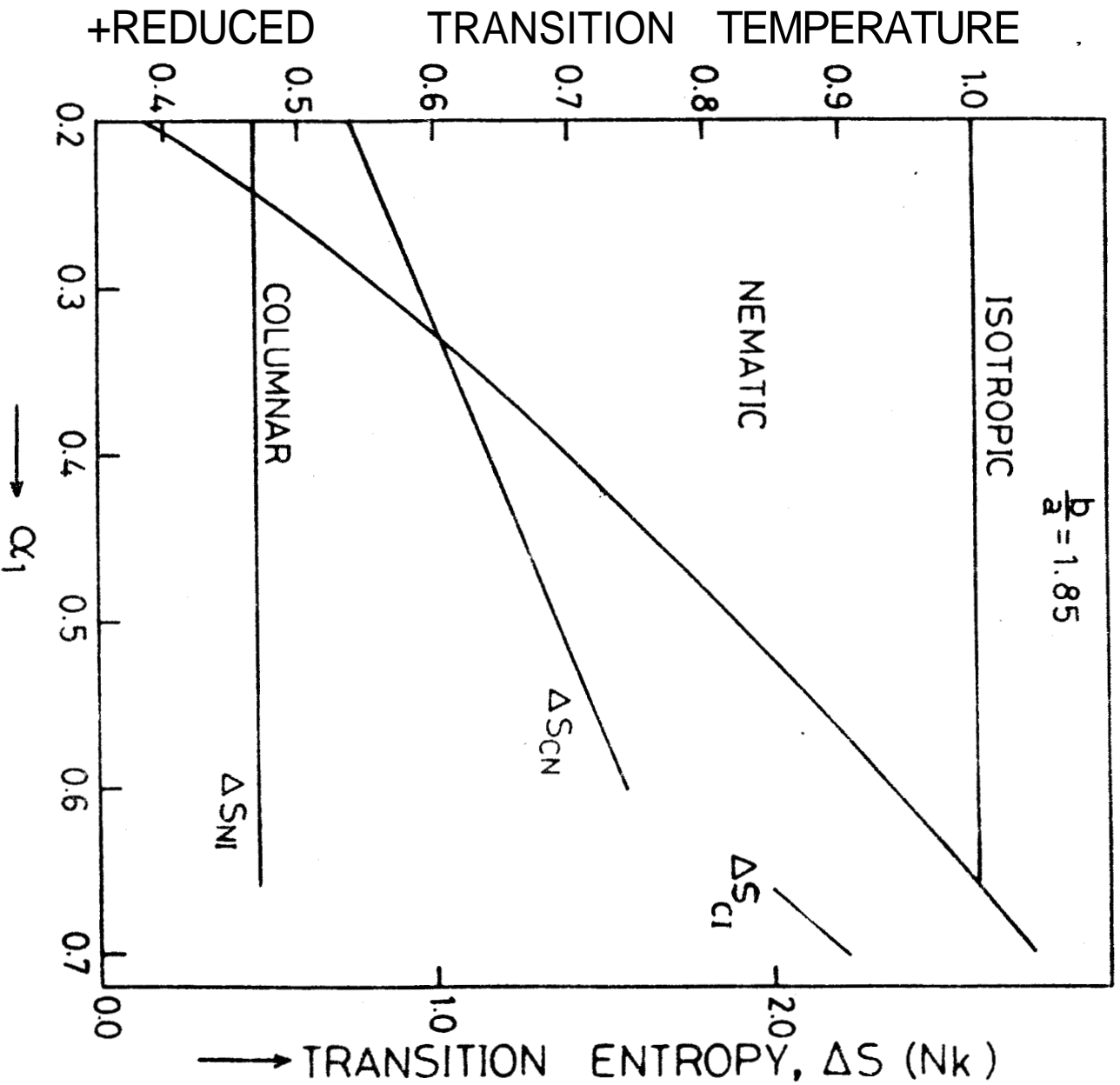   increase with increasing value of b/a (see figures
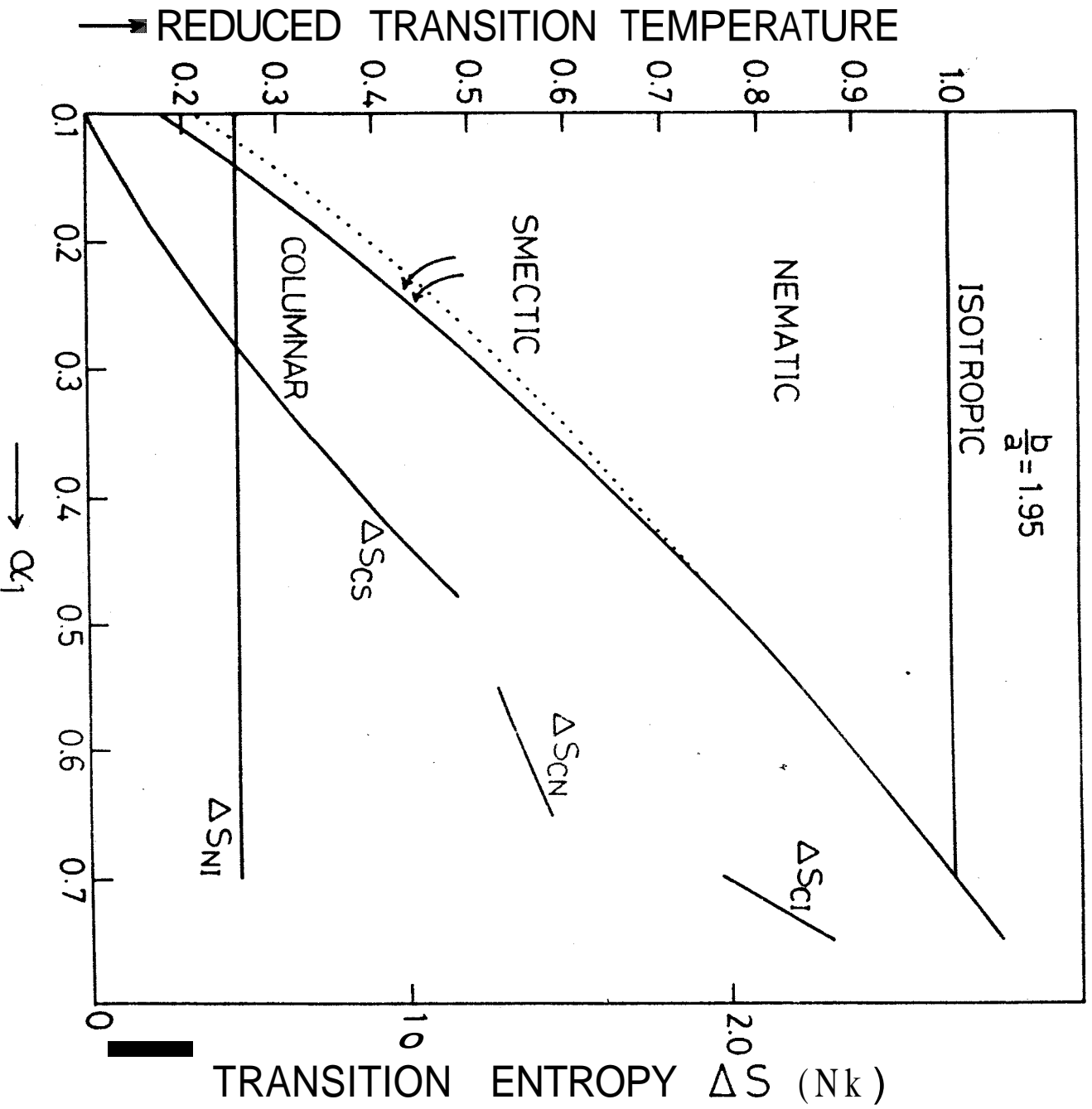
FIG.9: Theoretical diagram for b/a = 1.5 showing rectangular columnar, nematic and isotropic phase boundaries and the corresponding transition entropies. All the transitions are of first order.
