

Short range orientational order in nematic liquid crystals

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Abstract. The different approximations that have been used in applying Bethe's cluster model to the nematic-isotropic phase transition are examined. It is shown that the introduction of a higher order term in the mean field potential of an outer molecule of the cluster improves the consistency of the theory considerably. In particular, the importance of satisfying Chang's relation is emphasized. Calculations are presented of the long and short range order parameters, heat of transition and specific heat for different values of z , the number of nearest neighbours around any given molecule, for both nonpolar and antiparallel near neighbour correlations. Even the new mean field potential appears to be inadequate for $z = 3$.

Keywords. Short range order; nematic liquid crystals.

1. Introduction

In previous papers we demonstrated that the molecular statistical theory of the nematic-isotropic transition is improved considerably when near neighbour orientational correlations are taken into account (Madhusudana and Chandrasekhar 1973 *a, b, c*). The treatment was based on Bethe's cluster model: each molecule is supposed to be surrounded by z nearest neighbours ($z \geq 3$), no two nearest neighbours being nearest neighbours of each other. Let $E(\theta_{ij})$ be the energy of interaction between the central molecule i and an outer molecule j , where θ_{ij} is the angle between i and j , and let $V(\theta_j)$ be the *mean field* potential energy of an outer shell molecule j due to the surrounding medium. If we postulate that the relative probability of a molecule pointing in any direction (θ_i, ϕ_i) should be the same whether it is a central or an outer molecule, we obtain the following consistency relation due to Chang (1937):

$$F^z(\theta_i, \phi_i) = g(\theta_i) \int \int F^{z-1}(\theta_0, \phi_0) f(\theta_{0i}) d(\cos \theta_0) d\phi_0 \quad (1)$$

where the first subscript in θ_{ij} refers to the central molecule,

$$F(\theta_i, \phi_i) = \int \int f(\theta_{ij}) g(\theta_j) d(\cos \theta_j) d\phi_j,$$

$$f(\theta_{ij}) = \exp[-E(\theta_{ij})/kT]$$

and

$$g(\theta_j) = \exp[-V(\theta_j)/kT].$$

Krieger and James (1954) expressed this in a slightly different form: they argued

that the relative probability of a pair of molecules occupying any given configuration must be the same irrespective of which molecule is considered as the central one, *i.e.*,

$$\psi(\theta_i, \phi_i; \theta_j, \phi_j) = \psi(\theta_j, \phi_j; \theta_i, \phi_i) \quad (2)$$

where

$$\psi(\theta_i, \phi_i; \theta_j, \phi_j) = f(\theta_{ij}) g(\theta_j) F^{z-1}(\theta_i, \phi_i). \quad (3)$$

Equations (1) and (2) should be satisfied for all pairs of orientations $(\theta_i, \phi_i; \theta_j, \phi_j)$. We applied the Krieger-James (KJ) method taking

$$E(\theta_{ij}) = -B^* P_2(\cos \theta_{ij}) \quad (4)$$

and

$$V(\theta_j) = -BP_2(\cos \theta_j) \quad (5)$$

and showed that $(T_o - T^*)$ is significantly reduced as compared with the Maier-Saupe value. Here T_o is the nematic-isotropic transition temperature and T^* the apparent second order transition point. However, as was rightly pointed out by Ypma and Vertogen (1976 *a, b*), (4) and (5) do not satisfy (2) [or equivalently (1)] exactly in the ordered phase. The maximum discrepancy is 2-3% for $z = 8$ near T_o . In order to derive a mathematically consistent theory, these authors made the *weaker* approximation that only the *average* orientation of the central and an outer molecule need be identical. In other words,

$$\begin{aligned} \frac{1}{D} \int \int P_2(\cos \theta_i) F^z(\theta_i, \phi_i) d(\cos \theta_i) d\phi_i \\ = \frac{1}{D} \int \dots \int P_2(\cos \theta_i) g(\theta_i) f(\theta_{oi}) F^{z-1}(\theta_o, \phi_o) d(\cos \theta_i) d\phi_i \\ \times d(\cos \theta_o) d\phi_o \end{aligned} \quad (6)$$

where

$$D = \int \int F^z(\theta_i, \phi_i) d(\cos \theta_i) d\phi_i. \quad (7)$$

This relation is exactly analogous to the Bethe-Peierls-Weiss (BPW) approximation in ferromagnetism (see Smart 1966, Strieb *et al* 1963). The calculations of Ypma and Vertogen for z between 3 and 12 indicated that $(T_o - T^*)$ as well as the heat of transition come closer to the experimental values for smaller z . However, these authors also obtained the somewhat surprising result that the specific heat change (ΔC_v) at T_o decreases as z decreases, contrary to the predictions of the original Bethe theory (see *e.g.*, Fowler and Guggenheim 1939, Münster 1974). As we shall see presently, the YV results do not fulfil the thermodynamic equilibrium condition for the cluster free energy exactly. For $z = 8$ their solutions satisfy (1) to only 4-5% (maximum error) near T_o . The discrepancy increases at lower temperatures and becomes quite pronounced for lower values of z .

With a view to obtaining solutions that satisfy Chang's relation (and hence the thermodynamic equilibrium condition) as accurately as possible we have refined the calculations by introducing a higher order term in the mean field

potential $V(\theta_j)$ [see equation (9) below]. Though there are now two parameters in $V(\theta_j)$ they can be derived in terms of B^* , the two particle interaction constant, so that as before all the properties of the system can be deduced in terms of a single parameter. This leads to a significant improvement in the theory.

Before presenting these results we may mention in passing yet another method employed in ferromagnetism. The average orientational order of a molecule is calculated in two ways: (a) by assuming that the molecule is in the *mean* field of all its z nearest neighbours and (b) by considering interactions between two neighbouring molecules exactly and replacing the rest of the interactions of this coupled pair by the effective mean field due to the $z-1$ neighbours on each of them. It is then assumed that (a) and (b) should give identical results, *i.e.*,

$$\frac{\int \int P_2(\cos \theta_i) \exp \left\{ \frac{zBP_2(\cos \theta_i)}{kT} \right\} d(\cos \theta_i) d\phi_i}{\int \int \exp \left\{ \frac{zBP_2(\cos \theta_i)}{kT} \right\} d(\cos \theta_i) d\phi_i} \\ = \frac{\int \dots \int P_2(\cos \theta_i) \exp \left\{ \frac{B^*}{kT} P_2(\cos \theta_{ij}) + \frac{(z-1)B}{kT} \right. \\ \left. \times [P_2(\cos \theta_i) + P_2(\cos \theta_j)] \right\} d(\cos \theta_i) d\phi_i d(\cos \theta_j) d\phi_j}{\int \dots \int \exp \left\{ \frac{B^*}{kT} P_2(\cos \theta_{ij}) + \frac{(z-1)B}{kT} \right. \\ \left. \times [P_2(\cos \theta_i) + P_2(\cos \theta_j)] \right\} d(\cos \theta_i) d\phi_i d(\cos \theta_j) d\phi_j} \quad (8)$$

In ferromagnetism this method is known to be equivalent to the 'constant coupling approximation'. Equations (8) and (6) yield practically identical results (see table 1). We shall not therefore discuss this particular method any further in this paper.

