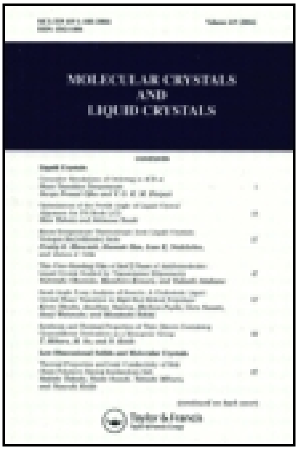

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A Molecular Statistical Calculation of Pretransitional Effects in Nematic Liquid Crystals

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A Molecular Statistical Calculation of Pretransitional Effects in Nematic Liquid Crystals

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A molecular statistical treatment is given of two pretransitional effects in the isotropic phase of nematic liquid crystals, namely of the magnetically induced birefringence and the scattering of light by orientational fluctuations. The calculations are based on the Maier–Saupe model, treated in the Bethe approximation in order to account for short range order. The ratio $(T_c - T_c^*)/T_c$ is improved considerably with respect to the mean field approximation. Also the cluster variation method is applied to the Maier–Saupe model. The differences between the results of the Bethe and the cluster variation method are discussed. A slight modification of the Bethe method produces close agreement with the cluster variation method.

I INTRODUCTION

In the isotropic phase of nematic liquid crystals a number of pretransitional effects have been observed,[1] e.g. the magnetically induced birefringence and the scattering of light by orientational fluctuations. Both the magnetic birefringence and the intensity of the scattered light appear to behave like $(T - T_c^*)^{-1}$, where T_c^* lies slightly below the transition point T_c. These pretransitional phenomena are usually described phenomenologically by a Landau model.[1,2] In a molecular statistical approach the frequently used mean field approximation fails because short range correlations are neglected. Quite apart from pretransitional effects the question can be raised to what extent the inclusion of short range order changes the properties of the nematic–isotropic transition as compared to the mean field results, e.g. the transition temperature T_c, the latent heat, the long range order parameter at T_c etc. In two recent papers[3,4] we presented a method, based on the Bethe–Peierls approximation,[5] which accounts in some way for short range order. The method was applied to the Maier–Saupe model of nematic liquid crystals. In Section 2 we give a brief review of the method and its results.

A different approach can be followed by extending the cluster variation method of magnetism,[6] as was done by Raich *et al.*[7] Unfortunately these authors based their calculations on the symmetry-broken version of the Maier–Saupe model. Consequently, no isotropic phase was found. For this reason we applied the cluster variation method to the rotationally invariant Maier–Saupe interaction, as is described in Section 3. The difference between the results of the Bethe and the cluster variation method are discussed in Section 4. It is shown that a slight modification of the Bethe approximation as used in Refs. 3 and 4 produces close agreement between the two approximations.

2 PRETRANSITIONAL EFFECTS IN THE BETHE APPROXIMATION

2.1 Bethe's approximation

Our starting point is an interaction energy between two neighbouring molecules i and j of the following form:

$$E_{ij} = -J(\mathbf{a}_i \cdot \mathbf{a}_j)^2 \tag{2.1}$$

where $\mathbf{a}_i$ and $\mathbf{a}_j$ are unit vectors pointing in the direction of the long axis of the molecules. This interaction is nothing but the rotationally invariant form of the well-known Maier–Saupe interaction,[8] which is symmetry-broken. Next, we consider a small cluster of $\gamma + 1$ molecules, consisting of a central molecule with orientation $\mathbf{a}_0$ and its γ nearest neighbours with orientations $\mathbf{a}_i$ $(i = 1, \ldots, \gamma)$, forming the outer shell. It is assumed that these nearest neighbours are not nearest neighbours of each other. The weight of a given configuration of the cluster is given by

$$P(\mathbf{a}_0; \mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_\gamma) = \frac{1}{Z} \prod_{i=1}^{\gamma} z(\mathbf{a}_i) \exp[\beta J(\mathbf{a}_0 \cdot \mathbf{a}_i)^2] \tag{2.2}$$

where $\beta = 1/kT$ and Z is a normalization constant. In this expression $z(\mathbf{a}_i)$ accounts for the influence of the remaining system on molecule i. The interaction with the remaining system is simply considered to be an effective field, acting only on the outer shell molecules. So we can write

$$z(\mathbf{a}_i) = \exp[\beta h S(\mathbf{a}_i)] \tag{2.3}$$

with

$$S(\mathbf{a}) = \tfrac{3}{2}a_z^2 - \tfrac{1}{2} \tag{2.4}$$

The strength h of the effective field is determined by the condition that the average orientation of the central molecule should be the same as the average orientation of its neighbours, i.e.