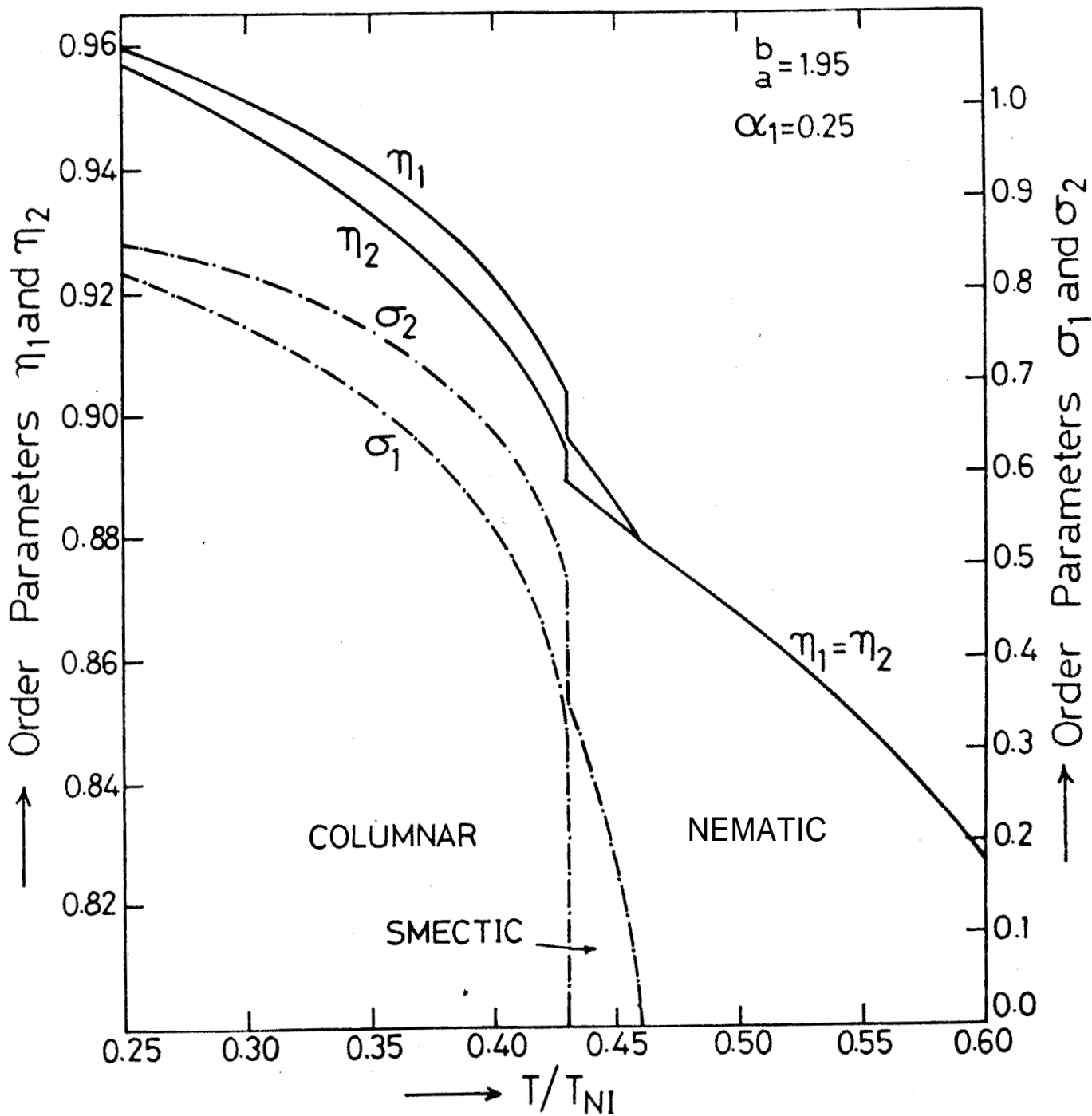
FIG. 10: Variation of long range order parameters η_1, η_2, σ_1 and σ_2 of the **biaxial rectangular columnar**, **biaxial smectic** and the **uniaxial** nematic phases as functions of T/T_{NI} for b/a = 1.95 and α_1 = 0.25. For clarity, diagram is not shown for T/T_{NI} > 0.60.