Table 1.

Z	B^*/kT		$\langle P_2(\cos \theta) \rangle$	
	Eq. (8)	Eq. (6)	Eq. (8)	Eq. (6)
8	0.6248	0.6248	0.426	0.424
4	1.452	1.452	0.420	0.413

2. The method

Let us first examine the nature of the error involved when the YV solutions based on (4), (5) and (6) are substituted into Chang's relation. The percentage error defined as $200 \times (\text{RHS} - \text{LHS}) / (\text{LHS} + \text{RHS})$ calculated from (1) is plotted as a function of $\cos \theta_i$ in figure 1. It is clear from the form of this curve that the introduction of a $P_4(\cos \theta)$ term in eq. (5) may be expected to compensate

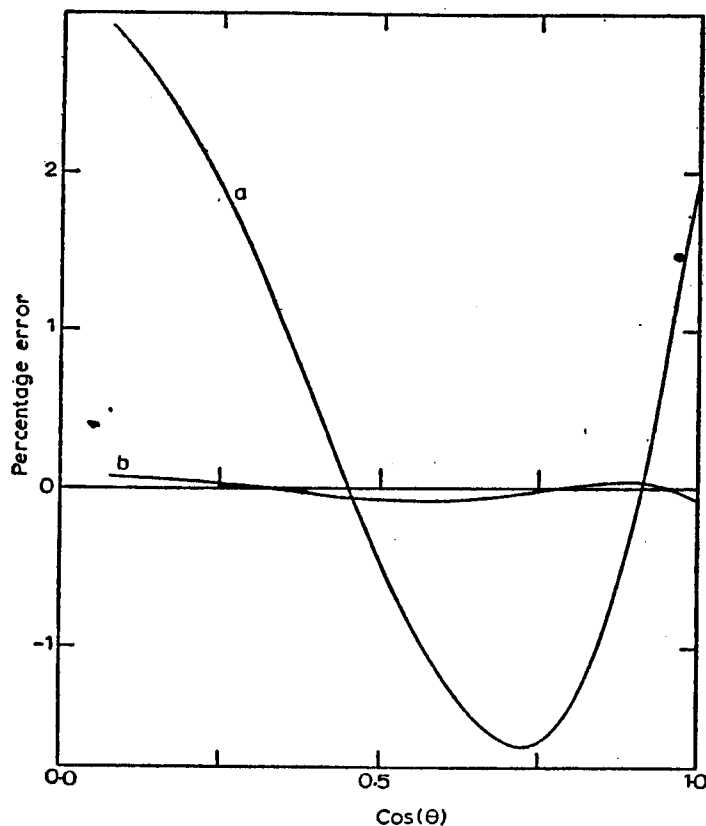


Figure 1. Percentage error in satisfying Chang's relation as a function of $\cos \theta$ for $z = 8$ at T_0 (a) when only B is taken into account and (b) when both B and C_{112} taken into account in the mean field potential energy (9).

for the error. We therefore write

$$V(\theta_j) = -BP_2(\cos \theta_j) - CP_4(\cos \theta_j). \quad (9)$$

We now impose the additional condition, similar to (6), that the average of $P_4(\cos \theta)$ should be the same for the central and outer shell molecules. This is an extension of the YV method and yields solutions which near T_0 satisfy Chang's relation (1) to better than 0.1% for $z = 8$ (figure 1). The new potential improves the results of the KJ method also to the same extent—indeed the parameters B and C derived by the two methods are practically identical and Chang's relation is fulfilled in both cases to the same degree of accuracy. Hence all results discussed hereafter will refer only to those obtained using the extended YV approximation.

The numerical calculations were made on an IBM-360 computer. The computational procedure was as follows: for a given value of B^*/kT we assume a pair of values of B/kT and C/kT to start with and iterate on the latter two numbers till the two consistency relations for $\langle P_2(\cos \theta) \rangle$ and $\langle P_4(\cos \theta) \rangle$ are satisfied. The integrations were performed using the Gaussian quadrature method in double precision, with 32 quadrature points. The properties of the system are finally expressible in terms of the single parameter B^* , the two particle interaction constant. The short range order parameter is given by

$$\langle P_2(\cos \theta_{ij}) \rangle = \frac{1}{D} \int \dots \int P_2(\cos \theta_{ij}) f(\theta_{ij}) g(\theta_j) F^{z-1}(\theta_i, \phi_i) d(\cos \theta_i) d\phi_i d(\cos \theta_j) d\phi_j. \quad (10)$$

Following Ypma and Vertogen, we evaluate the free energy of a cluster. The internal energy of the cluster is

$$\begin{aligned} U &= z \langle E(\theta_{ij}) \rangle + \frac{z}{2} \langle V(\theta_j) \rangle \\ &= -zB^* \langle P_2(\cos \theta_{ij}) \rangle - \frac{z}{2} B \langle P_2(\cos \theta_j) \rangle - \frac{z}{2} C \langle P_4(\cos \theta_j) \rangle \end{aligned} \quad (11)$$

and its entropy is given by

$$\begin{aligned} TS &= z \langle E(\theta_{ij}) \rangle + z \langle V(\theta_j) \rangle + kT \ln D \\ &= -zB^* \langle P_2(\cos \theta_{ij}) \rangle - zB \langle P_2(\cos \theta_j) \rangle - zC \langle P_4(\cos \theta_j) \rangle + kT \ln D \end{aligned} \quad (12)$$

and the free energy

$$F = U - TS. \quad (13)$$

As the expression for the specific heat C_V turns out to be rather long and involves two different kinds of averages, it is given separately in the appendix.