$$\langle S(\mathbf{a}_0)\rangle = \langle S(\mathbf{a}_1)\rangle \tag{2.5}$$

The thermal averages, denoted by $\langle\quad\rangle$, have to be evaluated with the distribution of orientations, given in (2.2). Equation (2.5) forms an implicit equation for h, which is solved numerically. If this equation allows for more than one solution, the free energy selects the correct one, corresponding to thermodynamic equilibrium. The Helmholtz free energy of the cluster is evaluated from its definition $F = U - TS$. The entropy of the cluster is given by:

$$S = -k\int d\mathbf{a}_0 \int d\mathbf{a}_1 \ldots\ldots d\mathbf{a}_\gamma\, P(\mathbf{a}_0; \mathbf{a}_1, \ldots, \mathbf{a}_\gamma)\ln P(\mathbf{a}_0; \mathbf{a}_1, \ldots, \mathbf{a}_\gamma) \tag{2.6}$$

The internal energy of the cluster equals

$$U = -\gamma J\langle(\mathbf{a}_0\cdot\mathbf{a}_1)^2\rangle - \tfrac{1}{2}\gamma h\langle S(\mathbf{a}_1)\rangle \tag{2.7}$$

where the last term represents the contribution of the internal field, which has to be distributed equally among the outer shell molecules and the surroundings of the cluster. This procedure yields for the free energy of the cluster

$$F = -\frac{1}{\beta}\ln Z + \tfrac{1}{2}\gamma h\langle S(\mathbf{a}_1)\rangle \tag{2.8}$$

with

$$Z = \int d\mathbf{a}_0\left[\int d\mathbf{a}_1\, z(\mathbf{a}_1)\exp[\beta J(\mathbf{a}_0\cdot\mathbf{a}_1)^2]\right]^\gamma \tag{2.9}$$

We note here that this form of the free energy, which is derived in close analogy with the mean field approximation, is open to question (see Section 4).

As a result a first order phase transition is found between the isotropic phase ($h = 0$) and the nematic phase ($h > 0$), provided the number of nearest neighbours γ is at least three. In Table I we compare the transition temperatures and the corresponding long range order S_c with the results of the mean

TABLE I

Transition temperature $\beta_c J$ and corresponding long range order S_c for the Bethe and the mean field (MF) approximation for various number of nearest neighbours γ.

γ	$(\beta_c J)_{\text{Bethe}}$	$(\beta_c J)_{\text{MF}}$	$(S_c)_{\text{Bethe}}$	$(S_c)_{\text{MF}}$
2	—	3.406	—	0.429
3	3.447	2.271	0.405	0.429
4	2.178	1.703	0.413	0.429
6	1.302	1.135	0.421	0.429
8	0.937	0.851	0.424	0.429
12	0.603	0.568	0.427	0.429

field approximation of Maier and Saupe. The variation of the order parameter with the number of nearest neighbours is remarkably small in Bethe's approximation. The latent heat of the transition[3] is reduced with respect to the value of the mean field approximation giving closer agreement with experiment. This reduction is most pronounced for a small number of nearest neighbours. Likewise the specific heat curve is improved with respect to the mean field result.[3]

2.2 Magnetic birefringence

When an external magnetic field is applied to the isotropic phase of a nematic, the anisotropic molecules will be slightly aligned, producing a birefringence Δn which can be calculated from the dielectric tensor ε_{ij}. It is easy to show[1] that for $S \ll 1$:

$$\Delta n = \frac{1}{2} \frac{\Delta\varepsilon}{\sqrt{\bar{\varepsilon}}} S \tag{2.10}$$