11 and 12), i.e., larger the asymmetry of the lattice, stronger is the biaxial order of the rectangular columnar phase.

d   From figure 10, we can see that at the columnar-smectic transition, σ_1, σ_2, η_1 and η_2 drop abruptly (σ_2 drops to 0) since the transition is of first order character. As the temperature is increased in the smectic phase, η_1 decreases more rapidly and becomes equal to η_2 at the smectic-nematic transition. σ_1 decreases continuously to zero value since the $\overset{SN}{\underset{\diagdown}{}}$transition is second order.   As one increases the temperature further $\eta(= \eta_1 = \eta_2)$ decreases and drops abruptly *to* zero at T_{NI}.

7.4   Conclusions

Rectangular phases have been observed with disc-like molecules having essentially circular cores;, but in these cases b/a does not depart significantly from $\sqrt{3}$. According to our theory the smectic A phase can intervene between the rectangular and nematic phase only if the lattice is significantly   a and moreover the α-values (and hence the chainolengths) have to be small. It is doubtful if an asymmetric distribution of relatively

FIG. 11: Variation of long range order parameters η_1, η_2, σ_1 and of the biaxial rectangular columnar and *the* uniaxial nematic phases as functions of T/T_{NI} for b/a = 1.85 and α_1 = *0.52*.
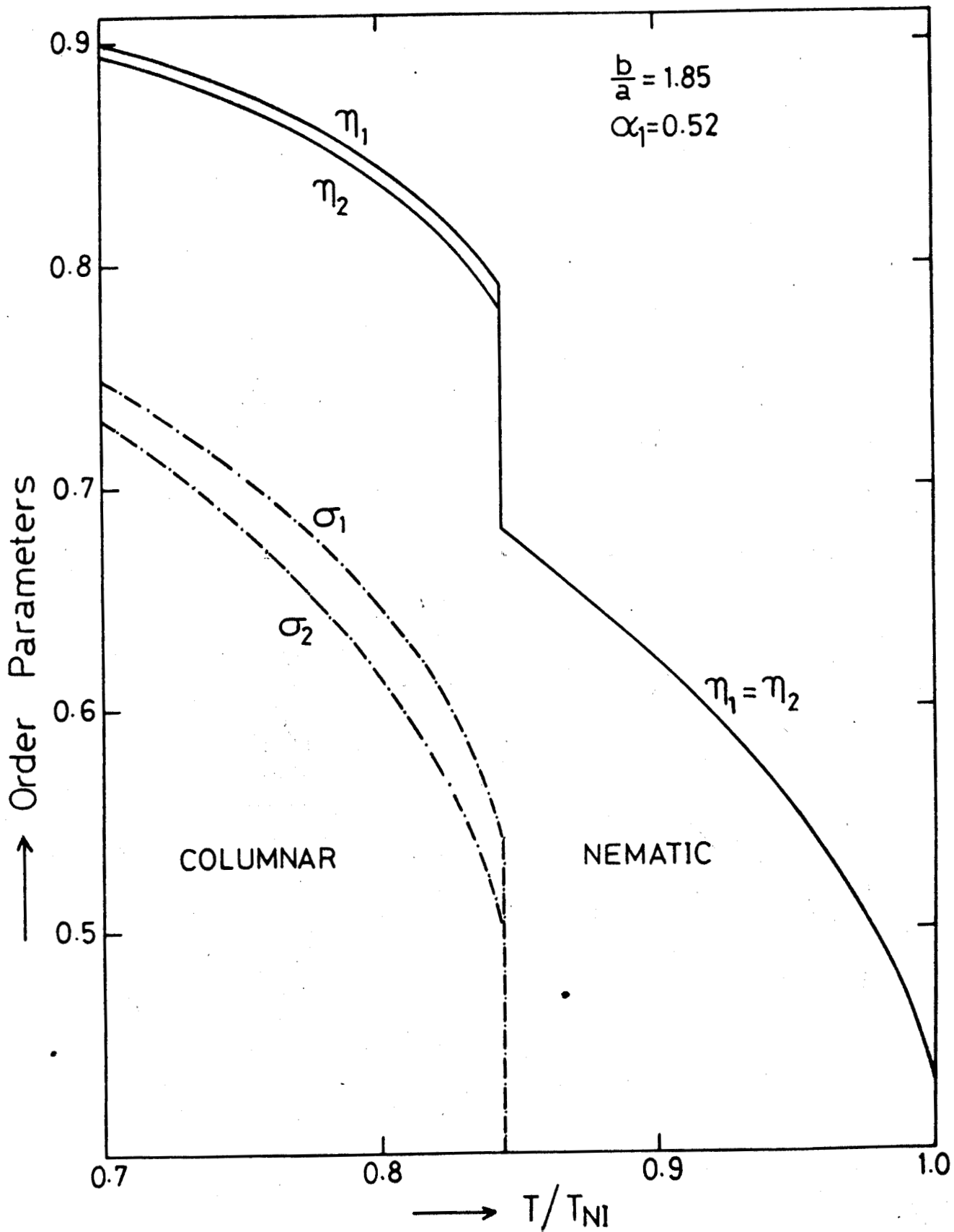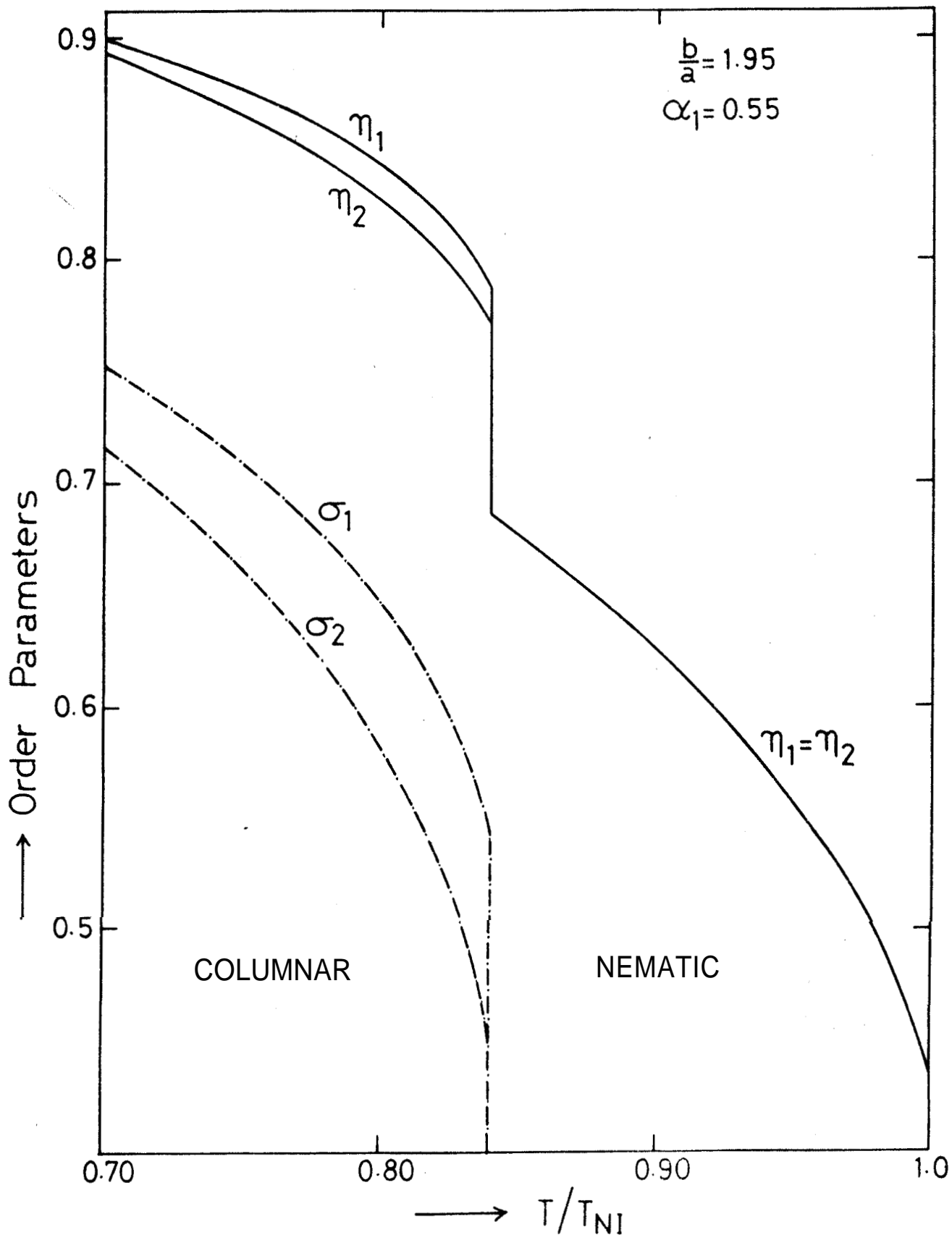
BIG. 12: **Variation of long** range **order parameters** η_1, η_2, σ_1 and σ_2 of the **biaxial rectangular columnar and the uniaxial nematic** phases as functions of T/T_{NI} for b/a = 1.95 and α_1 = 0.55.