Similar relations hold good for the isotropic phase ($B = C = 0$), which is always a solution of the consistency relations. The properties of the isotropic phase, *e.g.*, the electric and magnetic birefringence, etc., are given by the same expressions as derived in an earlier paper (Madhusudana and Chandrasekhar 1973 *c*) since in this case $\langle P_4 \rangle \ll \langle P_2 \rangle$ and therefore it is enough to retain only the B -term in (9).

3. Results and Discussion

The calculations are presented in table 2 and figures 2-6 for $z = 12, 8, 4$ and 3. We note the following points:

- (a) $(T_c - T^*)/T_c$ decreases as z is decreased, but not as rapidly as reported by Ypma and Vertogen. The present value is 0.030 as against their 0.011

Table 2.

Z	B^*/kT	B/kT	C/B	ΔH Joules/ mole	C_V Joules/ mole K	ΔC_V Joules/ mole K	δ^*_{\max}	$\frac{T_c - T^*}{T_c}$
12	0.4002	1.7155	-0.01509	1195.5	71.63	69.88		0.070
8	0.6212	1.6009	-0.02304	1090.0	79.96	76.90	0.088%	0.062
4	1.436	1.2590	-0.04827	719.3	83.47	80.31	0.29%	0.040
3	2.254	1.0603	-0.06714	483.8	77.32	65.85	0.4%	0.030

* δ^*_{\max} is the maximum error in satisfying Chang's relation at T_c .

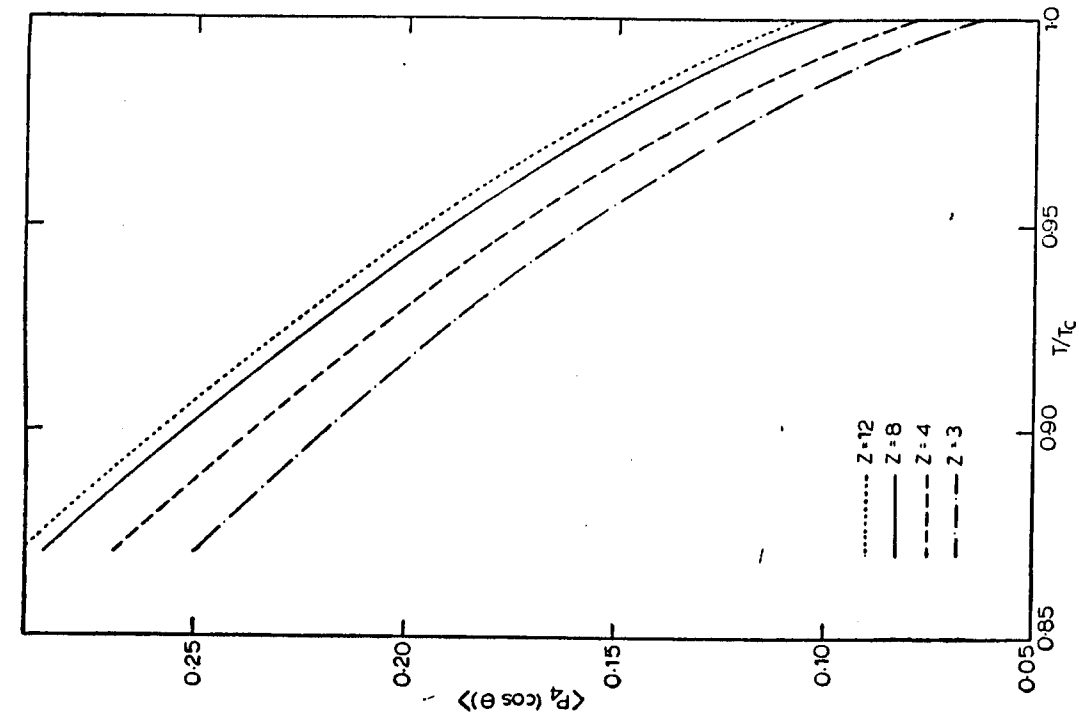


Figure 3. Long range order parameter $\langle P_4 \rangle$ as a function of the reduced temperature T/T_c for different values of z .

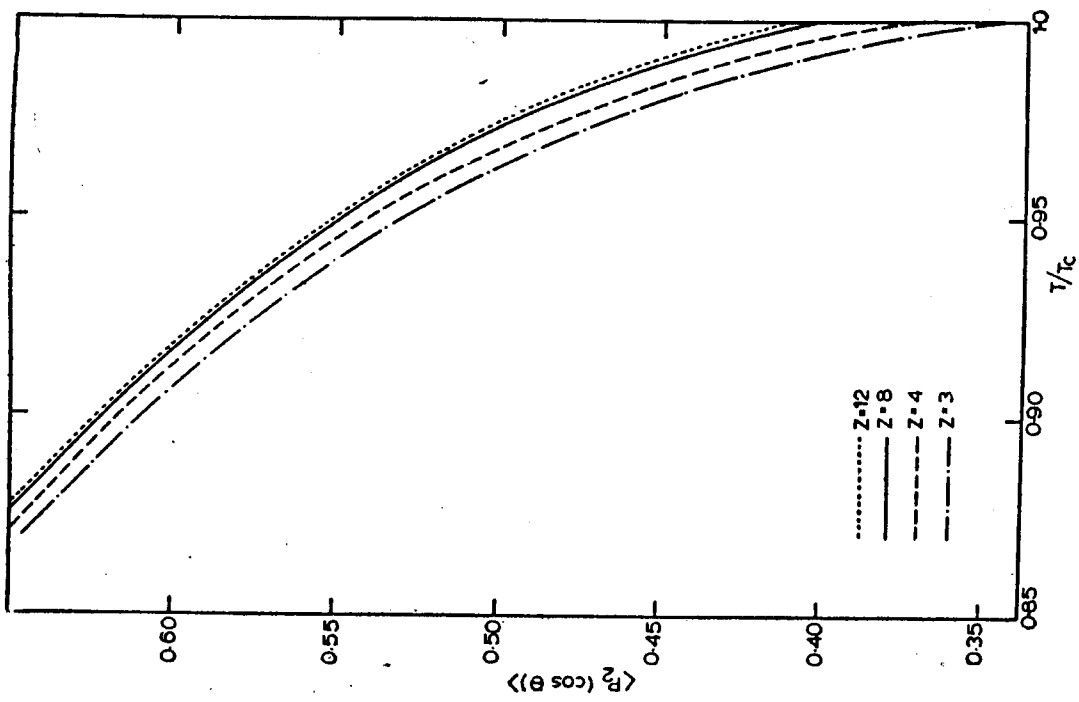


Figure 2. Long range order parameter $\langle P_2 \rangle$ as a function of the reduced temperature T/T_c for different values of z .

