CHAPTER 2

BETHE CLUSTER MODEL CALCULATIONS ON NEMATIC LIQUID CRYSTALS: I. NON-POLAR MOLECULES

2.1 Introduction

The first successful theory to explain qualitatively the thermodynamic properties of the nematic phase was given by Maier and Saupe (1957, 1958, 1959, 1960). In this theory the van der Waals forces between anisotropically polarizable molecules are considered. The electrostatic interaction between two molecules i and j is given by

$$H_{ij} = \sum_{k,l} \frac{e_{ik}\, e_{jl}}{\left|(\vec{r}_i + \vec{\rho}_{ik}) - (\vec{r}_j + \vec{\rho}_{jl})\right|} \qquad (1)$$

where e_{ik} and e_{jl} are the systems of point charges belonging to the molecules i and j respectively, $\vec{r}_i$ and $\vec{r}_j$ denote the positions of the centres of gravity of the molecules i and j, and $\vec{\rho}_{ik}$ and $\vec{\rho}_{jl}$ are the positions of the charges relative to the origin of the coordinate system located at the centres of gravity of the two molecules respectively. The intermolecular potential energy V_{ij} due to the dipole-dipole contribution of the dispersion forces is obtained as a second order perturbation. The internal energy of a molecule i is obtained by summing V_{ij} over all other molecular coordinates. Maier and Saupe used the mean-field approximation and assumed that (a) the distribution of the molecules a——— the reference m——— i is spherically symmetric and (b) the position and the orientation of the molecules are independent of each other. The orientation-dependent part of the potential energy of a given molecules i will then take the form

$$V_i = -\frac{A}{v^2} SP_2(\cos\theta_i) \qquad (2)$$

where v is the molar volume, A is a constant dependent on the anisotropic interaction strength mentioned above, $P_2(\cos\theta)$ is the second order Legendre polynomial and S is the degree of orientational order. The Helmholtz free energy is given by

$$F = -\frac{A}{2v^2} S^2 + kT \langle \ln f(\cos\theta)\rangle \qquad (3)$$

where (lo $f(\cos\theta)\rangle = \int_0^1 f(\cos\theta)[\ln f(\cos\theta)]d(\cos\theta)$. The normalized distribution function $f(\cos\theta)$ which minimizes this free energy is given by

$$f(\cos\theta) = \frac{\exp[\frac{A}{kTV^2} S\, P_2(\cos\theta)]}{\int_0^1 \exp[\frac{A}{kTV^2} S\, P_2(\cos\theta)]\, d(\cos\theta)} \qquad (4)$$

The consistent value of the order parameter is now given by

$$S = \int_0^1 P_2(\cos\theta)\, f(\cos\theta)\, d(\cos\theta) \qquad (5)$$

The theory predicts a first order NI transition at $A/kTV^2 = 4.5415$ and $S = 0.429$. $S = 0$ is a trivial solution of equation (5) and corresponds to the isotropic phase. For temperatures less than the NI transition temperature (T_{NI}), non-zero values of S corresponding to the nematic phase minimise the free energy. The theory is successful in predicting the qualitative behaviour of the thermodynamic properties of the nematic phase, but has some drawbacks. For instance, the theory predicts a universal curve for the variation of S as a function of A/kTV^2 and gives $S = 0.429$ at T_{NI} for all nematic compounds. However the experimental value of S at T_{NI} is generally different for different liquid crystals. Since there is a finite (though small) volume change at T_{NI}, the Gibb's free energies (rather than the Helmholtz free energies) of the nematic and isotropic phases should be equalized in locating T_{NI} (Maier and Saupe, 1960). However, the resulting value of S at T_{NI} is not significantly different from the universal value of $S = 0.429$.

This drawback was overcome by Chandrasekhar and Madhusudana (1971, 1973) by extending the orientational potential to include higher order terms. The interaction energy of a pair of molecules V_{ij} is obtained by taking into account the contributions from (i) permanent dipole-dipole interaction, (ii) dipole-dipole and dipole-quadrupole parts of the dispersion energy, (iii) energy due to the induction effect, and (iv) repulsion energy. The total internal energy of the molecule i with all its neighbouring molecules is given in the mean field approximation after truncating to the $\cos^4 \theta_i$ term by

$$V_i = - v^{-3}(a \cos^4 \theta_i + b \cos^2 \theta_i + C) \qquad (6)$$

Later Humphries and Luckhurst (1972) argued that it is mathematically more appropriate to take V_i in the following form

$$V_i = - v^{-3}[\lambda_4 P_4(\cos \theta_i) + \lambda_2 P_2(\cos \theta_i) + \lambda_0] \qquad (7)$$

where λ_4, λ_2 and λ_0 are functions of $\langle P_2(\cos \theta)\rangle$ and $\langle P_4(\cos \theta)\rangle$. $P_4(\cos \theta) = (35\cos^4 \theta - 30\cos^2 \theta + 3)/8$ is the fourth order Legendre polynomial. $\langle P_2(\cos\theta)\rangle = S$ and $\langle P_4(\cos\theta)\rangle$ vary from 1 to 0 over the range of perfect ordering to complete disorder. Depending upon the ratio of λ_4/λ_2, the values of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ at T_{NI} vary. $\lambda_4 = 0$ $(a = 0)$ corresponds to the Maier-Saupe theory. The values of the heat of transition and the isothermal compressibility obtained from all these mean field theories are considerably greater than the experimental values. This discrepancy arises because short range order effects between neighbouring molecules are not taken into account in the mean field theories. A crude way of including near neighbour correlations is to assume that clusters of 2-3 molecules act as independent units (Maier and Saupe, 1960; Chandrasekhar and Madhusudana, 1973).

The short range order effects are also observed in the isotropic phase. For instance, the magnetic and electric birefringence (Δn_M and Δn_E) of the isotropic phase exhibit strong anomalies as the temperature is lowered to T_{NI}. Foex (1933) observed many years ago that the magnetic birefringence exhibits a dependence of $(T - T^*)^{-1}$, where T^* is a temperature below T_{NI}. de Gennes (1971) has proposed a phenomenological description of these pretransition effects on the basis of the Landau theory (1969) of phase transitions. The excess free energy of the nematic phase can be written as

$$F = \frac{a_o}{2}(T - T^*)\, S^2 - \frac{B}{3} S^3 + \frac{C}{4} S^4 + \dots \qquad (8)$$

T^* here is recognized as the hypothetical second order transition point. For $B > 0$, it predicts a first order phase transition. T^* is given by

$$(T_{NI} - T^*) = 2B^2/9a_oC\,.$$

By applying an external magnetic field (H), a weak orientational order can be induced even in the isotropic phase and the resulting magnetic birefringence can be shown to be

$$\Delta n_H = D/a_o(T - T^*)$$

where D which is a function of material properties has a relatively small temperature dependence. Hence Δn_H varies essentially as $(T - T^*)^{-1}$. Experimentally (Stinson and Litster, 1970) this is found to be the case with $(T_{NI} - T^*) \simeq 1$°K.

The electric birefringence is also found to vary essentially as $(T - T^*)^{-1}$ for positively dielectric molecules. Hence for such molecules, Δn_H and Δn_E are expected to behave similarly over a wide range of temperature. Experimentally this is found to be the case (see for example Hatna et al, 1973, 1976). The mean field theories are able to predict the qualitative behaviour of Δn_M and Δn_E as functions of $(T - T^{*})$. For example, the Maier-Saupe free energy of the weakly ordered 'isotropic' phase can be written as

$$\frac{F}{NkT} = \frac{AS^2(T-T^{*})}{2kT^2v^2} - 0.0762\,\frac{A^3S^3}{8k^3T^3v^6} + \frac{0.0122A^4S^4}{16k^4T^4v^8} - \frac{\chi_a H^2 S}{3kT}$$

where $T^{*} = A/5kv^2_{NI}$ and the expansion is restricted to the S^4 term. Putting $A/kT_{NI}v^2_{NI} = 4.5415$, we get $T^{*}/T_{NI} = 0.908$. For paraazoxyanisole (PAA), $(T_{NI} - T^{*}) \sim 40K$ $(T_{NI} = 409°K)$ whereas experimentally $(T_{NI} - T^{*}) \sim 1°K$. This number remains the same even if one assumes that clusters of 2-3 molecules behave as independent units. It is necessary to consider in detail the short range order effects to account for these discrepancies.