short chains can give rise to the necessary values of
b/a. On the other hand, rectangular lattices of high
anisotropy may be expected if the molecular core itself
is elliptical as in the case of rufigallal (see
Jueguiner, 1979) (or in effect elliptical as in the
tilted columnar structure which of course would give
rise to a smectic C phase). The extension of the model
to allow for the ellipticity of the cores and also to
explicitly take into account the herringbone arrangement
will result in a very large number of order parameters
(as well as free parameters) and the calculations will
no doubt be extremely tedious. Nevertheless, the simple
model discussed above serves to illustrate two points,
namely that (a) the origin of the two-dimensional trans-
lational order in the columnar phase is similar to that
of one-dimensional order in smectic A in so far as the
large mutual attraction between the aromatic cores and
the role of the end chains are concerned, and (b) the
possibility exists of observing smectic phases in certain
discotic systems.

REFERENCES

Destrade, C., Tinh, N.H., Gasparoux, H., Malthete, J.
and Levelut, A.M. 1981a Mol. Cryst. Liq. Cryst. 71, 111.

Destrade, C., Gasparoux, H., Babeau, A., Tinh, N.H. and
Malthete, J. 1981b Mol. Cryst. Liq. Cryst. 67, 37.

Feldkamp, G.E., Handschy, M.A. and Clark, N.A. 1981
Phys. Lett. 85A, 359.

Katz, E.I. 1978 Sov. Phys. JETP 48, 916.

Levelut, A.M. 1980 Proc. Int. Liquid Crystals Conf.,
Bangalore, 1979, Ed. S. Chandrasekhar, Heyden, London
p. 21.

McMillan, W.L. 1971 Phys. Rev. A4, 1238.

Tinh, N.H., Gasparoux, H. and Destrade, C. 1981 Mol. Cryst.
Liq. Cryst. 68, 101.

Queguiner, A., Zann, A., Dubois, J.C. and Billard, J.
1980 Proc. Int. Liquid Crystals Conf., Bangalore, 1979,
Ed. S. Chandrasekhar, Heyden, London, p. 35.

APPENDIX I

Two Site Cluster Approximation

In chapters II and III, we have used the free energy
expression derived from a two-site cluster approximation
which was originally developed by Strieb et al (1963) to
treat cluster models encountered in magnetism. Subsequently
the argument has been used by Ypma (1977) specifically in
the case of nematic liquid crystals.

As in chapter II, the nearest neighbour interaction
is taken to be of the form

$$E(\theta_{ij}) = - B^* P_2(\cos \theta_{ij}) \tag{1}$$

The Hamiltonian of the system is now written as

$$H = - B^* \sum_{\langle ij \rangle} P_2(\cos \theta_{ij})$$

where $\langle ij \rangle$ represents the summation over the nearest
neighbours i and j oriented along directions (θ_i, φ_i) and
(θ_j, φ_j) respectively with respect to the nematic director
and θ_{ij} is the angle between their long axes. $P_2(\cos \theta_{ij})$
is the second order Legendre polynomial and is written as

$$P_2(\cos \theta_{ij}) = P_2(\cos \theta_i) P_2(\cos \theta_j) + W_{ij}$$

where

$$W_{ij} = \frac{3}{4}\sin^2 \theta_i \sin^2 \theta_j \cos 2\varphi_{ij}$$

$$+ 3\sin \theta_i \cos \theta_i \sin \theta_3 \cos \theta_j \cos \varphi_{ij}$$

and

$$\varphi_{ij} = |\varphi_i - \varphi_j|. \tag{2}$$

Following Strieb et al, the Hamiltonian of the system is divided into an unperturbed part (H_0) and a perturbation term (V) by introducing an expansion parameter

$$\Delta_i = \bar{S} - P_2(\cos \theta_i) \tag{3}$$

where $\bar{S}$ is a variational parameter whose best value will be determined by minimizing the free energy. The unperturbed Hamiltonian H_0 is taken to be

$$H_0 = -B^* \sum_{\langle i,j \rangle} [\ \bar{S}^2 - \bar{S}(\Delta_i + \Delta_j)] \tag{4}$$

so that only linear terms in Δ are used in H_0. The total Hamiltonian H is now written as

$$H = H_0 + V \tag{5}$$

where

$$V = -B^* \sum_{\langle i,j \rangle} (\Delta_i \Delta_j + W_{ij}) = \sum_{\langle i,j \rangle} V_{ij} \text{ say.} \tag{6}$$