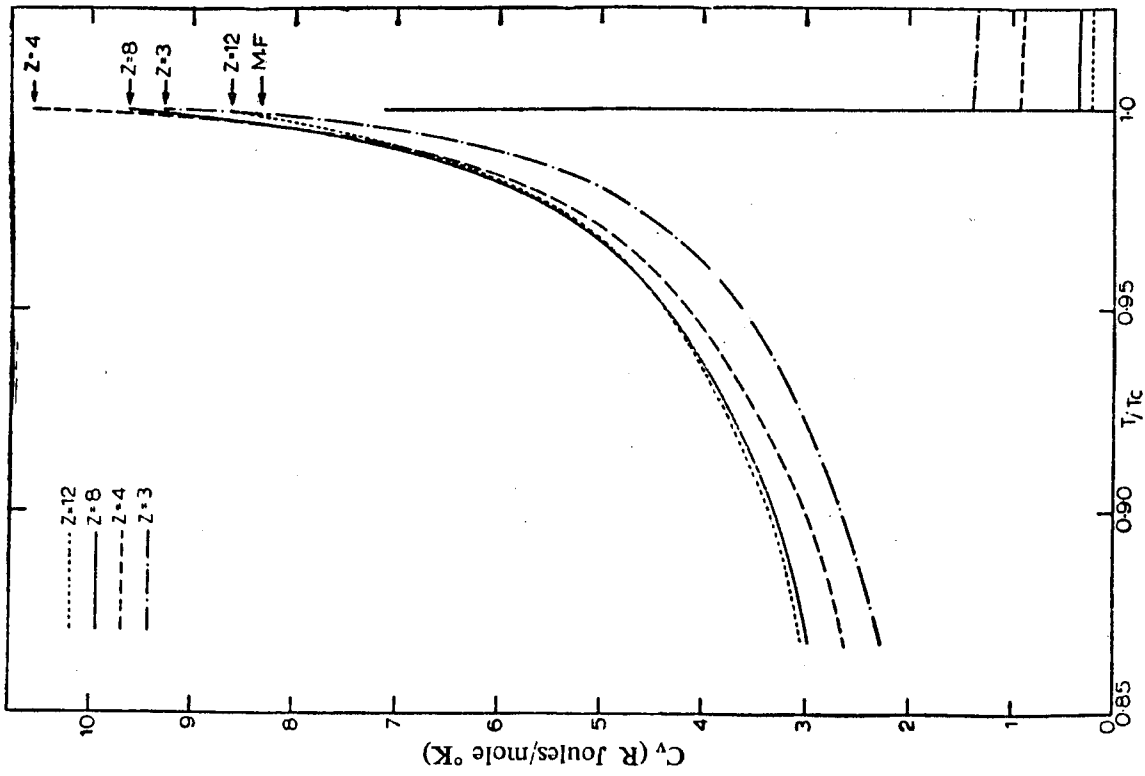


Figure 5. Specific heat C_V as a function of the reduced temperature T/T_c in the nematic and isotropic phases for different values of z . The arrows indicate C_V in the nematic phase at T_c . M.F. stands for the mean field theory.

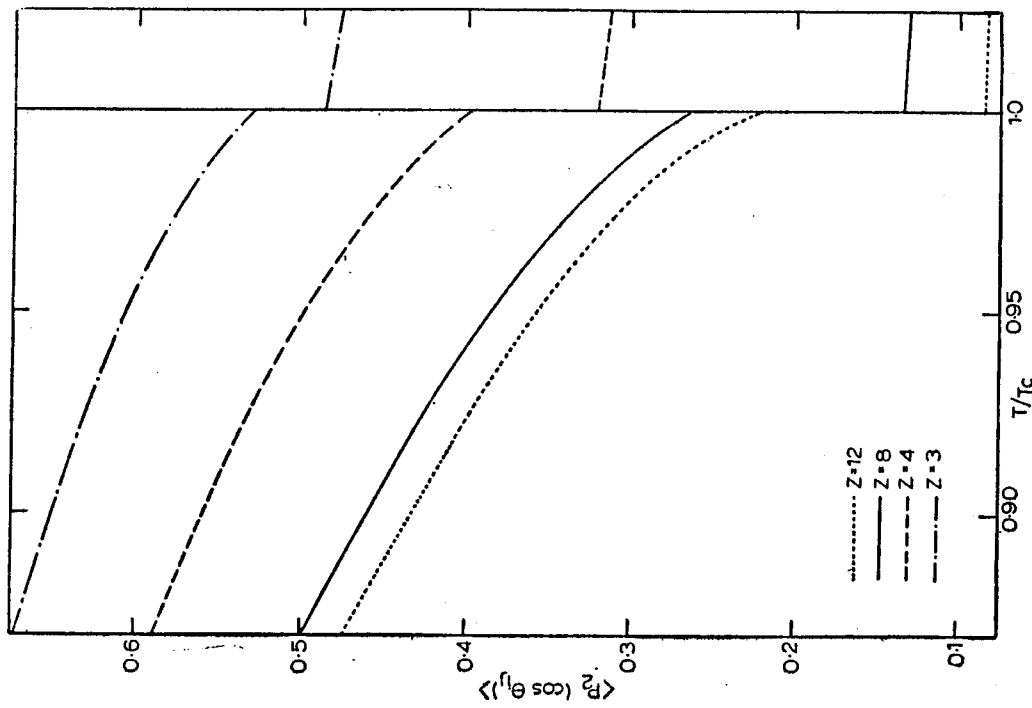


Figure 4. Short range order parameter $\langle P_2(\cos \theta_{ij}) \rangle$ as a function of the reduced temperature T/T_c in the nematic and isotropic phases for different values of z .