2.2 The Bethe cluster models for short range order in nematics

A theory including short range orientational correlations was given by Madhusudana and Chandrasekhar (1973) by adapting the Bethe's cluster model. In the cluster model, each molecule is assumed to be surrounded by s nearest neighbours $(s \geqslant 3)$, no two nearest neighbours being nearest neighbours of each other. It is implied in this method that the molecules essentially lie on a lattice. The interaction of the central molecule with its z nearest neighbours is considered in detail and that of an outer molecule with the rest of the medium is treated in the cam field fashion. Let $E(\cos\theta_{ij})$ be the energy of interaction between the central molecule i and an outer molecule j, where θ_{ij} is the angle between the long axes of the molecules i and j. Let $V(\theta_j)$ be the mean field potential energy of an outer molecule j due to the surrounding medium. At this stage, different approximations are possible and are mentioned below.

a. Chang's consistency condition: Chang (1937) postulated 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. The relative probability of the central molecule which is in the direction (θ_i, φ_i) is given by

$$P^z(\theta_i,\varphi_i) = \left[\iint f(\cos\theta_{ij})g(\theta_j)d(\cos\theta_j)d\varphi_j\right]^z$$

where

$$\begin{aligned} f(\cos\theta_{ij}) &= \exp[-E(\cos\theta_{ij})/kT], \\ g(\theta_j) &= \exp[-V(\theta_j)/kT] \end{aligned} \qquad (10)$$

and the first subscript in θ_{ij} refers to the central molecule. The assumed form of $E(\cos\theta_{ij})$ (and thus $f(\cos\theta_{ij})$) depends only on $\varphi = (\varphi_i - \varphi_j)$, the difference between the azimuthal angles. It can be noted that an integration over φ_i or φ_j is equivalent to an integration over φ and F as defined in equation (10) can be written as $F(\theta_i)$. Now, the probability of finding an <u>outer</u> molecule in the same orientation (θ_i, φ_i) is given by

$$g(\theta_i) \iint F^{z-1}(\theta_1) f(\cos\theta_{1i}) d(\cos\theta_1) d\varphi$$

where (θ_1, φ_1) is the orientation of the central molecule. Hence according to the Chang's approximation we get

$$F^{z}(\theta_i) = g(\theta_i) \iint F^{z-1}(\theta_1) f(\cos\theta_{1i}) d(\cos\theta_1) d\varphi \ . \qquad (11)$$

b. <u>Krieger and James approximation:</u> Krieger and James (1954) generalised the consistency requirement by arguing 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 molecule. The relative probability that the central molecule and one of its nearest neighbours, say 1, are oriented along (θ_i, φ_i) and (θ_1, φ_1) respectively is then

$$\Psi(\theta_i, \varphi_i; \theta_1, \varphi_1) = f(\cos\theta_{i1}) g(\theta_1) F^{z-1}(\theta_i) \ .$$

Since this probability should be the same irrespective of which molecule is regarded as the central one,

$$\Psi(\theta_i,\varphi_i; \theta_j,\varphi_j) = \Psi(\theta_j,\varphi_j; \theta_i,\varphi_i)$$

Since $f(\cos \theta_{ij}) = f(\cos \theta_{ji})$, we get after simplification

$$\frac{g(\theta_i)}{F^{(z-1)}(\theta_i)} = \frac{g(\theta_j)}{F^{(z-1)}(\theta_j)} = \text{constant} \qquad (12)$$

which is the Krieger-James (KJ) consistency condition.

c. Bethe-Peierls-Weiss approximation: The Bethe-Peierls-Weiss (BPW) approximation was used in the case of ferromagnetism (Smart 1966; Strieb et al, 1963) and was adapted by Ypma and Vertogen (1976, 1977) for the description of the nematic phase. In fact this is a weaker approximation compared to the two approximations mentioned above. It states that the average orientation of the central molecule and an outer molecule must be identical. In other words,

$$\frac{1}{D}\int P_{2n}(\cos \theta_i)\, F^{z}(\theta_i)\, d(\cos \theta_i)$$
$$= \frac{1}{D}\iiint P_{2n}(\cos \theta_i) g(\theta_i) f(\cos \theta_{ij})$$
$$\times F^{z-1}(\theta_j) d(\cos \theta_i) d(\cos \theta_j) d\varphi \qquad (13)$$

where $P_{2n}(\cos \theta_i)$ is the $(2n)^{th}$ order Legendre polynomial and

$$D = \int F^2(\theta_i)d(\cos\theta_i) .$$

d. <u>Constant coupling approximation:</u> This is yet another method employed in ferromagnetism and was used by Sheng and Wojtowicz (1976) for the nematic phase. The average orientational order of a molecule is calculated in two ways: (i) by assuming that the molecule is in the <u>mean</u> field of all its z nearest neighbours and (ii) by considering interaction between two neighbouring molecules exactly and replacing the rest of the interactions of this coupled pair by the <u>effective</u> mean field due to (z-1) neighbours on each of them. It is then assumed that (i) and (ii) should give identical results, i.e.,

$$\frac{\int P_2(\cos\theta_i)[g(\theta_i)]^{z/(z-1)}d(\cos\theta_i)}{\int[g(\theta_i)]^{z/(z-1)}d(\cos\theta_i)}$$

$$= \frac{\iiint P_2(\cos\theta_i)f(\cos\theta_{ij})g(\theta_i)g(\theta_j)d(\cos\theta_i)d(\cos\theta_j)d\varphi}{\iiint f(\cos\theta_{ij})g(\theta_i)g(\theta_j)d(\cos\theta_i)d(\cos\theta_j)d\varphi}$$

$$= \frac{\int P_2(\cos\theta_i)F(\theta_i)\,g(\theta_i)d(\cos\theta_i)}{\int F(\theta_i)\,g(\theta_i)\,d(\cos\theta_i)} \qquad (14)$$

which is the constant coupling (CC) approximation. Among all these approximations, the KJ approximation uses the most general consistency condition, since satisfying KJ condition is equivalent to satisfying all the other consistency conditions. This can be analytically tested as follows.

Substituting for $F^{(z-1)}(\theta_1)$ from eq.(12) in eq.(11), we get

$$F^{z}(\theta_i) = g(\theta_i)\iint \frac{g(\theta_1)}{g(\theta_i)}\, F^{z-1}(\theta_i) f(\cos\theta_{1i}) d(\cos\theta_1) d\varphi$$

$$= F^{z-1}(\theta_i)\iint f(\cos\theta_{1i}) g(\theta_1) d(\cos\theta_1) d\varphi \quad .$$

Thus KJ approximation involves the Chang's approximation and hence the BPW approximation also. Further by substituting KJ relation, viz., $F(\theta_i) = [g(\theta_i)/g(\theta_1)]^{1/z-1} \times F(\theta_1)$ in the RHS of equation (14), it can be seen that it is reduced to an identity. Thus the KJ approximation also implies the CC approximation.

Madhusudana and Chandrasekhar (1973) applied the KJ method (eqn. 12) to the nematic phase by taking

$$E(\theta_{ij}) = -B^{*}P_2(\cos\theta_{ij}) \qquad (16)$$

and

$$V(\theta_j) = -B_2P_2(\cos\theta_j). \qquad (17)$$

For $z = 8$, they derived theoretical relations for the electric and magnetic birefringence of the isotropic phase on the basis of the above mentioned model. The calculations showed that $(T_{NI} - T^{*})$ is considerably reduced as compared with the mean field theories. However, as was rightly pointed out by Ypma and Vertogen (1976), equations (16) and (17) do nut satisfy KJ relation, or equivalently, Chang's relation (eq.11) exactly in the ordered phase. The maximum discrepancy is of the order of 2-3% for $z = 8$ near T_{NI} (see fig. 1). In order to derive a mathematically consistent theory, Ypma and Vertogen used the weaker BPW approximation (eq.13). They made calculations for different values of z between 3 and 12 and showed that $(T_{NI}-T^{*})$ as well as the heat of transition come closer to the experimental values for lower values of z. However, as we shall see later, the above method does not satisfy Chang's relations. For $z = 8$ near T_{NI}, tho maximum error in satisfying Chang's condition is 4 - 5%. The discrepancy increases at lower temperatures for a given value of z and moreover it becomes quite pronounced for lower values of z. Further, these authors also obtained the somewhat surprising result that the specific heat change (ΔC_v) at T_{NI} decreases as z decreases, contrary to the predictions of the original Bethe theory [see e.g., Fowler and Guggenheim (1939),