The choice of the perturbation is reasonable since $\Delta_i \Delta_j$ is likely to be quite small and the value of W_{ij} is always

close to zero. The configurational Helmholts free energy is given by

$$F = -kT \ln[\text{Tr}\{\exp(-H/kT)\}]$$

$$= -kT \ln\left[\frac{\text{Tr}[\exp\{-(H_0 + V)/kT\}]}{\text{Tr}[\exp(-H_0/kT)]}\right] - kT \ln\{\text{Tr}[\exp(-H_0/kT)]\}$$

$$= -kT \ln \langle\exp(-V/kT)\rangle_{H_0} - kT \ln\{\text{Tr}[\exp(-H_0/kT)]\}$$

$$= F_1 + F_0 . \tag{7}$$

The unperturbed portion of the free energy, viz., F_0 is easily evaluated and gives

$$F_0 = \frac{N z \, B^* \bar{S}^2}{2} - NkT \ln \int d(\cos\theta)\exp[zB^* \, \bar{S}P_2(\cos\theta_1)/kT]$$

$$..(8)$$

where z is the number of nearest neighbours.

Identifying $NzB^* = A/V^2$ and $S = \bar{S}$, F_0 is the free energy according to the mean field approximation used by Maier and Saupe (see chapter II).

To calculate F_1, a two-site cluster approximation is used. It is assumed that

$$\langle\exp(-V/kT)\rangle_{H_0} = \left\langle\prod_{\langle ij\rangle} \exp(-V_{ij}/kT)\right\rangle_{H_0}$$

$$= \left[\langle\exp(-V_{12}/kT)\rangle_{H_0}\right]^{Nz/2} . \tag{9}$$

Substituting equations (9) and (8) in eq.(7), we get by following some algebra

$$F = NkT(z - 1)\ln Z_1 - NkT \frac{z}{2} \ln Z_{12} \qquad (10)$$

where

$$Z_{12} = \iiint d(\cos \theta_1)d\varphi_1 \, d(\cos \theta_j)d\varphi_j \, f(\theta_{1j})g(\theta_1)g(\theta_j) \, ,$$

$$Z_1 = \int d(\cos \theta_1)[g(\theta_1)]^{z/(z-1)} \, , \qquad (11)$$

$$f(\theta_{1j}) = \exp[+B^* P_2(\cos \theta_{1j})/kT] \, ,$$

$$g(\theta_1) = \exp[B^* \bar{3} (z - 1) P_2(\cos \theta_1)/kT] \qquad (12)$$

which are identical to equations $\lfloor$(10), (16) and (17) of chapter II, if $B_2 = B^* \bar{3} (z - 1)$. Equation (10) is thermodynamically consistent as we have shown in chapter II.

REFERENCES

Strieb, B., Callen, H.B. and Horowitz, G.   1963
   Phys. Rev. 130, 1798.

Ypma, J.G.J.   1977   Thesis 'A Molecular Statistical
   Description of Nematic Liquid Crystals'.
   University of Groningen.

APPENDIX II

EXPRESSIONS FOR THE

SPECIFIC HEAT AT CONSTANT VOLUME C_v USED IN CHAPTERS II & III

The specific heat at constant volume C_v is defined as

$$C_v = + \left(\frac{\partial U}{\partial T}\right)_v \qquad (1)$$

where U is the internal energy of the system which is given by (see Chapters II & III)

$$U = -\frac{Ng}{2}\left[B^* \langle P_2(\cos\theta_{ij})\rangle - A^* \langle P_1(\cos\theta_{ij})\rangle \right]$$

$$C_v = -\frac{Ng}{2}\left\{ B^*\left[\frac{\partial\langle P_2(\cos\theta_{ij})\rangle}{\partial T}\right]_v - A^*\left[\frac{\partial\langle P_1(\cos\theta_{ij})\rangle}{\partial T}\right]_v \right\} \qquad (2)$$

$$\langle P_m(\cos\theta_{ij})\rangle = \frac{\iiint P_m(\cos\theta)_2 \, f(\theta_{ij}) \, g(\theta_i) \, g(\theta_j) \, r(\theta_{ij}) \, d(\cos\theta_i) \, d(\cos\theta_j) \, d\varphi}{\iiint f(\theta_{ij}) \, g(\theta_i) \, g(\theta_j) \, d(\cos\theta_i) \, d(\cos\theta_j) \, d\varphi} \; , \qquad (3)$$

where

$$f(\theta_{ij}) = \exp[\{B^* P_2(\cos\theta_{ij}) - A^* P_1(\cos\theta_{ij})\}/kT] \; , \qquad (4)$$

$$g(\theta_i) = \exp[\sum (B_{2n} P_{2n}(\cos\theta_i)/kT] \; .$$

From equations (3) and (4), after some algebra, we get

$$\left[\frac{\partial \langle P_2(\cos\theta_{ij})\rangle}{\partial T}\right]_N = -\frac{B^*}{kT^2}[\langle P_2(\cos\theta_{ij})^2\rangle - \langle P_2(\cos\theta_{ij})\rangle^2]$$

$$+\frac{A^*}{kT^2}[\langle P_2(\cos\theta_{ij})P_1(\cos\theta_{ij})\rangle - \langle P_2(\cos\theta_{ij})\rangle \langle P_1(\cos\theta_{ij})\rangle]$$

$$+\frac{2}{kT}\sum\left(\frac{\partial B_{2n}}{\partial T} - \frac{B_{2n}}{T}\right)[\langle P_{2n}(\cos\theta_i)P_2(\cos\theta_{ij})\rangle - \langle P_{2n}(\cos\theta_i)\rangle\langle P_2(\cos\theta_{ij})\rangle]$$

... (5)

Similarly we can write

$$\left[\frac{\partial \langle P_1(\cos\theta_{ij})\rangle}{\partial T}\right]_V = -\frac{B^*}{kT^2}[\langle P_2(\cos\theta_{ij})\,P_1(\cos\theta_{ij})\rangle - \langle P_2(\cos\theta_{ij})\rangle \langle P_1(\cos\theta_{ij})\rangle]$$

$$+\frac{A^*}{kT^2}[\langle P_1(\cos\theta_{ij})^2\rangle - \langle P_1(\cos\theta_{ij})\rangle^2]$$

$$+\frac{2}{kT}\sum\left(\frac{\partial B_{2n}}{\partial T} - \frac{B_{2n}}{T}\right)[\langle P_{2n}(\cos\theta_i)P_1(\cos\theta_{ij})\rangle - \langle P_{2n}(\cos\theta_i)\rangle\langle P_1(\cos\theta_{ij})\rangle]$$

... (6)

Substituting equations (5) and (6) in eq. (2), we get

Differentiating both parts of this equation with respect to T, we get a (mxn) matrix

$$\iiint f(\theta_i) f(\theta_j) g(\theta_i) g(\theta_j) f(\theta_i) g(\theta_j) d(\cos \theta_i) d(\cos \theta_j) d\phi$$

$$\overline{\iiint P_{2m}(\cos \theta_i) f(\theta_i) g(\theta_j) f(\theta_{ij}) g(\theta_i) g(\theta_j) d(\cos \theta_i) d(\cos \theta_j) d\phi}$$

.