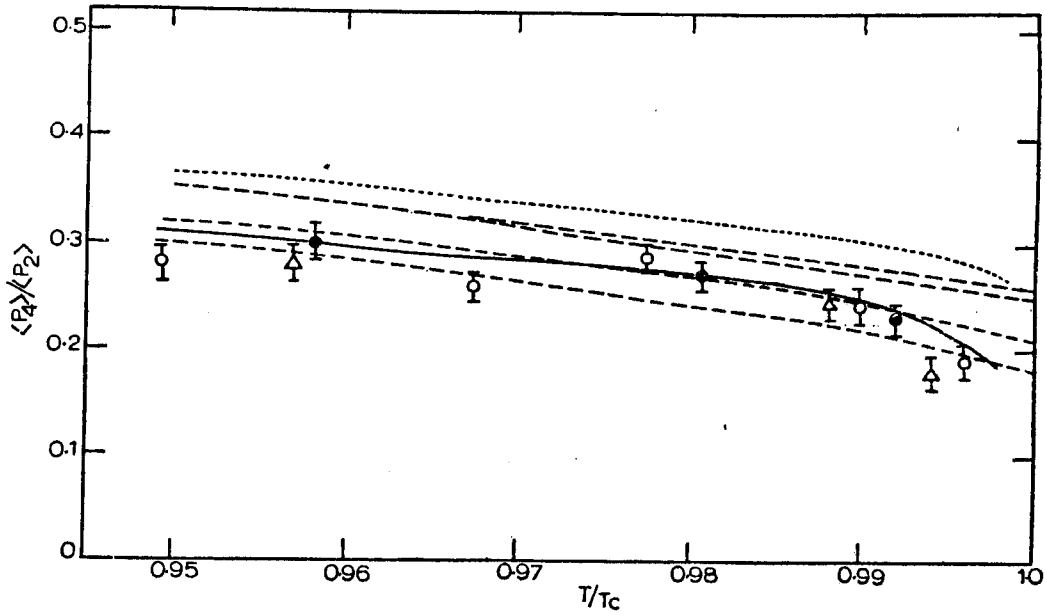


Figure 6. Comparison of experimental values of $\langle P_4 \rangle / \langle P_2 \rangle$ in the case of *p*-azoxyanisole as a function of reduced temperature T/T_c with theoretical values. Continuous line, Δ , \circ and \bullet stand for experimental values and the dotted line, the mean field result (from Kohli *et al* 1976). Dashed lines represent the theoretical values in the Bethe approximation for $z = 12, 8, 4$ and 3 from top to bottom.

for $z = 3$. (It may be mentioned however that $z = 3$ is an unphysical situation in a real system).

- (b) The absolute values and the temperature variation of $\langle P_2 \rangle$ for $z = 3$ and 4 are in good agreement with experimental data for common nematic compounds like PAA, MBBA (Saupe and Maier 1961, Chandrasekhar and Madhusudana 1969, Lee *et al* 1974). Recently, Kohli *et al* (1976) have determined the temperature variation of the ratio $\langle P_4 \rangle / \langle P_2 \rangle$ for PAA using neutron scattering. Again the agreement with the theoretical variation is reasonably good for $z = 3$ and 4 (figure 6).
- (c) Taking $C = 0$ in (13) and imposing the equilibrium condition $\partial F / \partial \langle P_2 \rangle = 0$ on the free energy of a cluster, we find that $B \propto \langle P_2 \rangle$. However, the actual numerical calculations of Ypma and Vertogen based on eqs (4), (5) and (6) do not lead to this result: the ratio $B / \langle P_2 \rangle$ steadily decreases as the temperature is increased. [A similar problem exists in the case of the BPW method in ferromagnetism (Strieb *et al* 1963)]. Another consequence of this discrepancy becomes apparent when the transition point T_c is located by the equal areas method from U vs. $(1/T)$ diagram (see Madhusudana and Chandrasekhar 1973). This method requires the thermodynamic equilibrium to be satisfied at all temperatures. It is found that T_c obtained by this method is slightly different from the value obtained by equating the excess cluster free energy ($F_N - F_I$) to zero.

When the C -term is introduced in the mean field potential, the equilibrium conditions $\partial F / \partial \langle P_2 \rangle = \partial F / \partial \langle P_4 \rangle = 0$ lead to expressions involving both B and C and we no longer get a simple relation like $B \propto \langle P_2 \rangle$. However, in this case, T_c obtained by the equal areas method agrees well with the

value obtained from the condition $F_N - F_I = 0$ (up to the 4th significant figure for $z = 8$; we have not tested this for lower values of z as the calculations are very lengthy). Thus it would appear that it is necessary for the detailed angular distribution functions of the central and outer molecules, and not merely their average orientations, to be identical for the system to be in thermodynamic equilibrium.

- (d) An even more sensitive test of the validity of the calculations is provided by the specific heat at constant volume (C_V). Ypma and Vertogen found that C_V at all temperatures and ΔC_V at T_c decrease systematically as z decreases from ∞ (mean field theory) to 3, contrary to the predictions of the original Bethe theory. In the present calculations, C_V at T_c as well as ΔC_V increase from the mean field to $z = 4$ (figure 5), but drop to lower values for $z = 3$. We believe that this reversal in the trend is because Chang's relation is relatively poorly satisfied ($\approx 0.4\%$) for $z = 3$ (see table 3). At sufficiently low temperatures, C_V is lower for smaller z , which again is in agreement with the Bethe theory.

4. Polar molecules: antiparallel correlations

In an earlier paper (Madhusudana and Chandrasekhar 1973 *c*) we proposed a theory of antiparallel near neighbour correlations in nematics composed of strongly polar molecules. Recent x-ray studies on the crystalline (Vani and Kalyani 1976), smectic (Lydon and Coakely 1975) and nematic (Leadbetter *et al* 1975) states of several strongly polar compounds have provided direct evidence for this kind of local ordering. An important consequence of such a correlation is that the mean dielectric constant in the nematic phase, $\langle \epsilon \rangle = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$, should be less than the extrapolated isotropic value. This again is found to be the case experimentally (Schadt 1972, Ratna and Shashidhar 1976).

We have now refined our earlier calculations in the light of the results of the previous sections. We re-write the near-neighbour interaction energy as

$$E(\theta_{ij}) = A^*P_1(\cos \theta_{ij}) - B^*P_2(\cos \theta_{ij}) \quad (14)$$

where the positive sign of A^* favours an antiparallel arrangement, and assume the mean field potential $V(\theta_j)$ to be given by (9) instead of (5) as in previous calculations. As in the non-polar case, there is now a significant improvement. The results are presented in table 3 and figures 7-11. The major points emphasized

Table 3.

	z	B^*/kT	B/kT	C/B	ΔH joules/ mole	ΔC_V joules/ mole K	δ_{maz}	$\frac{T_c - T^*}{T_c}$	$\delta\bar{\epsilon}/\bar{\epsilon}^*$
Eq. (5) $C=0$	8	0.5954	1.6818	..	1279.4	72.50	2.93%	0.055	0.073
	4	1.317	1.4005	..	1005.5	60.44	4.6%	0.028	0.190
Eq. (9) $C \neq 0$	8	0.5924	1.6016	-0.02311	1137.02	84.97	0.088%	0.059	0.078
	4	1.3035	1.2774	-0.04927	810.4	91.53	0.29%	0.038	0.156
	3	1.9750	1.0568	-0.06769	522.0	71.75	0.39%	0.028	0.191

* $\delta\bar{\epsilon}/\bar{\epsilon}$ is the relative jump in the mean dielectric constant at T_c .

in (a), (c) and (d) of the previous section hold good in this case also. The order parameters $\langle P_2 \rangle$ of several cyanobiphenyls, which are strongly polar materials, agree well with the theoretical values for $z = 3$ or 4 (Heger 1975, Karat and Madhusudana 1976). However, the experimental $\langle P_4 \rangle$ -values of 4'-n-heptyl-4-cyano biphenyl are lower than the theoretical values even for $z = 3$.