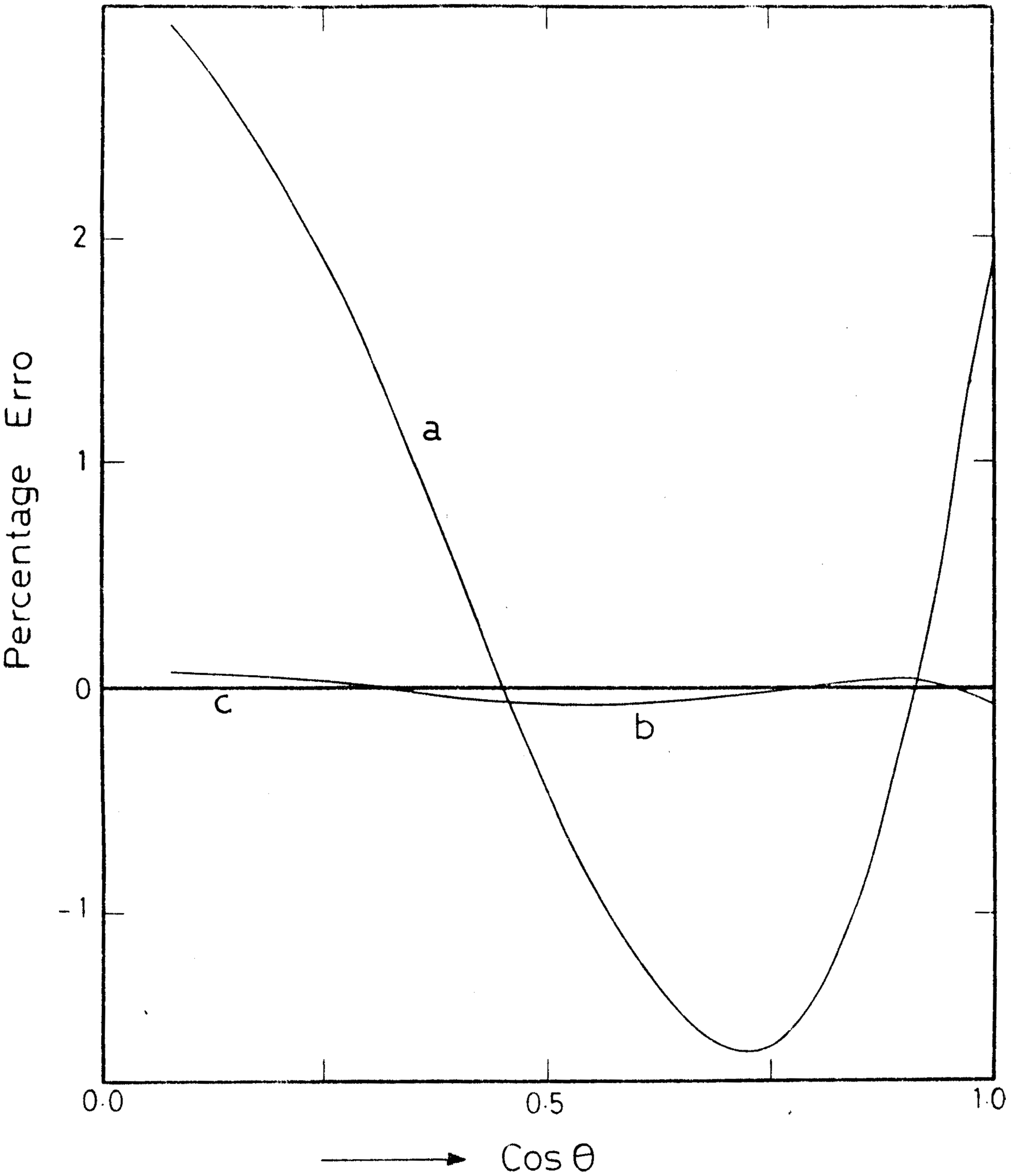


FIG. 1: Percentage error in satisfying Krieger-James approximation for $z = 8$ (a) when terms only up to $P_2(\cos\theta)$ is taken into account, (b) when $P_4(\cos\theta)$ tern is also taken into account, (c) when terms up to $P_{12}(\cos\theta)$ are taken into account.

Münster (1974)]. As we will see in later sections, it is necessary to satisfy the KJ relation as accurately as possible, to achieve a thermodynamically consistent description of the nematic phase. It is interesting to note that in magnetism, the KJ approximation is equivalent to the CC approximation (Savithramma and Madhusudana 1978). In magnetism, the CC approximation is known to be thermodynamically consistent whereas the BPW approximation is not. In the following section, we discuss an extension of the calculations mentioned above such that the KJ relations are satisfied quite accurately.

2.3 Extension of the calculations based on the Bethe cluster method

With the aim of obtaining solutions to satisfy the KJ consistency condition and hence the thermodynamic consistency condition as accurately as possible, we include higher order terms in the potential $V(\theta)$, i.e., we assume

$$V(\theta_i) = -\sum_{n=1}^{m} B_{2n}P_{2n}(\cos\theta_i) \quad . \qquad (18)$$

Retaining terms up to $P_4(\cos\theta)$ as well as $P_{12}(\cos\theta)$, we have made calculations using the KJ and BPW approximations. The two particle distribution functions in these approximations are given by

$$\chi(\theta_i,\varphi_i;\ \theta_j,\varphi_j)_{KJ} = \frac{f(\cos\theta_{ij})g(\theta_i)g(\theta_j)}{\iiint f(\cos\theta_{ij})g(\theta_i)g(\theta_j)d(\cos\theta_i)d(\cos\theta_j)d\varphi} \qquad (19$$

$$\chi(\theta_i,\varphi_i;\theta_j,\varphi_j)_{BPW} = \frac{F^{z-1}(\theta_i)g(\theta_j)f(\cos\theta_{ij})}{\iiint F^{z-1}(\theta_i)g(\theta_j)f(\cos\theta_{ij})d(\cos\theta_i)d(\cos\theta_j)d\varphi} \qquad (20$$

and an average of any angle dependent function x is given by

$$\langle x\rangle = \iiint x\chi(\theta_i,\varphi_i;\ \theta_j,\varphi_j)d(\cos\theta_i)d(\cos\theta_j)d\varphi\ .$$

Three different methods have been used to locate T_{NI}.

1. Two-site cluster approximation: The procedure was originally developed for magnetism (Strieb et al, 1963). It has also been used by Ypma (Thesis, 1977) and Sheng and Wojtowicz (1976). The intermolecular potential which describes the nearest neighbour interaction of the Bethe cluster can be written as

$$H = -B^{*}\sum_{(i,j)} P_2(\vec{a}_i\cdot\vec{a}_j)$$

where $\vec{a}_i$ is a unit vector pointing in the direction of the long axis of the molecule i. Introducing a variational parameter $\bar{S}$ such that

$$\Delta_i = \bar{S} - P_2(a_{iz})$$

where a_{iz} is the projection of $\vec{a}_i$ along the nematic director, the Hamiltonian is written as

$$H = H_o(\Delta_i, \Delta_j, \bar{S}) + \sum_{(i,j)} V_{ij}(\Delta_i \Delta_j, \bar{S})$$

The free energy of the system is given by

$$\begin{aligned} -F/kT &= \ln \mathrm{Tr}[\exp(-H/kT)] \\ &= \ln \left\langle \exp\left(- \sum_{(i,j)} V_{ij}/kT\right) \right\rangle_{H_o} + \ln \mathrm{Tr}[\exp(-H_o/kT)] \end{aligned}$$

where $\langle \ \rangle_{H_o}$ means the average over the distribution function given by

$$\exp(-H_o/kT)/\mathrm{Tr}[\exp(-H_o/kT)] .$$

In the two-site cluster approximation, a pair of interacting nearest neighbour molecules is assumed to be embedded in an effective internal field due to the average alignment of the remaining system, i.e., for a Bethe cluster $\left\langle \prod_{ij} \exp(-V_{ij}/kT) \right\rangle_{H_o}$ is replaced by $\left[\left\langle \exp(-V_{12}/kT) \right\rangle_{H_o}\right]^{\frac{Nz}{2}}$. After this, the free energy is simplified to

$$F/NkT = (z - 1) \ln Z_1 - z/2 \ln Z_{12} \qquad (21)$$

where

$$Z_{12} = \iiint f(\theta_{ij})g(\theta_i)g(\theta_j)d(\cos\theta_i)d(\cos\theta_j)d\varphi$$

$$Z_1 = \int [g(\theta_i)]^{z/(z-1)} d(\cos\theta_i) \ .$$

The detailed derivation of these expressions is given in Appendix I. T_{NI} is obtained by equating the free energy of the nematic phase to that of the isotropic phase. Further the above free energy [eq.(21)] is thermodynamically consistent as it satisfies the following conditions

$$\text{(i)} \quad \left[\frac{\partial F/kT}{\partial(1/kT)}\right]_{\bar{S}} = -\frac{Nz}{2} B^* \langle P_2(\cos\theta_{ij})\rangle = U \qquad (22)$$

where U is the international energy of the system, and

$$\text{(ii)} \quad \left[\frac{\partial F/kT}{\partial \bar{S}}\right]_T = 0 \ .$$