In this expression $\Delta\varepsilon$ denotes the anisotropy and $\bar{\varepsilon}$ an arithmetic mean of the dielectric constant in the completely aligned material. The induced long range order

$$S = \tfrac{3}{2}\langle a_z^2 \rangle - \tfrac{1}{2} \tag{2.11}$$

was calculated by De Gennes[2] and Stinson and Litster[1] from a Landau model. We derived it[4] from the microscopic Maier–Saupe model and related it to the short range order parameter, defined as

$$\sigma = \tfrac{3}{2}\langle(\mathbf{a}_0 \cdot \mathbf{a}_1)^2\rangle - \tfrac{1}{2} \tag{2.12}$$

With the aid of (2.10) we found for the Cotton-Mouton coefficient:

$$\frac{\Delta n}{H^2} = \frac{\Delta\varepsilon\Delta\chi}{6kT\sqrt{\bar{\varepsilon}}}\langle S^2(\mathbf{a}_0)\rangle\frac{1+\sigma}{1-(\gamma-1)\sigma} \tag{2.13}$$

where $\Delta\chi$ is the anisotropy of the molecular susceptibility. The reciprocal of this coefficient appeared to behave as

$$\frac{H^2}{\Delta n} = C(T - T_c^*), \tag{2.14}$$

in qualitative agreement with experimental results.[1] Table II shows the ratio $(T_c - T_c^*)/T_c$ and an estimate of the coefficient C for MBBA. Also the calculated mean field results and the experimental values are given.

TABLE II

The ratio $(T_c - T_c^*)/T_c$ and the coefficient C for MBBA, as defined in (2.14), for various numbers of nearest neighbours in the Bethe approximation, and compared with the experimental and the mean field (MF) results.

γ	$(T_c - T_c^*)/T_c$	$C(10^{12}\mathrm{G}^2/{}^\circ\mathrm{K})$
3	0.011	43
4	0.029	58
6	0.047	66
8	0.057	69
12	0.067	71
MF	0.092	74
Exp.[a]	0.003	45

[a] See Ref. 1.

2.3 Light scattering

The scattering of light in the isotropic phase is much smaller than in the nematic phase. Just above T_c, however, there will be a sizeable scattering intensity due to orientational fluctuations. Experimentally,[1] two intensities have been measured with polarizations parallel and perpendicular to the polarization of the incident light. They are given by

$$I_{\parallel} = \frac{N}{\lambda^4}\sum_i \langle Q_{zz}^0 Q_{zz}^i\rangle \tag{2.15a}$$

$$I_{\perp} = \frac{N}{\lambda^4}\sum_i \langle Q_{xz}^0 Q_{xz}^i\rangle \tag{2.15b}$$

where λ denotes the wavelength of the incident light and $Q_{\alpha\beta}$ is the anisotropic part of the molecular polarizability tensor $\boldsymbol{\alpha}$:

$$Q_{\alpha\beta} = \Delta\alpha(a_\alpha a_\beta - \tfrac{1}{3}\delta_{\alpha\beta}), \tag{2.16}$$

a_α denoting a component of the molecular orientation $\mathbf{a}$. $Q^0_{\alpha\beta}$ belongs to a particular molecule, while the index i runs over all the other molecules of the sample. The intensities can be related to the short range order σ, giving[4]

$$I_\| = \frac{4}{45}\frac{N(\Delta\alpha)^2}{\lambda^4}\frac{\gamma\sigma}{1-(\gamma-1)\sigma} \tag{2.17}$$

$$I_\perp = \tfrac{3}{4}I_\| \tag{2.18}$$

Both quantities appear to behave as $(T - T_c^*)^{-1}$ where T_c^* is the same as that found for the magnetic birefringence (see Table II).