These results bring out the necessity of fulfilling Chang's consistency relation in order to develop a satisfactory theory of near neighbour correlations in the Bethe approximation. An attempt is being made to generalize this model and will be discussed in a separate paper.

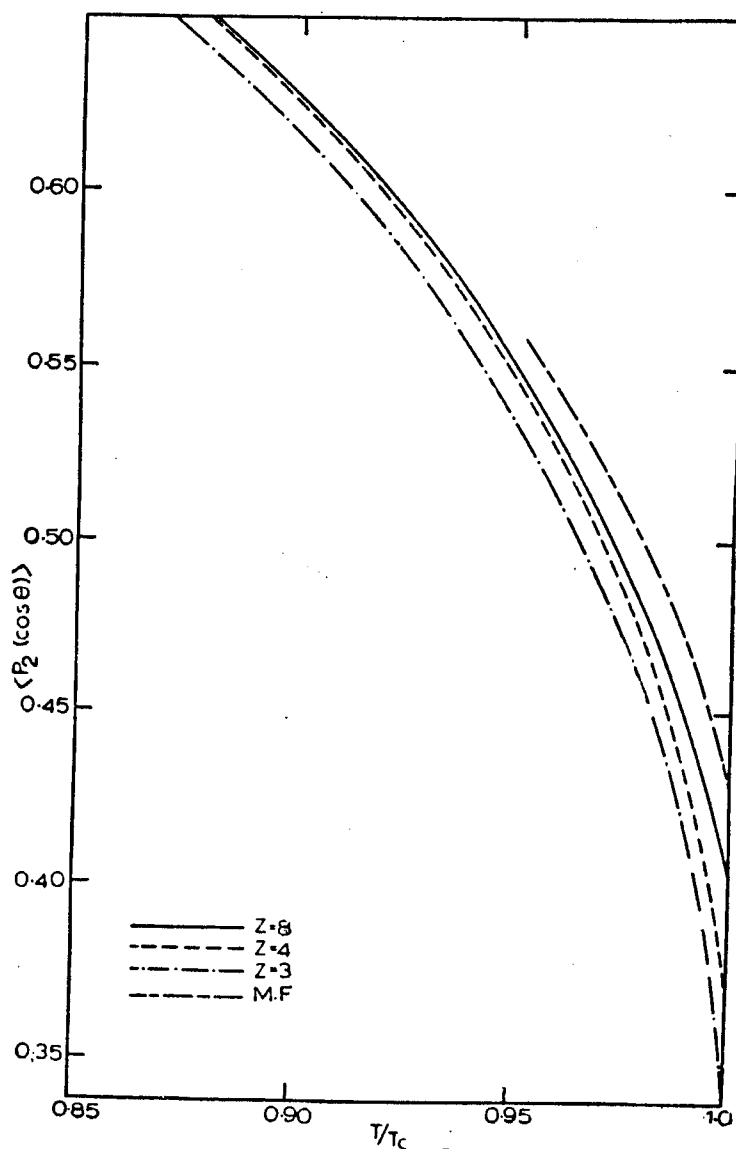


Figure 7. Long range order parameter $\langle P_2 \rangle$ for polar molecules with antiparallel correlation ($A^*/B^* = 0.5$) as a function of the reduced temperature T/T_c for different values of z .

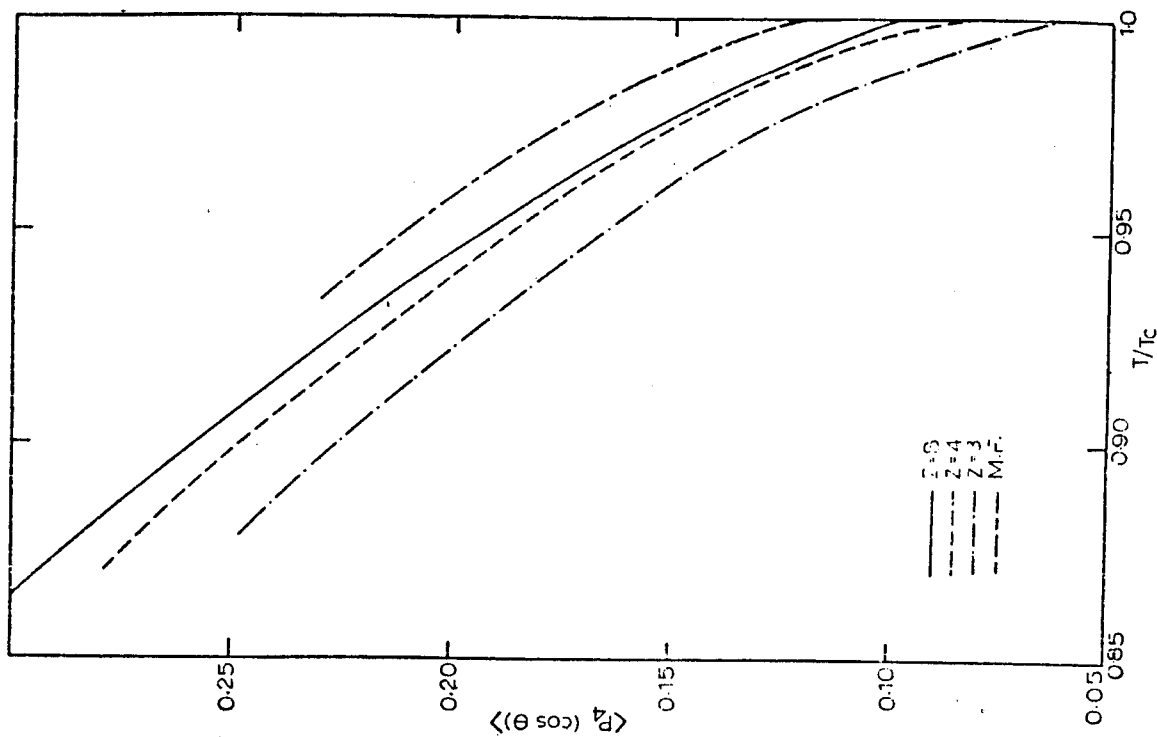


Figure 8. Long range order parameter $\langle P_4 \rangle$ as a function of the reduced temperature T/T_c for different values of z ($A^*/B^* = 0.5$).