2. <u>Free energy of a Bethe cluster:</u> Ypma and Vertogen (1976) located T_{NI} by calculating the free energy of a Bethe cluster in the following manner. The internal energy of a cluster of z molecules is given by (Ypma and Vertogen, 1976)

$$U_c = z\langle E(\theta_{ij})\rangle + \frac{z}{2}\langle V(\theta_j)\rangle \qquad (23)$$

and the entropy is given by

$$TS_c = z\langle E(\theta_{ij})\rangle + z\langle V(\theta_j)\rangle + kT\ln D$$

where D is defined as in the equation (13). The free energy of a Bethe cluster is then written as

$$\begin{aligned} F_c &= U_c - TS_c \\ &= -\frac{z}{2}\langle V(\theta_j)\rangle - kT \ln D . \end{aligned} \qquad (24)$$

T_{NI} is located by equating the above free energy of the nematic phase to that of the isotropic phase. Further checking for the thermodynamic consistency, it gives the following results

i) $$\left[\frac{\partial F_c/kT}{\partial(1/kT)}\right]_N = z\langle E(\theta_{ij})\rangle + \frac{z}{2}\langle V(\theta_j)\rangle = U_c$$

ii) $$\left[\frac{\partial F_c/kT}{\partial B_2}\right] = 0$$ gives the condition that $B_2 \propto \langle P_2(\cos\theta)\rangle$

when the term with $P_2(\cos\theta)$ only is retained in the potential given in equation (18). By including higher order terms this method gives complicated coupled equations involving $\langle P_2\rangle$, $\langle P_4\rangle$, ... $\langle P_{2m}\rangle$

3. <u>Graphical method</u>: Using the thermodynamic relation (12) (Krieger and James, 1954) it can be shown that the first order nematic-isotropic transition is determined by satisfying the condition

$$\int_{1/T_E}^{1/T_{NI}} U d(1/kT) = \int_{1/T^*}^{1/T_{NI}} U d(1/kT) \qquad (25)$$

where T_E is the temperature corresponding to the point E in figure 2. The internal energy of the system U is plotted as a function of $1/kT$ for the required range of temperatures. The first order transition point (T_{NI}) is obtained by adjusting the shaded areas to have equal values. This ensures that the Helmholtz free energies of the ordered and the disordered phases are the same.

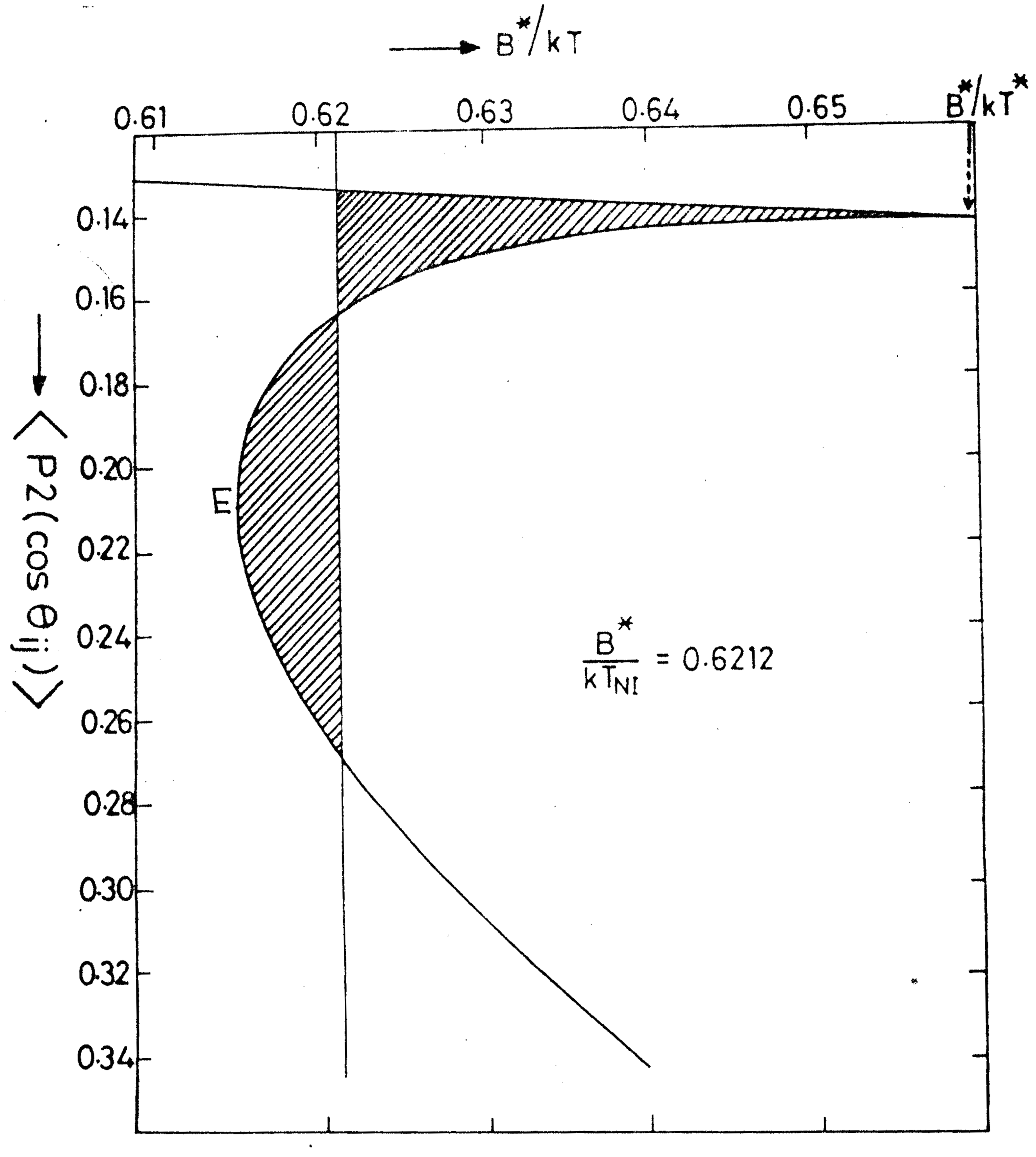
As we discussed earlier, the other point of interest in calculations based on short range effect is the estimation of ($T_{NI} - T^*$). The hypothetical second order transition point T^* can be evaluated in the following manner. T^* is the temperature at which the internal energies of the nematic and the isotropic phases are equal (see figure 2). As the temperature approaches T^*, the coefficients of higher order terms, viz., B_4, B_6 ... B_{12} become negligibly small compared to B_2. Hence one can write

$$g(\theta) \simeq 1 + B_2 P_2(\cos\theta)/kT \qquad (26)$$

In this limit of approximation, it satisfies all the four consistency conditions (i.e., equations 11-14).

Using the KJ approximation, viz.,

$$\frac{g(\theta_1)}{F^{z-1}(\theta_1)} = \frac{g(\theta_j)}{F^{z-1}(\theta_j)}$$



PIG.2: Plot of $\langle P_2(\cos\theta_{ij})\rangle$ ($= -2U/NzB^*$) versus B^*/kT *for* $z = 8$. At the first order transition temperature (T_{NI}) the shaded areas are equal so that the Helmholtz free energy of the ordered and disordered phases are the sane. At the secmd order transition temperature (T^*), $\langle P_2(\cos\theta_{ij})\rangle = 1/(z-1)$.

and substituting equation (26) in eq.(10), we get

$$F(\theta_i) = \iint \exp[B^M P_2(\cos\theta_{ij})/kT] \times [1 + B_2P_2(\cos\theta_j)/kT]\,d(\cos\theta_j)\,d\varphi$$

After some simplification, we get

$$F(\theta_i) = 2\pi D_o[1 + C_2B_2P_2(\cos\theta_i)/kT] \qquad (27)$$

where

$$C_2 = \frac{1}{D_o}\int P_2(\cos\theta)\exp[B^M P_2(\cos\theta)/kT]\,d(\cos\theta)$$

and

$$D_o = \int \exp[B^M P_2(\cos\theta)/kT]\,d(\cos\theta) \quad .$$

Substituting eqns. (26-27) in the KJ relation, we get

$$\frac{1 + \frac{B_2}{(z-1)kT}P_2(\cos\theta_i)}{1 + B_2C_2P_2(\cos\theta_i)/kT} = \frac{1 + \frac{B_2}{(z-1)kT}P_2(\cos\theta_1)}{1 + B_2C_2P_2(\cos\theta_1)/kT}$$

By retaining only the linear terms in B_2, we get

$$C_2 = 1/(z-1) \qquad (28)$$

The other properties that can be obtained from the theory are the specific heat C_v at constant volume and the heat of transition ΔU;

$$C_v = (\partial U/\partial T)_v$$

and

$$\Delta U = U_{nem} - U_{iso} \qquad (29)$$

where U_{nem} is the molar internal energy given by eq.(22) for the nematic phase. The corresponding internal energy of the isotropic phase is obtained by putting $B_{2m} = 0$. The detailed expression for C_v is given in the Appendix II.