... (8)

To calculate $\left(\dfrac{\partial B_{2n}}{\partial T} - \dfrac{B_{2n}}{T}\right)$, we proceed as follows. The O-O approximation

is given by

$$\frac{\int (P_{2m}(\cos \theta_i)) [g(\theta_i)]^{z/z-1} d(\cos \theta_i)}{\int [g(\theta_i)]^{z/(z-1)} d(\cos \theta_i)} =$$

$$- A^{*} \left\{ \langle P_{2n}(\cos\theta_i) P_1(\cos\theta_{ij}) \rangle - \langle P_{2n}(\cos\theta_i) \rangle \langle P_1(\cos\theta_{ij}) \rangle \right\}$$

$$+ \frac{2}{kT} \sum_{T} \left(\frac{\partial B_{2n}}{\partial T} - \frac{B_{2n}}{T}\right) \left[B^{*} \left\{ \langle P_{2n}(\cos\theta_i) P_2(\cos\theta_{ij}) \rangle - \langle P_{2n}(\cos\theta_i) \rangle \langle P_2(\cos\theta_{ij}) \rangle \right\} \right.$$

$$+ \frac{2A^M B^M}{kT^2} \left[\langle P_2(\cos\theta_{ij}) P_1(\cos\theta_{ij}) \rangle - \langle P_1(\cos\theta_{ij}) \rangle \ \langle P_2(\cos\theta_{ij}) \rangle \right]$$

$$C_v = - \frac{Nk}{2} \left[-\frac{B^{*2}}{kT^2} [\langle P_2(\cos\theta_{ij})^2 \rangle - \langle P_2(\cos\theta_{ij}) \rangle^2] + \frac{A^{*2}}{kT^2} [\langle P_1(\cos\theta_{ij})^2 \rangle - \langle P_1(\cos\theta_{ij}) \rangle^2] \right]$$

equation of the form,

$$
\begin{pmatrix}
a_{11} & a_{12} & \cdot & \cdot & \cdot & \cdot \\
a_{21} & & & & & \\
\cdot & & & & & \\
\cdot & & & & & \\
\cdot & & & & & \\
a_{m1} & & & & & a_{mm}
\end{pmatrix}
\begin{pmatrix}
b_1 \\
b_2 \\
\cdot \\
\cdot \\
\cdot \\
b_m
\end{pmatrix}
=
\begin{pmatrix}
c_1 \\
c_2 \\
\cdot \\
\cdot \\
\cdot \\
c_m
\end{pmatrix}
\qquad (9)
$$

where

$$b_n = \frac{1}{kT}\left\{\frac{\partial B_{2n}}{\partial T} - \frac{B_{2n}}{T}\right\}$$

$$c_n = -\frac{B^*}{kT^2}\left[\langle P_{2n}(\cos\theta_i)\, P_2(\cos\theta_{ij})\rangle - \langle P_{2n}(\cos\theta_i)\rangle \langle P_2(\cos\theta_{ij})\rangle\right]$$
$$+\frac{A^*}{kT^2}\left[\langle P_{2n}(\cos\theta_i)\, P_1(\cos\theta_{ij})\rangle - \langle P_{2n}(\cos\theta_i)\rangle \langle P_1(\cos\theta_{ij})\rangle\right]$$

and

$$a_{nm} = \frac{1}{(z-1)}\left[\langle P_{2n}(\cos\theta_i)\, P_{2m}(\cos\theta_i)\rangle - \langle P_{2n}(\cos\theta_i)\rangle \langle P_{2m}(\cos\theta_i)\rangle\right]$$
$$-\left[\langle P_{2n}(\cos\theta_i)P_{2m}(\cos\theta_j)\rangle - \langle P_{2n}(\cos\theta_i)\rangle \langle P_{2m}(\cos\theta_j)\rangle\right] \qquad (10)$$

Equations (9) are solved alongwith equation (10) to determine the values of b_n.

APPENDIX III

EXPRESSIONS FOR SECOND DERIVATIVES OF THE CHEMICAL POTENTIAL USED IN CHAPTER IV

The pressure is given by the relation (see chapter IV)

$$\frac{Pv_0}{kT} = \frac{d[1 + d + \frac{2}{3}d^2(1 + q - q^2/2)]}{(1 - d)^3}$$

$$+ \frac{\frac{N\pi d^2}{2}[1 + (1 + 2q)d/3](1 - 5/8 \langle P_2 \rangle^2)}{(1 - d)^3}$$

$$- \frac{1}{2}\frac{\mathcal{V}_0 d^2}{v_0 kT} - \frac{\mathcal{V}_2 d^2}{2v_0 kT}\langle P_2 \rangle^2 . \qquad (1)$$

The isothermal compressibility β is given by

$$\beta = -\frac{1}{v}\left(\frac{\partial V}{\partial P}\right)_{N,T}$$

$$= \frac{v_0}{kT}\left[d\left(\frac{\partial Pv_0/kT}{\partial d}\right)_{N,T}\right]^{-1} .$$

By differentiating P with respect to d keeping T constant in equation (1), we get after simplification

$$d\left(\frac{\partial Pv_d/kT}{\partial d}\right)_{N,T} = \frac{d[1 + 4d + 3d^2(1 + \frac{2}{3}q - \frac{q^2}{3}) + \pi r d[1 + (1 + q)d](1 - 5/8\langle P_2\rangle^2)]}{(1 - d)^4}$$

$$-\frac{d^2}{v_o kT}(\vartheta_o + \vartheta_2\langle P_2\rangle^2) - \left\{\frac{\vartheta_2 d^2}{v_o kT} + \frac{5\pi r d(1+(1+2q)d/3)}{8(1 - d)^3}\right\}d\langle P_2\rangle\left(\frac{\partial\langle P_2\rangle}{\partial d}\right)_T .$$

...(2)