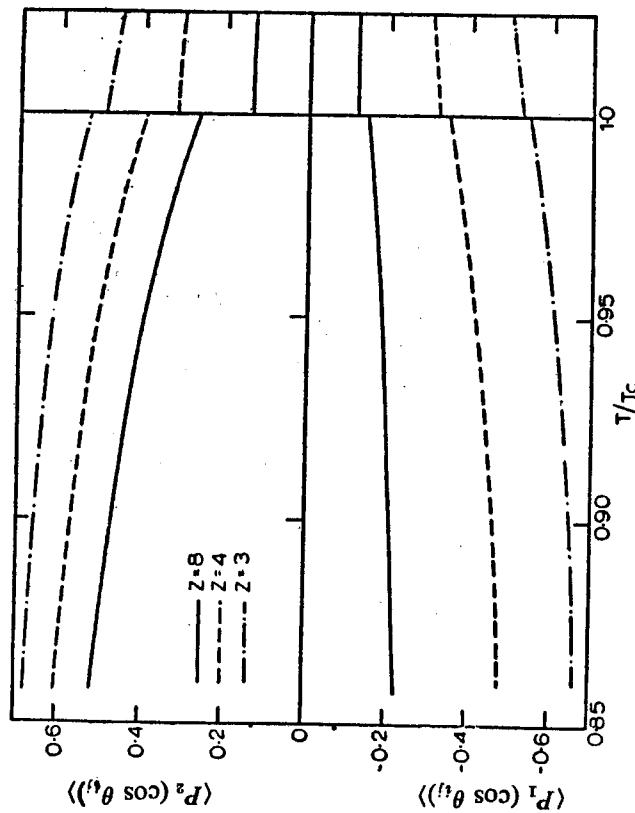


Figure 9. Short range order parameters $\langle P_2(\cos \theta_{ij}) \rangle$ and $\langle P_1(\cos \theta_{ij}) \rangle$ as functions of the reduced temperature T/T_c for different values of z . ($A^*/B^* = 0.5$).

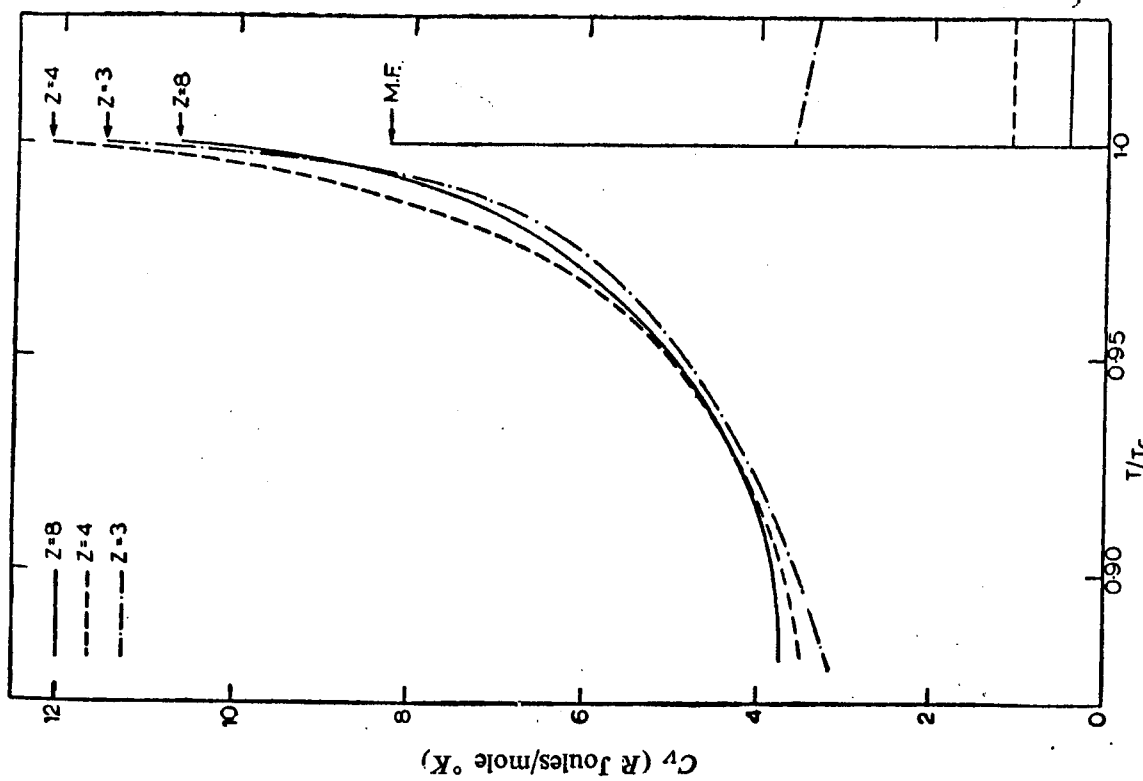


Figure 10. Specific heat C_V as a function of the reduced temperature T/T_c in the nematic and isotropic phases for different values of z . The arrows indicate C_V at T_c . ($A^*/B^* = 0.5$).