2.4 Results and Discussion

All the integrals have been evaluated by using the 32-points Guassian quadrature method. The consistency conditions are solved by a least square fitting procedure. The calculations were carried out in double precision on an IBM-360 computer. For a given value of m and retaining terms up to a given value of m in the long range potential [eq.(18)], we made the calculations as follows:

Assuming a reasonable value of B^*/kT to start with, in the BPW approximation the coefficients B_2, B_4, ... B_{2m} are calculated by equating $\langle P_2\rangle$, $\langle P_4\rangle$, ... $\langle P_{2m}\rangle$ obtained from the one particle distribution function to those got by using the two particle distribution function (see eqn.13). Following Ypma and Vertogen (1976 a,b) T_{NI} is located by using the free energy of a Bethe cluster. The value of B^*/kT_{NI} is obtained by iterating on the assumed value of B^*/kT to equalise the free energies of the nematic and isotropic phases. The procedure is repeated for several values of m by retaining terms up to P_2(cos a), P_4(cos θ) and P_{12}(cos θ) respectively in the long range potential. As we have mentioned already, for m = 1, minimization of free energy of a Bethe cluster demands that $B_2 \propto \langle P_2 \rangle$. However the actual numerical calculations using the BPW ximation do not lead to this result. It turns out that the ratio $B_2 / \langle P_2 \rangle$ steadily decreases (by ~ 0.3%) as the temperature is increased (by ~ 33%) (a similar problem exists in the BPW method in ferromagnetism (Strieb et al, 1963)). When the P_4(cos θ) term is introduced in the long range potential, the equilibrium conditions using the free energy of a Bethe cluster lead to expressions involving both B_2 and B_4 and we no longer get a simple relation like $B_2 \propto \langle P_2 \rangle$.

In the KJ approximation, we made the calculations as follows. For a given value of and B^*/kT, the coefficients B_2, B_4, ... B_{2m} are chosen such that the KJ relations (eq.12) are satisfied as accurately as possible at 32 values of θ ranging from 0 to π/2. By iterating an the assumed value of B^*/kT, the value of B^*/kT_{NI} is determined by equating the two-site cluster free energy of the nematic phase to that of the isotropic phase (eq.21). This procedure is repeated for several values of m and also by retaining terms up to P_2(cos θ), P_4(cos θ) and P_{12}(cos θ) respectively in the long range potential.

For $z = 8$, B^*/kT_{NI} has also been calculated by the graphical method. The short range order parameter $\langle P_2(\cos\theta_{ij})\rangle$ (eq. 19) and hence the internal energy U (eq. 22) of the system are determined for the required range of values of B^*/kT. Plotting U versus B^*/kT, T_{NI} is located by the equal areas method (see figure 2).

We have also estimated the error involved in satisfying the KJ consistency condition for different values of m and z. From eq.(12), the percentage error defined as $6 = 200 \times (RHS-LHS)/(RHS + LHS)$ is calculated and the result for $z = 8$ at T_{NI} as a function of Cos θ Is plotted in figure 1, for m = 1, 2 and 6. For m = 1, the maximum error in satisfying the KJ relation is found to be 2-3%. By including the $P_4(\cos\theta)$ term in the long range potential, the maximum error is reduced to 0.08%. When terms up to $P_{12}(\cos\theta)$ are included, the error is almost zero ($\sim 10^{-9}$) and hence cannot be distinctly shown in figure 1.

Results obtained by retaining terms only up to $P_2(\cos\theta)$ in the long range potential, are given in table I. We can see that the value of $\langle P_2\rangle$ got from the KJ approximation is slightly greater than that got

TABLE I

Results obtained by retaining terms up to $P_2(\cos\theta)$

z	$\langle P_2 \rangle$ at T_{NI}		B^*/kT_{NI}		
	BPW	KJ	BPW[a]	KJ[b]	Graphical method
8	0.424	0.426	0.6248	0.621	0.6212
4	0.413	0.420	1.452	1.437	-

[a] by using the free energy of a Beth. cluster, Eq.(24)

[b] by using the free energy given by the two-site cluster approximation, Eq. (21).

from the BPW approximation for any value of B^*/kT. For $z = 8$, using the KJ approximation the value of B^*/kT_{NI} is found to be the same whether we use two-site cluster free energy or the equal areas method. Compared to this, the BPW approximation (wherein the free energy of a Bethe cluster is used) yields a slightly larger value of B^*/kT_{NI}.

When terms up to $P_4(\cos\theta)$ are included in the long range potential, KJ approximation and BPW approximation give practically the same values of $\langle P_2\rangle$ and $\langle P_4\rangle$. Moreover, the two-site cluster free energy, equal areas method and the free energy of a Bethe cluster will all lead to almost an identical value for B^*/kT_{NI}, showing the importance of including higher order terms in the long range potential for achieving thermodynamic consistency. All the results that are discussed further were obtained by using the KJ approximation.

Including the $P_4(\cos\theta)$ term in the long range potential, various properties of both nematic and isotropic phases like $\langle P_2\rangle$, $\langle P_4\rangle$, $\langle P_2(\cos\theta_{ij})\rangle$, $(T_{NI} - T^*)/T_{NI}$, heat of transition ΔU, specific heat at constant volume (C_v), etc. are calculated for $z = 12$, 8, 4 and 3. The values are listed in table 32 for various values of Or The variation of $\langle P_2\rangle$, $\langle P_4\rangle$, $\langle P_2(\cos\theta_{ij})\rangle$ and C_v of both nematic and isotropic phases are plotted respectively

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TABLE II

Results obtained by retaining term up to $P_4(\cos\theta)$ (our results)

Properties at T_{NI}	$z = 3$	$z = 4$	$z = 8$	$z = 12$	M. F. ($z = \infty$)
B^*/kT	2.254	1.436	0.6212	0.4002	–
B_2/kT	1.0603	1.259	1.6009	1.7155	–
$-B_4/B_2$	0.06714	0.04827	0.02304	0.01509	–
$\langle P_2 \rangle$	0.3437	0.3554	0.3991	0.4103	0.429
$\langle P_4 \rangle$	0.0634	0.0768	0.0990	0.1061	–
ΔU joules/mole	483.8	709.3	1080.0	1185.5	1400
C_v joules/mole °K	77.32	83.47	79.96	71.63	69
ΔC_v joules/mole °K	65.85	80.31	76.90	69.88	69
δ_{max} at T_{NI}	0.38%	0.27%	0.085%	0.04%	–
$(T_{NI} - T^*)/T_{NI}$	0.030	0.040	0.062	0.070	* 0.[illegible]7

in figures 3 to 6. The calculated values of long range order parameters are compared with some of the experimental data in figure 7.

From figures 3 and 4, we see that $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are lower for lower values of z, particularly near The rate of decrease of the long range order parameter with temperature increases for lower values of z. The absolute value of $\langle P_2 \rangle$ and its temperature variation for! z = 3 and 4 are in good agreement with experimental data on common nematic compounds like p-azoxyanisole (PAA) and n-p-methoxybenzylidene-p'-butylaniline (Saupe and Maier, 1961; Chandrasekhar and Madhusudana, 1969; Lee et al, 1974). The calculated values of $\langle P_4 \rangle / \langle P_2 \rangle$ are compared with experimental results given by Kohli et al (1976) for PAA. The agreement between them is again good for a = 3 and 4.