The long range order parameter $\langle P_2\rangle$ is given by

$$\langle P_2\rangle = \frac{\int P_2(\cap)\exp\left[\left\{\frac{\vartheta_2 d}{v_o kT} + \frac{5\pi r d[1-(1-q)d4/3]}{8(1 - d)^2}\right\}\langle P_2\rangle P_2(\cap)\right]d\cap}{\int \exp\left[\left\{\frac{\vartheta_2 d}{v_o kT} + \frac{5\pi r d[1-(1-q)d/3]}{8(1-d)^2}\right\}\langle P_2\rangle P_2(\cap)\right]d\cap} .$$

(3)

Differentiating the above equation with respect to d at constant T, we get

$$d\left(\frac{\partial\langle P_2\rangle}{\partial d}\right)_T = \frac{\left\{\frac{5\pi r d[1 + (1 + 2q)d/3]}{3(1 - d)^3} + \frac{\vartheta_2 d}{v_o kT}\right\}\langle P_2\rangle[\langle P_2^2\rangle - \langle P_2\rangle^2]}{1 - \left\{\frac{5\pi r d[1 + (1 + 2q)d/3]}{8(1 - d)^3} + \frac{\vartheta_2 d}{v_o kT}\right\}[\langle P_2^2\rangle - \langle P_2\rangle^2]} .$$

(4)

Substituting this expression for $\left(\frac{\partial \langle P_2 \rangle}{\partial \rho}\right)_T$ in equation (2), we can calculate the isothermal compressibility β. The thermal expansivity α is defined as

$$\alpha = \frac{1}{v}\left(\frac{\partial V}{\partial T}\right)_{H,p} = \left(\frac{\partial T}{\partial T}\right)_\rho = \frac{kJ}{v_0}\left(\frac{\partial P v_0/k}{\partial T}\right)_p . \qquad (5)$$

Differentiating P in equation (1) with respect to T keeping ρ constant, we get after simplification

$$\left(\frac{\partial P v_0/k}{\partial T}\right)_\rho = \frac{d[1+d+\frac{2}{3}d^2(1+q-\frac{d^2}{2})+\frac{\pi r d}{2}(1+(1+2q)d/3)(1-\frac{5}{8}\;\langle P_2\rangle^2)]}{(1-d)^3}$$

$$-\left\{\frac{5\pi r d^2(1+(1+2q)d/3)}{8(1-d)^3} + \frac{\vartheta_2 d^2}{v_0 k T}\{T\langle P_2\rangle\left(\frac{\partial\langle P_2\rangle}{\partial T}\right)\right)_\rho . \qquad (6)$$

Differentiating $\langle P_2 \rangle$ (equation 3) with respect to T at constant P, we got

$$T\left(\frac{\partial\langle P_2\rangle}{\partial T}\right)_\rho =$$

$$\frac{-\frac{\vartheta_2 d}{v_0 k T}\langle P_2\rangle[\langle P_2^2\rangle - \langle P_2\rangle^2]}{1-\left\{\frac{5\pi r d[1-(1-q)d/3]}{8(1-d)^2}\langle P_2\rangle[\langle P_2^2\rangle - \langle P_2\rangle^2] + \frac{\vartheta_2 d}{v_0 k T}\{[\langle P_2^2\rangle - \langle P_2\rangle^2]\right\}} . \qquad (7)$$

Substituting equations (6) and (7) in equation (5), we can calculate the thermal expansivity α. The specific heat at constant volume C_V and at constant pressure C_p are given by

$$\frac{C_V}{Nk} = \left(\frac{\partial U/Nk}{\partial T}\right)_{N,V} = -\frac{\vartheta_2 d}{V_0 k}\langle P_2\rangle\left(\frac{\partial \langle P_2\rangle}{\partial T}\right)_\rho \qquad (8)$$

and

$$\frac{C_p}{Nk} = \frac{C_V}{Nk} + \frac{T\alpha^2}{\rho k\kappa_\tau} \,. \qquad (9)$$

APPENDIX IV

EXPRESSIONS FOR SECOND DERIVATIVES OF THE CHEMICAL POTENTIAL USED IN CHAPTER V

The pressure of the system is given by

$$\frac{Pv_0}{kT} = -\ln(1-d) + \frac{Ad^2}{1 - \sum \omega_n d^{n+1}/v_0^{n+1}} - A \int_0^d \frac{ydy}{1 - \sum \omega_n y^{n+1}/v_0^{n+1}}$$

$$- \frac{1}{2} \frac{\vartheta_0 d^2}{v_0 kT} - \frac{1}{2} \frac{\vartheta_2 d^2}{v_0 kT} \langle P_2 \rangle^2 \; . \qquad (1)$$

By differentiating this equation with respect to the packing fraction d at constant temperature we get

$$\left(\frac{\partial Pv_0/kT}{\partial d}\right)_T = \frac{1}{(1-d)} + \frac{2Ad}{1 - \sum \omega_n d^{n+1}/v_0^{n+1}} + \frac{Ad^2 \left[-\sum (n+1)\omega_n d^n/v_0^{n+1}\right]}{\left[1 - \sum \omega_n d^{n+1}/v_0^{n+1}\right]^2}$$

$$+ \frac{d^2 (\partial A/\partial d)_T}{1 - \sum \omega_n d^{n+1}/v_0^{n+1}} - \left(\frac{\partial A}{\partial d}\right)_T \int_0^d \frac{ydy}{1 - \sum \omega_n y^{n+1}/v_0^{n+1}} - \frac{Ad}{1 - \sum \omega_n d^{n+1}/v_0^{n+1}}$$

$$- \frac{\vartheta_0 d}{v_0 kT} - \frac{\vartheta_2 d}{v_0 kT} \langle P_2 \rangle^2 - \frac{\vartheta_2 d^2}{v_0 kT} \langle P_2 \rangle \left(\frac{\partial \langle P_2 \rangle}{\partial d}\right)_T$$

$$= \frac{1}{(1-d)} + \frac{Ad}{1 - \sum \omega_n d^{n+1}/\Psi_o^{n+1}} - \frac{Ad^2 \sum (n+1)\omega_n d^{n+1}/\Psi_o^{n+1}}{\left[1 - \sum \omega_n d^{n+1}/\Psi_o^{n+1}\right]^2}$$

$$+ \left(\frac{\partial A}{\partial d}\right)_T \left\{ \frac{d^2}{1 - \sum \omega_n d^{n+1}/\Psi_o^{n+1}} - \int_0^d \frac{y\,dy}{1 - \sum \omega_n y^{n+1}/\Psi_o^{n+1}} \right\}$$

$$= -\frac{\vartheta_o d}{\Psi_o} \frac{\langle P_2 \rangle}{kT} - \frac{\vartheta_2 d \langle P_2 \rangle}{\Psi_o kT} \left\{ \langle P_2 \rangle + d\left(\frac{\partial \langle P_2 \rangle}{\partial d}\right)_T \right\} \qquad (2)$$

where

$$A = \frac{14 + 21(x-1) + \frac{24}{x}(x-1)^2 \sum_i \sum_k |\sin \theta_{ik}| f(\cup_i) f(\cup_k)}{(3x-1)} \quad . \qquad (3)$$