3 THE CLUSTER VARIATION METHOD

In this Section we apply the cluster variation method[6] to the rotationally invariant interaction (2.1). Raich *et al.*[7] used the symmetry-broken interaction

$$E_{ij} = -JS(\mathbf{a}_i)S(\mathbf{a}_j) \tag{3.1}$$

with

$$S(\mathbf{a}_i) = \tfrac{3}{2}a_{iz}^2 - \tfrac{1}{2} \tag{3.2}$$

and did not find a nematic–isotropic phase transition. This is not surprising because this interaction cannot produce an isotropic phase, except in the mean field approximation. In terms of the interaction (2.1) the model is described by the Hamiltonian

$$H = -J\sum_{\langle ij\rangle}(\mathbf{a}_i\cdot\mathbf{a}_j)^2 \tag{3.3}$$

where the summation is over all pairs of neighbouring molecules. Next H is divided into an unperturbed part H_0 and a perturbation term V by introducing an expansion parameter

$$\Delta_i = \bar{S} - S(\mathbf{a}_i). \tag{3.4}$$

$\bar{S}$ is a variational parameter, whose best value will be determined by minimizing the free energy. With the help of the relations

$$\begin{aligned} a_{ix}^2 &= \tfrac{1}{2}(1 - a_{iz}^2) + \tfrac{1}{2}(a_{ix}^2 - a_{iy}^2),\\ a_{iy}^2 &= \tfrac{1}{2}(1 - a_{iz}^2) - \tfrac{1}{2}(a_{ix}^2 - a_{iy}^2), \end{aligned} \tag{3.5}$$

holding for a unit vector $\mathbf{a}_i$, we devide $(\mathbf{a}_i \cdot \mathbf{a}_j)^2$ into leading terms and small terms in the following way

$$(\mathbf{a}_i \cdot \mathbf{a}_j)^2 = \tfrac{1}{3} + \tfrac{2}{3}S(\mathbf{a}_i)S(\mathbf{a}_j) + W_{ij} \tag{3.6}$$

with

$$\begin{aligned} W_{ij} = {} & \tfrac{1}{2}(a_{ix}^2 - a_{iy}^2)(a_{jx}^2 - a_{jy}^2) + 2a_{ix}a_{iy}a_{jx}a_{jy} \\ & + 2a_{ix}a_{iz}a_{jx}a_{jz} + 2a_{iy}a_{iz}a_{jy}a_{jz}. \end{aligned} \tag{3.7}$$

Because W_{ij} contains products of two terms, which both fluctuate around zero, W_{ij} will presumably be small. With the help of (3.4) we can rewrite H as

$$H = -J\sum_{\langle ij\rangle}[\tfrac{1}{3} + \tfrac{2}{3}(\bar{S} - \Delta_i)(\bar{S} - \Delta_j) + W_{ij}] \tag{3.8}$$

and choose the unperturbed Hamiltonian to be linear in Δ_i and Δ_j:

$$H_0 = -J\sum_{\langle ij\rangle}[\tfrac{1}{3} - \tfrac{2}{3}\bar{S}(\Delta_i + \Delta_j) + \tfrac{2}{3}\bar{S}^2] \tag{3.9}$$

The perturbation term reads

$$V = -J\sum_{\langle ij\rangle}(\tfrac{2}{3}\Delta_i\Delta_j + W_{ij}) \equiv \sum_{\langle ij\rangle} V_{ij} \tag{3.10}$$

The free energy F is written in the following way:

$$\begin{aligned} -\beta F &= \ln Tr[\exp(-\beta H)] \\ &= \ln \frac{Tr[\exp(-\beta H_0 - \beta V)]}{Tr[\exp(-\beta H_0)]} + \ln Tr[\exp(-\beta H_0)] \\ &= \ln\langle\exp(-\beta V)\rangle_{H_0} + \ln Tr[\exp(-\beta H_0)] \end{aligned} \tag{3.11}$$

The second term is easily evaluated and gives

$$-\beta F_0 \equiv \ln Tr[\exp(-\beta H_0)] = -\tfrac{1}{6}N\gamma\beta J(2\bar{S}^2 - 1) + N \ln Z_1 \tag{3.12}$$

with

$$Z_1 = \int d\mathbf{a}\, \exp[\tfrac{2}{3}\gamma\beta J\bar{S}S(\mathbf{a})] \tag{3.13}$$

with γ denoting the number of nearest neighbours.