From table 11, we can see that the coefficient B_4 has a negative sign. The ratio $|B_4/B_2|$ increases considerably as the temperature is lowered for a value of z. Further it increases rapidly as z decreases. And the error in satisfying the KJ relation also increases as z decreases (see table II). The ratio $(T_{NI} - T^*)/T_{NI}$ and ΔU decrease from the mean field limit

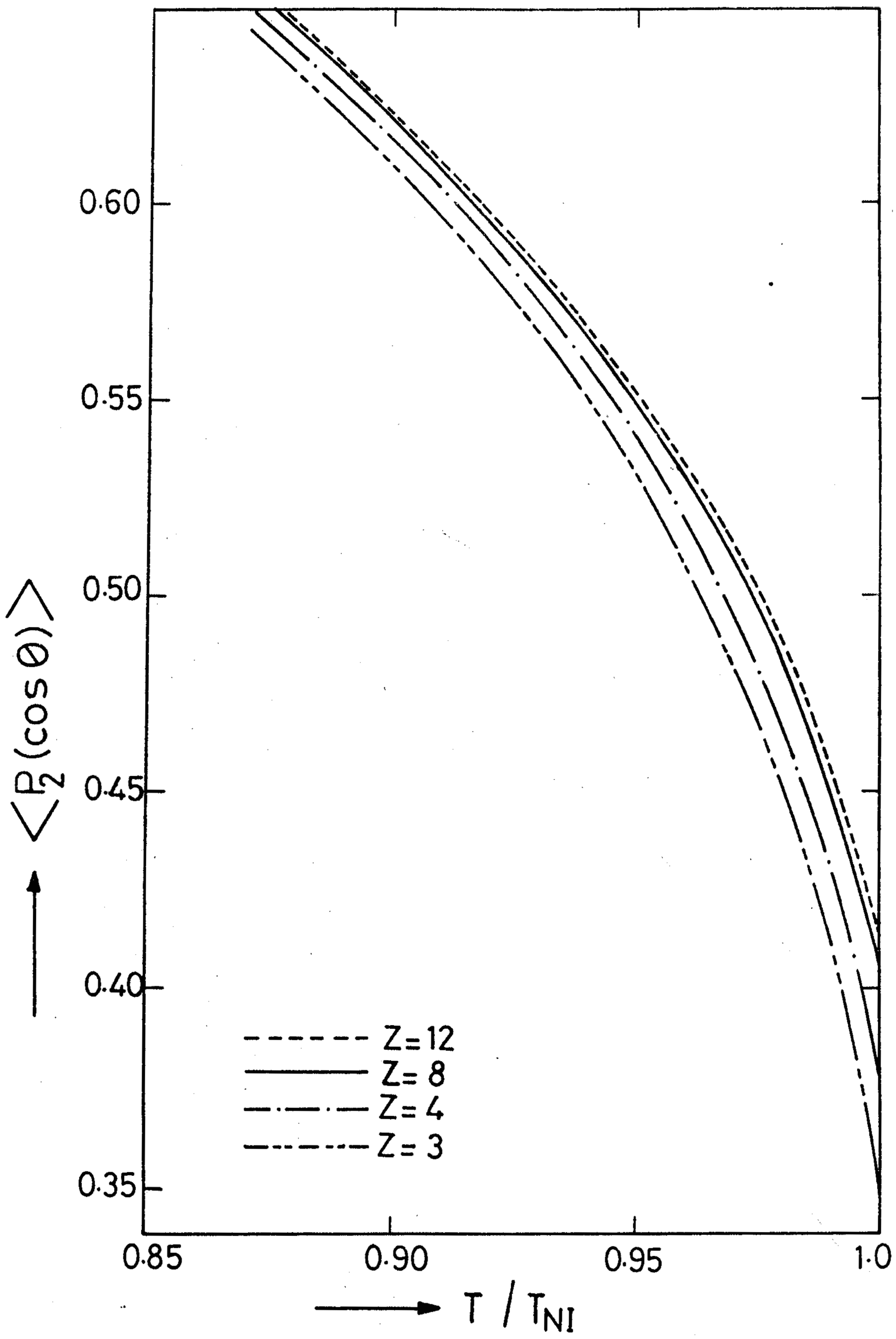

FIG.3: Long range order parameter $\langle P_2 \rangle$ as a function of temperature for different values of z.

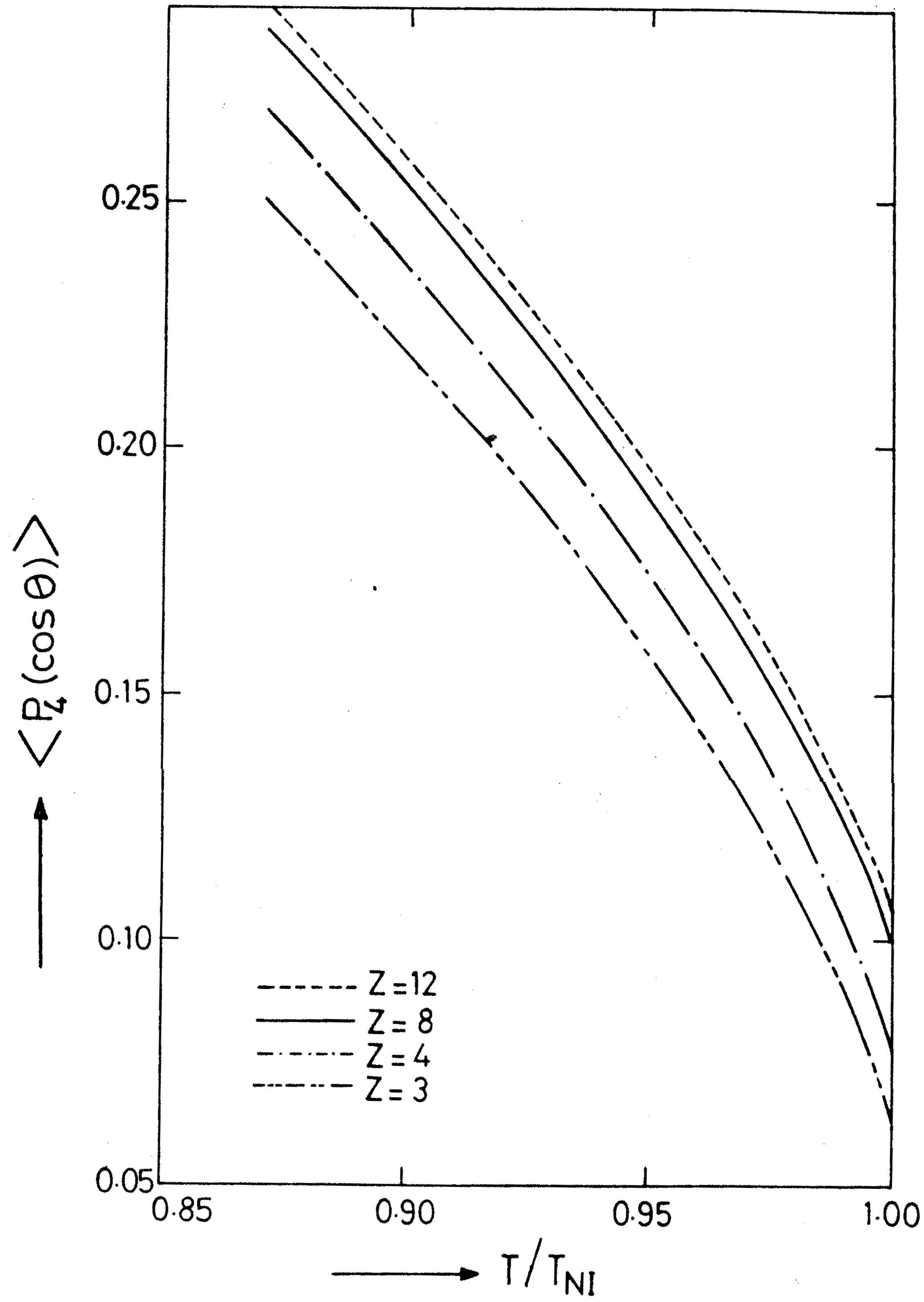

FIG.4: Variation of long range order parameter $\langle P_4 \rangle$ as a function of temperature for different values of z.

