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Monte Carlo simulations and pair approximations on the phase transition of the restricted orientational lattice model for liquid crystals

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Abstract. The nematic–isotropic phase transition on the sc lattice model of uniaxial molecules is studied by Monte Carlo simulations and the pair approximation method. The interaction between nearest-neighbour sites is assumed to be proportional to $(1 - 3 \cos^2 \theta)/2$ where θ is the angle between the long axes of molecules. The models of restricted orientation with 3, 4, 6 and 10 directions are systematically investigated. The phase transitions are shown to be of first order. Analytical estimations by a pair approximation are in agreement with Monte Carlo results.

1. Introduction

There are many theoretical works on phase transitions of liquid crystals. Flory (1956) has studied the system of hard rods by using the lattice model and found the phase separation caused by the asymmetry of molecules. Onsager's (1942) prediction of first-order transition of the gas of long thin rods has been verified by Zwanzig (1963) by calculating the virial coefficients to seventh order. This transition follows jumps not only in the volume but also in the orientational order parameter of the long axis of molecules.

The model of Maier and Saupe (1959, 1960) is a simple molecular model which allows isotropic and nematic phase transitions. In this model the interactions between the molecules are only dependent on the mutual angles between long axes of molecules. They were successful in describing the first-order phase transition on the basis of the molecular field approximation, but the quantitative agreement was not satisfactory.

McMillan (1972) has extended this model to a smectic A phase. Meyer and McMillan (1974) have also considered soft-core repulsive interaction in addition to dipole–dipole interaction and smectic B and H phases.

In this paper Monte Carlo simulations on the Maier–Saupe model on the sc lattice are performed systematically on the restricted orientational model. Furthermore the analytical studies by means of pair approximation (Takagi 1941, 1942, 1944) are given and compared with the Monte Carlo results in order to check on the reliability of this approximation.

In § 2 we briefly explain our Hamiltonian of the lattice model for liquid crystals and the restricted orientational model. Some of these models turn out to be identical to Potts models. Monte Carlo simulations carried out systematically on these models are

described in § 3. Analytical calculations for the isotropic–nematic phase transition are developed on the basis of the pair approximation in § 4. The final section is devoted to conclusions and discussions.

2. Hamiltonian of lattice model for liquid crystals and restricted orientational models

A lattice model for liquid crystals is a statistical model which may allow a phase transition between isotropic and nematic phases. In this model each molecule is permitted to pivot around its centre of mass which is fixed on the site of some regular lattices.

In this paper we deal with the SC lattice on which uniaxial molecules like a columnar rod or spheroid are located. Nearest neighbouring molecules are submitted to the following Hamiltonian:

$$H = -\varepsilon \sum_{\langle ij \rangle} P_2(\cos \theta_{ij}) = -\varepsilon \sum_{\langle ij \rangle} (3 \cos^2 \theta_{ij} - 1)/2, \quad (2.1)$$

where P_2 is the second Legendre polynomial, θ_{ij} is the angle between long axes of nearest neighbouring molecules. Since we have assumed that the molecule has an inversion centre of symmetry, the interaction never includes the odd-power terms in $\cos \theta_{ij}$ unlike a spin system. From a general point of view the above interaction would not be satisfactory when hardcore interaction becomes important. The above Hamiltonian involves only a leading term of the quadrupole–quadrupole interaction.

Hereafter we will specifically concentrate on restricted orientational models in which the axis of the molecule is restricted to have 3, 4, 6 and 10 directions. They are selected to point to the centre of faces or vertices of some polyhedra as shown in figure 1, so as

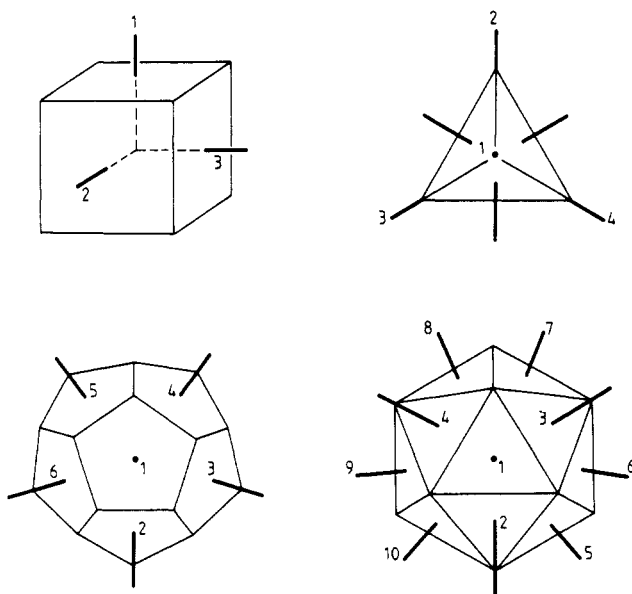


Figure 1. Restricted orientations of the axes of molecules. The 3-, 4-, 6-, and 10-direction models are associated with the centre of faces of hexa-, tetra-, dodeca-, and icosahedra, respectively. Attached figures are the numbering of the states. Directional cosines of the axes are described in Appendix 1.

to make mutually equivalent directions. Their directional cosines are supplemented in Appendix 1. These restrictions allow us to save much Monte Carlo computing time, and also give us an opportunity to investigate systematically how to depend on the number of divisions with these phase transitions.