If the first term in (3.11) is neglected and the remaining free energy F_0 is minimized with respect to $\bar{S}$, we have

$$\bar{S} = \langle S(\mathbf{a})\rangle_{Z_1} \tag{3.14}$$

The thermal average $\langle\quad\rangle_{Z_1}$ has to be evaluated with the distribution function

$$P(\mathbf{a}) = \frac{1}{Z_1}[\exp \tfrac{2}{3}\gamma\beta J\bar{S}S(\mathbf{a})] \tag{3.15}$$

The zero-order free energy F_0 thus simply leads to the mean field approximation, as used by Maier and Saupe.[8] The two-site cluster approximation consists in nothing but a replacement of

$$\langle \exp(-\beta V) \rangle_{H_0} = \left\langle \prod_{\langle ij \rangle} \exp(-\beta V_{ij}) \right\rangle_{H_0} \tag{3.16}$$

by

$$\prod_{\langle ij \rangle} \langle \exp(-\beta V_{ij}) \rangle_{H_0} = [\langle \exp(-\beta V_{12}) \rangle_{H_0}]^{1/2N\gamma} \tag{3.17}$$

After this simplification the evaluation of the free energy is straightforward, giving

$$-\beta F = \tfrac{1}{2} N\gamma \ln Z_{12} - N(\gamma - 1) \ln Z_1 \tag{3.18}$$

with

$$Z_{12} = \int d\mathbf{a}_1 \int d\mathbf{a}_2 \exp[\beta J(\mathbf{a}_1 \cdot \mathbf{a}_2)^2 + \tfrac{2}{3}(\gamma - 1)\beta J \bar{S}(S(\mathbf{a}_1) + S(\mathbf{a}_2))] \tag{3.19}$$

Minimization of F with respect to variations of $\bar{S}$ yields

$$\tfrac{1}{2}\langle S(\mathbf{a}_1) + S(\mathbf{a}_2) \rangle_{Z_{12}} = \langle S(\mathbf{a}_1) \rangle_{Z_1} \tag{3.20}$$

The thermal average $\langle \quad \rangle_{Z_{12}}$ in the left hand side is evaluated with the distribution function

$$P(\mathbf{a}_1; \mathbf{a}_2) = \frac{1}{Z_{12}} \exp[\beta J(\mathbf{a}_1 \cdot \mathbf{a}_2)^2 + \tfrac{2}{3}(\gamma - 1)\beta J \bar{S}(S(\mathbf{a}_1) + S(\mathbf{a}_2))], \tag{3.21}$$

the right hand side with the distribution (3.15). Equation (3.20), which is an implicit equation for $\bar{S}$, expresses a kind of translational invariance: the average orientation of a molecule inside the cluster is the same as the average orientation of a molecule that is subjected only to the internal field $\bar{S}$ outside the cluster. It should be noted that $\bar{S} \neq \langle S(\mathbf{a}) \rangle$. As a result a first order phase transition is found between the nematic and the isotropic phase. Table III shows the transition temperature, the long range order S_c at T_c and the ratio $(T_c - T_c^*)/T_c$. The rather strong variation of S_c with the number of nearest neighbours is remarkable.

The expectation value $\langle \exp(-\beta V) \rangle_{H_0}$ in (3.16) can also be decoupled in the following way:

$$\left\langle \prod_{\langle ij \rangle} \exp(-\beta V_{ij}) \right\rangle_{H_0} \simeq \prod_{i=1}^{N/2} \left\langle \exp\left(-\beta \sum_{j=1}^{\gamma} V_{ij} \right) \right\rangle_{H_0}, \tag{3.22}$$

where j runs over the nearest neighbours of molecule i, which are assumed not to be nearest neighbours of each other. The free energy of this Bethe-type cluster approximation reads

$$-\beta F = \tfrac{1}{2} N \ln Z - N(\gamma - 1) \ln Z_1 \tag{3.23}$$

TABLE III

Transition temperature $\beta_c J$, corresponding long range order S_c and the ratio $(T_c - T_c^*)/T_c$ for various numbers of nearest neighbours γ in the two-site cluster approximation.