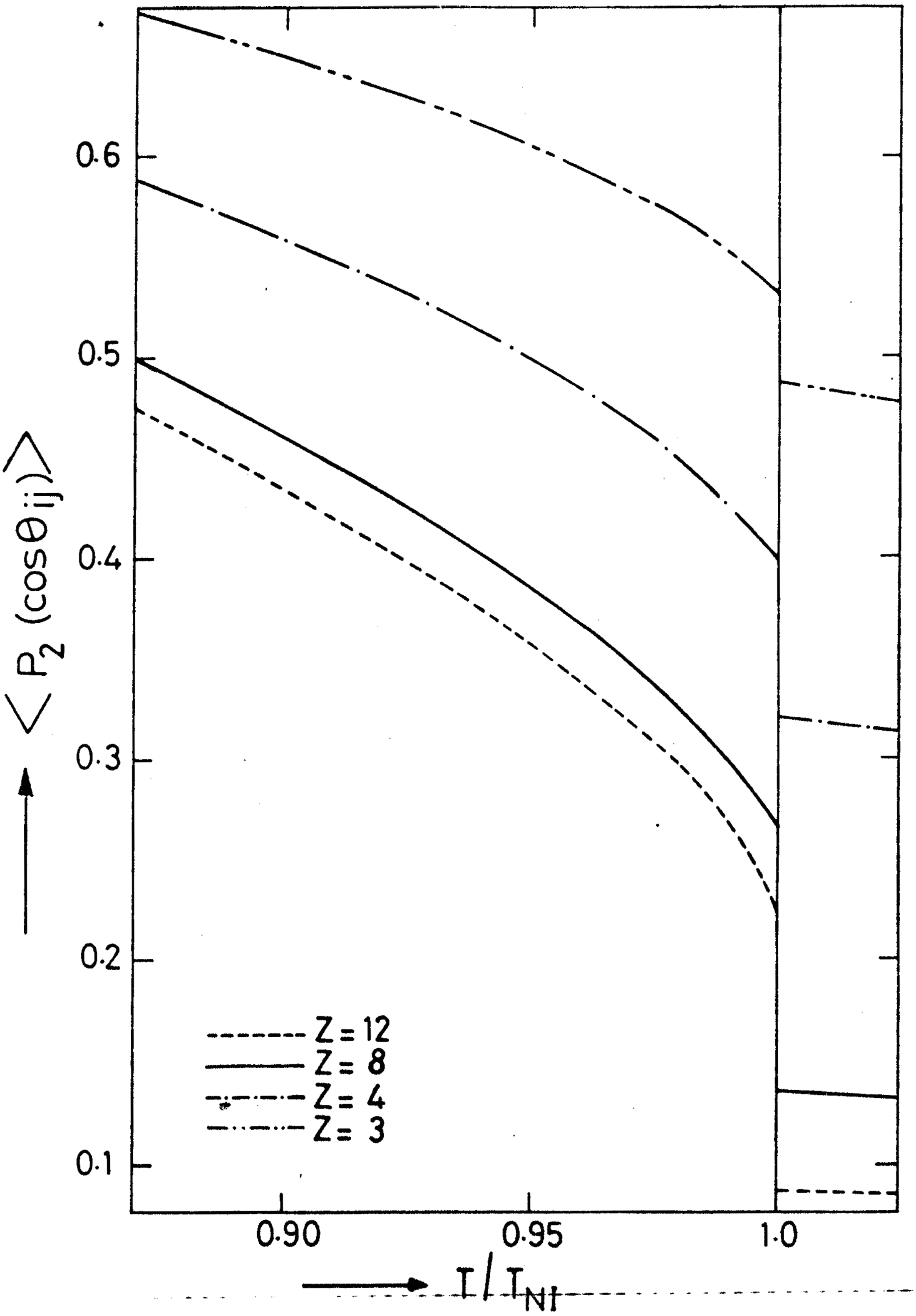

FIG.5: Short range order parameter $\langle P_2(\cos\theta_{ij})\rangle$ as a function of temperature for different values of z.

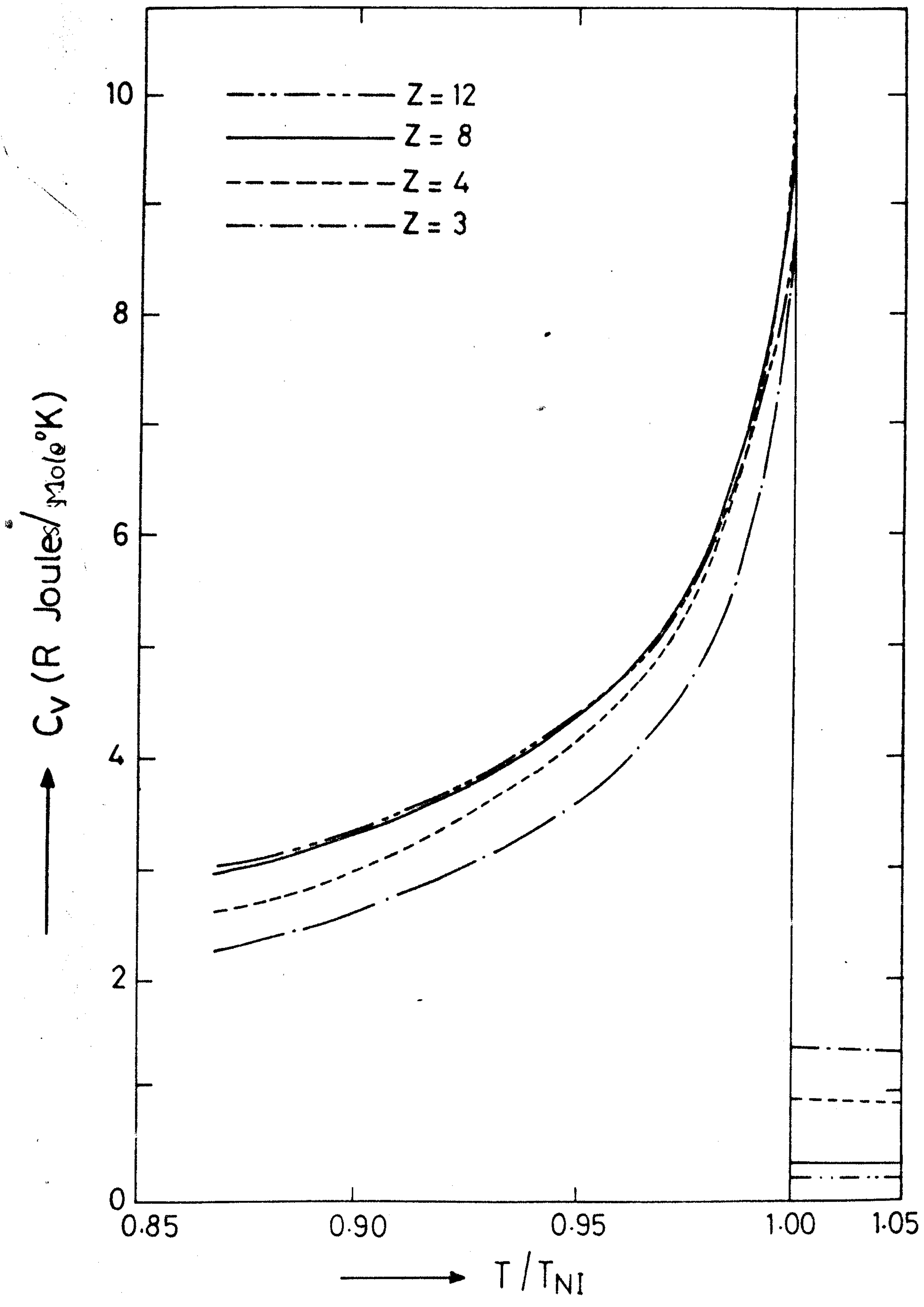

FIG.6: Specific heat at constant volume (C_V) versus T/T_{NI} for different values of z.