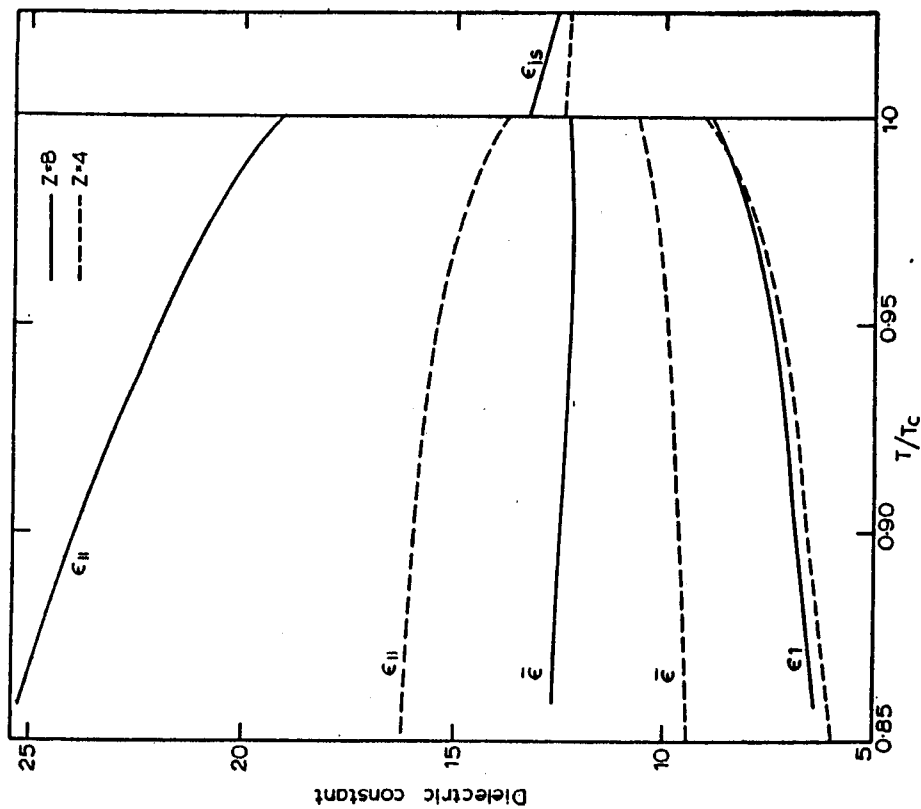


Figure 11. Dielectric constants $\epsilon_{||}$ and ϵ_{\perp} and the mean dielectric constant $\bar{\epsilon} = (\epsilon_{||} + 2\epsilon_{\perp})/3$ as functions of the reduced temperature T/T_c . ($A^*/B^* = 0.5$).

Appendix

The specific heat C_V :

$$\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T} \right)_V = -\frac{Nz}{2} \left[B^* \frac{\partial}{\partial T} \langle P_2(\cos \theta_{ij}) \rangle - A^* \frac{\partial}{\partial T} \langle P_1(\cos \theta_{ij}) \rangle \right] \\
&= -\frac{Nz}{2} \left[\frac{B^{*2}}{kT^2} \{ z \langle P_2(\cos \theta_{ij}) \rangle^2 - \langle P_2^2(\cos \theta_{ij}) \rangle \right. \\
&\quad - (z-1) \langle P_2(\cos \theta_{ij}) P_2(\cos \theta_{jk}) \rangle' \} \\
&\quad - \frac{2A^* B^*}{kT^2} \{ z \langle P_2(\cos \theta_{ij}) \rangle \langle P_1(\cos \theta_{ij}) \rangle - \langle P_2(\cos \theta_{ij}) P_1(\cos \theta_{ij}) \rangle \\
&\quad - (z-1) \langle P_2(\cos \theta_{ij}) P_1(\cos \theta_{jk}) \rangle' \} \\
&\quad + \frac{A^{*2}}{kT^2} \{ z \langle P_1(\cos \theta_{ij}) \rangle^2 - \langle P_1^2(\cos \theta_{ij}) \rangle \\
&\quad - (z-1) \langle P_1(\cos \theta_{ij}) P_1(\cos \theta_{jk}) \rangle' \} \\
&\quad + \frac{B^*}{kT} \left(\frac{B}{T} - \frac{\partial B}{\partial T} \right) \{ z \langle P_2(\cos \theta_{ij}) \rangle \langle P_2(\cos \theta_i) \rangle \\
&\quad - \langle P_2(\cos \theta_i) P_2(\cos \theta_{ij}) \rangle \\
&\quad - (z-1) \langle P_2(\cos \theta_{ij}) P_2(\cos \theta_k) \rangle' \} \\
&\quad + \frac{B^*}{kT} \left(\frac{C}{T} - \frac{\partial C}{\partial T} \right) \{ z \langle P_2(\cos \theta_{ij}) \rangle \langle P_4(\cos \theta_i) \rangle \\
&\quad - \langle P_4(\cos \theta_i) P_2(\cos \theta_{ij}) \rangle \\
&\quad - (z-1) \langle P_2(\cos \theta_{ij}) P_4(\cos \theta_k) \rangle' \} \\
&\quad - \frac{A^*}{kT} \left(\frac{B}{T} - \frac{\partial B}{\partial T} \right) \{ z \langle P_2(\cos \theta_i) \rangle \langle P_1(\cos \theta_{ij}) \rangle \\
&\quad - \langle P_2(\cos \theta_i) P_1(\cos \theta_{ij}) \rangle \\
&\quad - (z-1) \langle P_1(\cos \theta_{ij}) P_2(\cos \theta_k) \rangle' \} \\
&\quad - \frac{A^*}{kT} \left(\frac{C}{T} - \frac{\partial C}{\partial T} \right) \{ z \langle P_1(\cos \theta_{ij}) \rangle \langle P_4(\cos \theta_i) \rangle \\
&\quad - \langle P_4(\cos \theta_i) P_1(\cos \theta_{ij}) \rangle \\
&\quad - (z-1) \langle P_1(\cos \theta_{ij}) P_4(\cos \theta_k) \rangle' \}
\end{aligned}$$

where $\langle \rangle$ indicates average values obtained by using the RHS of eq. (8) and $\langle \rangle'$ indicates the following type of average:

$$\langle A \rangle' = \frac{1}{D} \int \dots \int A f(\theta_{ij}) f(\theta_{jk}) g(\theta_i) g(\theta_k)$$

$$F^{z-2}(\theta_j, \phi_j) d(\cos \theta_i) d\phi_i$$

$$d(\cos \theta_j) d\phi_j d(\cos \theta_k) d\phi_k$$

$\left(\frac{B}{T} - \frac{\partial B}{\partial T}\right)$ and $\left(\frac{C}{T} - \frac{\partial C}{\partial T}\right)$ can be evaluated by differentiating the consistency relation (8) and the analogous one involving $P_4(\cos \theta_i)$. The specific heat in the non-polar case is obtained by putting A^* equal to zero.

Note added in proof

We have recently received a preprint of a paper by Sheng and Wojtowicz, who have used the constant coupling approximation (8) with the more general form of the potential (9) and have obtained results very similar to those discussed here.

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