γ	$\beta_c J$	S_c	$(T_c - T_c^*)/T_c$
3	3.387	0.320	0.028
4	2.155	0.358	0.040
6	1.294	0.387	0.054
8	0.932	0.399	0.063
12	0.600	0.410	0.071

where Z_1 is defined in (3.13) and Z is identical to the expression (2.9) of the Bethe approximation if we set

$$h = \tfrac{2}{3}(\gamma - 1)J\bar{S} \tag{3.24}$$

If we require this free energy to be minimal with respect to $\bar{S}$ the consistency relation reads

$$\langle S(\mathbf{a}_1)\rangle_Z = \langle S(\mathbf{a})\rangle_{Z_1} \tag{3.25}$$

The left hand side, which has to be evaluated with the distribution (2.2) of the Bethe approximation, measures the average orientation of an outer shell molecule of a Bethe cluster, while the right hand side gives the average of a molecule that is only subjected to the internal field $\bar{S}$ outside the cluster. It should be noted that the consistency relation within the Bethe approximation (2.5) requires translational invariance within the cluster. In Table IV we give the results for this Bethe-type cluster approximation.

TABLE IV

Transition temperatures $\beta_c J$, corresponding long range order S_c and the ratio $(T_c - T_c^*)/T_c$ for various numbers of nearest neighbours γ in the Bethe-type cluster approximation, as defined in (3.22).

γ	$\beta_c J$	S_c	$(T_c - T_c^*)/T_c$
3	3.385	0.328	0.029
4	2.154	0.362	0.040
6	1.293	0.388	0.054
8	0.932	0.399	0.063
12	0.600	0.410	0.071

4 DISCUSSION

In the preceding Section we studied the influence of short range order on the nematic–isotropic transition in the Maier–Saupe model. We made use of the Bethe approximation and cluster variation methods. These approximations are identical in the isotropic phase, i.e. they give the same value of T_c^*, connected with the pretransitional phenomena. The pretransitional phenomena, namely the magnetically induced birefringence and the scattering of light by orientational fluctuations, are qualitatively well described in these approximations. Quantitative agreement with experimental results is not too bad for a small number of nearest neighbours γ and gets worse with increasing γ. It should be realized, however, that the correlation between the orientations of the molecules are heavily underestimated in both approximations. The two-site cluster approximation (TSC) only takes into account correlations between a pair of neighbouring molecules; a similar reduction of correlations takes place in the Bethe approximation because it is assumed that nearest neighbours of a molecule are not nearest neighbours of each other.

Two surprising differences turn up between the Bethe and the cluster variation methods. The ratio $(T_c - T_c^*)/T_c$ is smaller in the former case while the variation of S_c with γ is larger in the latter case. Both deviations can be traced back to the form of the free energy, which differs for the two approximations. In both approximations a small cluster of molecules is embedded in an internal field due to the remaining system; in the TSC-approximation it is a pair of molecules, in the Bethe approximation a cluster consisting of a molecule with all its nearest neighbours. The strength of the internal field acting on the cluster is in the cluster variation method determined from a variational principle, in the Bethe approximation from the requirement of translational invariance. The free energy in the latter case (expression (2.8)) will not necessarily be minimal with respect to variation of the field strength h. This arouses doubts whether the fundamental thermodynamic relationship

$$U = \frac{\partial(\beta F)}{\partial\beta} \tag{4.1}$$

will be satisfied. This equality, if applied to the internal and free energy of a Bethe cluster, given by (2.7) and (2.8) respectively, holds if we differentiate F only explicitly with respect to β, without taking into account the implicit β-dependence of h and $\langle S(\mathbf{a}_1)\rangle$. If the implicit temperature dependence of h and $\langle S(\mathbf{a}_1)\rangle$ is taken into account, the equality (4.1) only holds if

$$\frac{\partial h}{\partial\beta}\langle S(\mathbf{a}_1)\rangle = h\frac{\partial\langle S(\mathbf{a}_1)\rangle}{\partial\beta} \tag{4.2}$$

It appears from the numerical calculations that this relation is not accurately satisfied. It should be remarked here that this difficulty does not appear in the mean field approximation because the selfconsistency relation $S = \langle S(\mathbf{a}) \rangle$ implies $\partial F/\partial S = 0$ and vice versa. As a result the implicit temperature dependence of F with β through S in (4.1) can be ignored. It is also clear that near the transition temperature small variations of the free energy produce rather different results, because the order parameter varies strongly in that region.