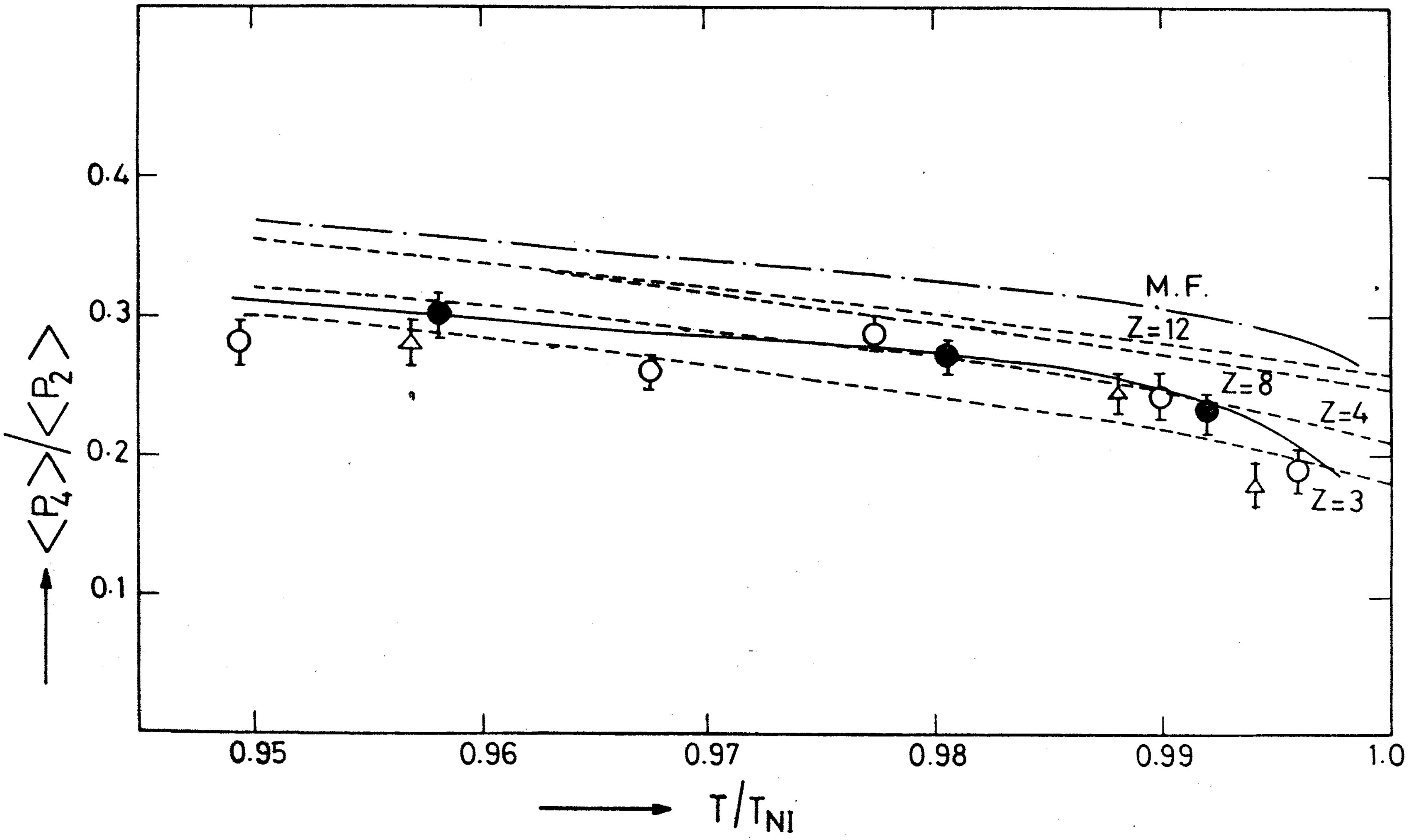

FIG.7: Experimental data on $\langle P_4 \rangle / \langle P_2 \rangle$ in the case of PAA from neutron scattering experiments (Kohli et al, 1976) compared with theory. Continuous line and different kinds of symbols are results of different experiments.

($z = \infty$) to $z = 3$. The value of ΔU decreases slightly but $(T_{NI} - T^*)/T_{NI}$ remains unaltered as the number of terms m increases (see table II).

The results obtained for the specific heat at constant volume when terms up to $P_4(\cos\theta)$ are taken in the long range potential are given in table II for various values of z. By retaining only $P_2(\cos\theta)$ term, Ipma and Vertogen (1976 a, b) found that C_v at all temperatures and ΔC_v at T_{NI} decrease systematically as z decreases from the mean field limit to 3, contrary to the predictions of the original Bethe theory. However, when terms up to $P_4(\cos\theta)$ are included in the long range potential, C_v at T_{NI} as well as ΔC_v increases from the mean field limit to $z = 4$ (see figure 6). But for $z=3$, both these quantities fall below the values for $z = 4$. This trend is true even when the long range potential is extended up to $P_{12}(\cos\theta)$. In any case $z = 3$ is not a realistic number for the cluster model. As the temperature is lowered, the C_v-curves for lower values of z cross over those for higher values of z, so that at sufficiently low temperatures C_v is lower if z is lower. This behaviour is also in agreement with the results of Bethe theory.

We made these calculations some years ago, and after the calculations were completed, we received a preprint from Sheng and Wojtowicz (1976) in which the CC approximation has been applied to calculate the NI transition properties as functions of z. They used the two-site cluster free energy to locate T_{NI} and terms up to $P_4(\cos\theta)$ in the long range potential. Their results at T_{NI} for various values of z are given in table III, and indeed are very close to our results (see table II). They also made calculations by including a $P_4(\cos\theta_{ij})$ term in the short range potential, i.e., by assuming that

$$E(\theta_{ij}) = -B^*[P_2(\cos\theta_{ij}) + \alpha P_4(\cos\theta_{ij})]$$

For z = 8, they calculated the value of $\langle P_2\rangle$ at T_{NI} for $\alpha = \pm 0.2$. It was found that $\alpha = 0.2$ increases the value of $\langle P_2\rangle$ at T_{NI} while $\alpha = -0.2$ decreases it.

When terms up to $P_{12}(\cos\theta)$ are included in the long range potential, all the four mechanical consistency conditions and the three methods of locating T_{NI} lead to the same numerical results for the properties of nematic and isotropic phases. The results are given in table IV. Comparing them with the results obtained by retaining terms up to $P_4(\cos\theta)$ only (table II), only some minor quantitative differences are observed in the transition properties.

TABLE III

Results obtained by retaining terms up to $P_4(\cos\theta)$ (by Sheng and Wojtowicz, 1976)

s	4	6	8	10
$\langle P_2 \rangle$	0.356	0.382	0.399	0.405
$\langle P_2(\cos\theta_{ij}) \rangle_{nem}$	0.393	0.298	0.264	0.245
$\langle P_2(\cos\theta_{ij}) \rangle_{iso}$	0.320	0.189	0.134	0.103
B^*/kT_{NI}	1.437	0.8622	0.6215	0.4866
ΔU joules/mole	703.40	944.5	1072.0	1159.10

TABLE IV

Results obtained by retaining terms up to $P_{12}(\cos\theta)$

Properties at T_{NI}	$z = 4$	$z = 3$
B^M/kT	1.4352	2.2532
B_2/kT	1.2657	1.0541
$B_4/B_2 \times 10$	- 0.6396	- 0.7434
$B_6/B_2 \times 10^2$	0.4959	0.7672
$B_8/B_2 \times 10^3$	- 0.4293	- 0.8784
$B_{10}/B_2 \times 10^4$	0.3889	1.0514
$B_{12}/B_2 \times 10^5$	- 0.3520	- 1.2463
$\langle P_2 \rangle$	0.3664	0.3414
$\langle P_4 \rangle \times 10$	0.7707	0.6248
$\langle P_6 \rangle \times 10$	0.1037	0.0674
$\langle P_8 \rangle \times 10^3$	0.9574	0.4574
$\langle P_{10} \rangle \times 10^4$	0.6363	0.2051
$\langle P_{12} \rangle \times 10^5$	0.6018	0.6320
ΔU joules/mole	680.9	443.1
C_v joules/mole °K	84.63	78.16
ΔC_v joules/mole °K	81.33	73.18
δ_{max} at T_{NI}	~ 0.0	~ 0.0
$(T_{NI} - T^M)/T_{NI}$	0.041	0.031

The order parameter $\langle P_2 \rangle$ goes up by ~ 3% for both z = 3 and 4. ΔU has decreased by ~ 9% for z = 3 and by ~ 4% for z = 4. Further C_v has increased by ~ 1.% for z = 3 and by ~ 1.5% for z = 4. ΔC_v also increases by ~ 10% for z = 3 and by ~ 1.2% for z = 4. The values of B^*/kT_{NI} and $(T_{NI} - T^*)/T_{NI}$ are not affected much.

Recently Lekkerkerker et al (1978) and Haegen et al (1980) have extended the cluster variation model for the NI transition to the three-particle and four-particle cluster approximations in analogy with a method followed in magnetism (Ballensiefen and Wagner, 1965). This is in effect an extension of the CC approximation. In these cases, the results depend on the type of lattice considered. For hexagonal layered (hl) and face centered cubic (fcc) lattices, in which a pair of nearest neighbours have common nearest neighbours, even the three particle cluster approximation leads to an appreciable improvement in the values of $(T_{NI} - T^*)/T_{NI}$ compared to the two particle cluster approximation. On the other hand, for simple cubic (sc) and body centered cubic (bcc) lattices for which nearest neighbours do not have common nearest neighbours, the three-particle approximation did not lead to any improvement over the two-particle cluster approximation. However, when a four-particle cluster approximation was used, there was a considerable reduction in the values of $\langle P_2 \rangle$ and $(T_{NI} - T^*)/T_{NI}$ for all the lattices: the value of $\langle P_2 \rangle$ at T_{NI} has come down to 0.274, 0.347, 0.350 and 0.360 for hl, sc, bcc and fcc respectively. Further $(T_{NI}-T^*)/T_{NI}$ has also reduced to 0.024, 0.038, 0.040 and 0.045 for these lattices respectively.

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