Assuming

$$\sum_i \sum_k |\sin \theta_{ik}| f(\cup_i) f(\cup_k) = \frac{\pi}{4} - \frac{5\pi}{32} \langle P_2 \rangle^2$$

so we get

$$\left(\frac{\partial A}{\partial \rho}\right)_T = -\frac{15}{2}\frac{(x-1)^2}{(3x-1)}\langle P_2\rangle\left(\frac{\partial \langle P_2\rangle}{\partial \rho}\right)_T \tag{4}$$

The long range order parameter $\langle P_2\rangle$ is given by

$$\langle P_2\rangle = \frac{\int P_2(\Omega)\exp\left[\left\{\frac{\vartheta_2\rho}{kT}+\frac{15}{2d}\frac{(x-1)^2}{(3x-1)}\right\}\langle P_2\rangle P_2(\Omega)\right]d\Omega \int_0^d \dfrac{ydy}{1-\sum_n\omega_n y^{n+1}/v_o^{n+1}}}{\int\exp\left[\left\{\frac{\vartheta_2\rho}{kT}+\frac{15}{2d}\frac{(x-1)^2}{(3x-1)}\right\}\langle P_2\rangle P_2(\Omega)\right]d\Omega \int_0^d \dfrac{ydy}{1-\sum_n\omega_n y^{n+1}/v_o^{n+1}}} \tag{5}$$

Differentiating $\langle P_2\rangle$ with respect to d at constant 2, we get after simplification

$$\left[\frac{\partial\langle P_2\rangle}{\partial\rho}\right]_T = \frac{\left[\frac{\vartheta_2}{v_o kT}+\frac{15}{2d}\frac{(x-1)^2}{(3x-1)}\right]\left\{\frac{d}{1-\sum_n\omega_n d^{n+1}/v_o^{n+1}}-\frac{1}{d}\int_0^d\dfrac{ydy}{1-\sum_n\omega_n y^{n+1}/v_o^{n+1}}\right\}\langle P_2\rangle\left[\langle P_2^2\rangle-\langle P_2\rangle^2\right]}{1-\left[\frac{\vartheta_2 d}{v_o kT}+\frac{15(x-1)^2}{2d(3x-1)}\right]\int_0^d\dfrac{ydy}{1-\sum_n\omega_n y^{n+1}/v_o^{n+1}}\left[\langle P_2^2\rangle-\langle P_2\rangle^2\right]} \tag{6}$$

Knowing $[\frac{\partial A}{\partial d}]_T$ and $[\frac{\partial \langle P_2\rangle}{\partial d}]_T$ from equations (4) and (6), $[\frac{\partial P v_o/kT}{\partial d}]_T$ can be obtained. The isothermal compressibility β is defined as

$$\beta = -\frac{1}{V}[\frac{\partial V}{\partial P}]_{N,T} = \frac{v_o}{dkT}[\frac{\partial P v_o/kT}{\partial \rho}]_{N,T}^{-1} \quad .$$

(7)

Differentiating P (eq. 1) with respect to T at constant density $\rho (\equiv d)$, we get

$$\left(\frac{\partial P v_o/k}{\partial T}\right)_d = -\ln(1-d) + \frac{Ad^2}{1-\sum_n \omega_n d^{n+1}/v_o^{n+1}} - A \int_0^d \frac{ydy}{1-\sum_n \omega_n y^{n+1}/v_o^{n+1}} - \frac{\vartheta_2 d^2}{v_o k}\langle P_2\rangle\left(\frac{\partial \langle P_2\rangle}{\partial T}\right)_d$$

$$+ T\left(\frac{\partial A}{\partial T}\right)_d \left\{ \frac{d^2}{1-\sum_n \omega_n d^{n+1}/v_o^{n+1}} - \int_0^d \frac{ydy}{1-\sum_n \omega_n y^{n+1}/v_o^{n+1}} \right\} \quad .$$

(8)

Differentiating A (eq.5) and $\langle P_2\rangle$ (eq. 5) with respect to T, we get

$$\left(\frac{\partial A}{\partial T}\right)_d = -\frac{15}{2}\frac{(x-1)^2}{(3x-1)}\langle P_2\rangle\left(\frac{\partial \langle P_2\rangle}{\partial T}\right)_d \quad ,$$

(9)

$$T\left(\frac{\partial \langle P_2\rangle}{\partial T}\right)_d = \frac{-\dfrac{\vartheta_2\rho}{kT}\langle P_2\rangle\left[\langle P_2^2\rangle - \langle P_2\rangle^2\right]}{1 - \dfrac{\vartheta_2\rho}{kT} + \dfrac{15(x-1)^2}{2d(3x-1)}\displaystyle\int_0^d \frac{ydy}{1 - \sum_n \omega_n y^{n+1}/v_0^{n+1}}\left\{\langle P_2^2\rangle - \langle P_2\rangle^2\right\}} \qquad (10)$$

By knowing $[\partial A/\partial T]_d$ and $[\partial\langle P_2\rangle/\partial T]_d$ from equations (9) and (10), we can calculate $\dfrac{\partial Pv_0/k}{\partial T}\Big)_d$ from equation (8). The thermal expansivity is defined as

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_{N\,P} = \frac{k\beta}{v_0}\left[\frac{\partial Pv_0/k}{\partial T}\right]_d . \qquad (11)$$

The specific heat at constant volume (U_v) and at constant pressure (U_p) are given by

$$\frac{c_v}{Nk} = \left(\frac{\partial U/Nk}{\partial T}\right)_{N,V} = -\frac{\vartheta_2}{v_0}\frac{\rho}{k}\,d\,\langle P_2\rangle\left(\frac{\partial\langle P_2\rangle}{\partial T}\right)_d , \qquad (12)$$

$$\frac{c_p}{Nk} = \frac{c_v}{Nk} + \frac{T\alpha^2}{\rho k\beta} . \qquad (13)$$