The inconsistency can be removed following the procedure of James and Krieger[11] to determine the free energy for the Bethe approximation. Their starting point is the internal energy per particle, which reads

$$U = -\tfrac{1}{2}\gamma J \langle (\mathbf{a}_0 \cdot \mathbf{a}_1)^2 \rangle \tag{4.3}$$

where the thermal average is evaluated using the distribution function (2.2); the effective field h acting on the outer shell molecules of the cluster is determined by

$$\langle S(\mathbf{a}_0) \rangle = \langle S(\mathbf{a}_1) \rangle \tag{4.4}$$

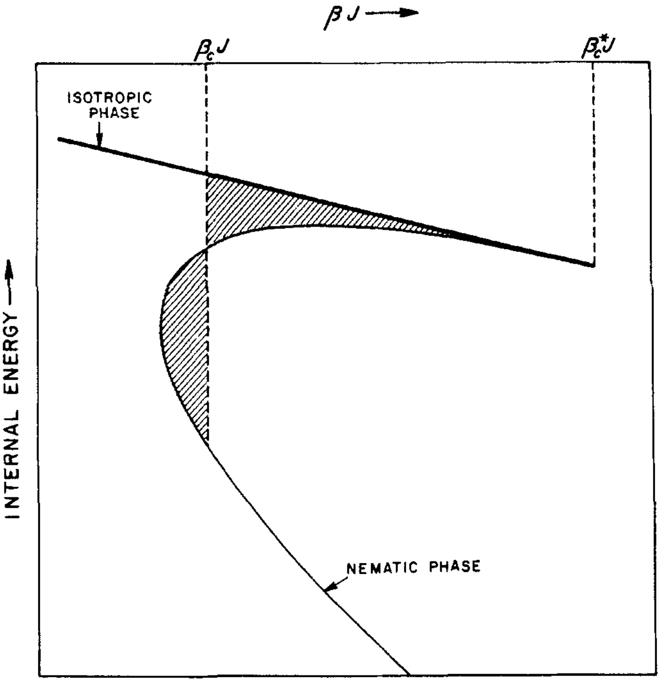

FIGURE 1 The internal energy in the Bethe approximation as a function of the inverse temperature βJ.

The free energy per particle F is determined by integrating the relation:

$$\frac{\partial(\beta F)}{\partial \beta} = U \tag{4.5}$$

with $\beta = 1/kT$. Figure 1 shows qualitatively the behaviour of U as a function of βJ. For each β a disordered solution ($h = 0$) of the consistency relation (4.4) exists. At a certain temperature β_c^*, which also appeared in the calculation of the pretransitional effects, the ordered solution ($h > 0$) branches from the disordered one. The transition from the isotropic to the nematic phase takes place at β_c, where the free energies of the two phases become equal. It can be shown easily[11] that β_c has to be chosen such that the two shaded areas in Figure 1 are equal. Following this approach the improved transition temperatures for the Bethe approximation were calculated. The results are given in Table V. Comparison with the results of the cluster variation methods (Tables III and IV) shows close agreement between the approximations.

TABLE V

Transition temperature $\beta_c J$, corresponding long range order S_c and the ratio $(T_c - T_c^*)/T_c$ for various numbers of nearest neighbours γ in the modified Bethe approximation.

γ	$\beta_c J$	S_c	$(T_c - T_c^*)/T_c$
3	3.391	0.304	0.027
4	2.156	0.354	0.039
6	1.294	0.384	0.054
8	0.932	0.398	0.062
12	0.600	0.409	0.071

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