It is also easily seen from Appendix 1 that these 3-, 4- and 6-direction models are equivalent to 3-, 4- and 6-state Potts (1952) models, respectively, because the interaction energy or its square of directional cosine of angle between the restricted orientations are permitted only to have either of two distinct values of 1 or 0 ($\frac{1}{3}$, $\frac{1}{6}$) for the 3- (4-, 6-) directional model.

3. Monte Carlo simulations

A simple cubic lattice of $8 \times 8 \times 8$ with a periodic boundary condition is employed in our Monte Carlo calculations. Generated uniform random numbers were used:

- (i) when picking up one site randomly from N lattice sites;
- (ii) when selecting randomly a new orientation of axis of the molecule on that site;
- (iii) when deciding whether that orientation will be acceptable or not.

With regards to the occasion (iii) a conventional rule is employed as usual Monte Carlo methods after the above-mentioned procedures have been repeated N times, a final configuration of states is joined to the 'Monte Carlo' ensemble. Every Monte Carlo step (MCS) makes one new member. These ensembles were used to evaluate the thermal averages and fluctuations of physical quantities.

We started with a random orientation at high temperature and gradually cooled the system so as to allow the ordered phase and then gradually heat up to high temperature.

Below a certain temperature the distribution of the orientation is expected to bias uniaxially like a nematic phase. An order parameter associated with this phase is conventionally defined by

$$\xi = \langle (3 \cos^2 \theta_i - 1)/2 \rangle, \quad (3.1)$$

where $\langle \dots \rangle$ means the thermal average, and θ_i is the angle between the axis of the i th molecule and the symmetry axis of the nematic phase. The order parameter will be 1 when molecules are aligned perfectly in parallel, and 0 with random orientation. Furthermore it may become negative up to $-\frac{1}{2}$ where the axes are all aligned in the plane perpendicular to the symmetric axis. We could not know in advance the axis of symmetry in performing the Monte Carlo simulation, so we have to evaluate the following tensor order parameter

$$\hat{\xi} = \begin{bmatrix} \langle x_i^2 \rangle & \langle x_i y_i \rangle & \langle x_i z_i \rangle \\ \langle y_i x_i \rangle & \langle y_i^2 \rangle & \langle y_i z_i \rangle \\ \langle z_i x_i \rangle & \langle z_i y_i \rangle & \langle z_i^2 \rangle \end{bmatrix} \quad (3.2)$$

where $x_i(y_i, z_i)$ is the $x(y, z)$ component of the directional cosine of the i th molecular axis and $\langle \dots \rangle$ indicates the average over all sites as well as Monte Carlo steps. We diagonalise (2.3) to get the three eigenvalues. It is expected that in the nematic phase one eigenvalue λ_1 is different from two other eigenvalues λ_2 and λ_3 which are supposed

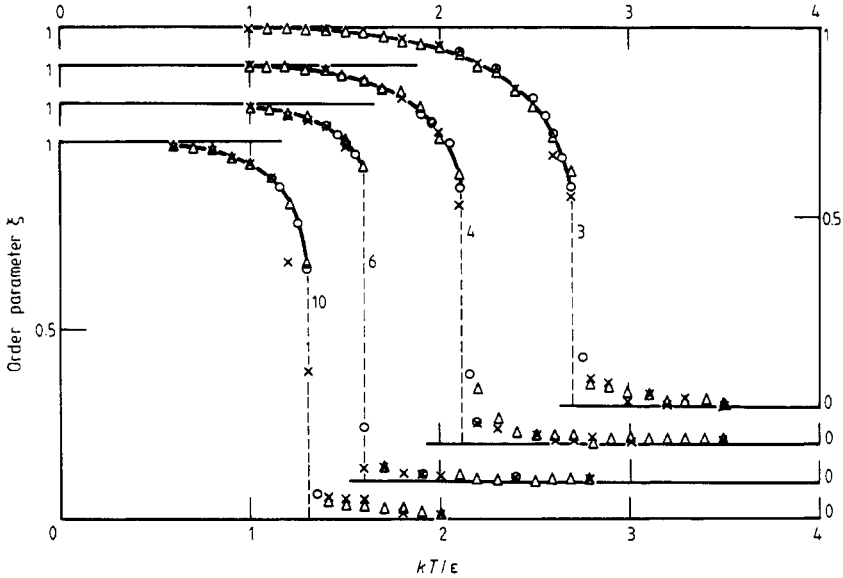


Figure 2. Temperature dependence of order parameter ξ obtained from Monte Carlo simulations on $8 \times 8 \times 8$ lattice. The figures indicate the number of restricted orientation. The marks \times and \triangle indicate the average over 100–300 MCS in the case of descending and increasing temperatures, respectively. Some hysteresis is found between them, open circles (\circ) means the average over between 1500 and 2000 MCS in another Monte Carlo sequence. Dotted lines indicate estimated transition temperatures and full curves are merely to aid the eyes.

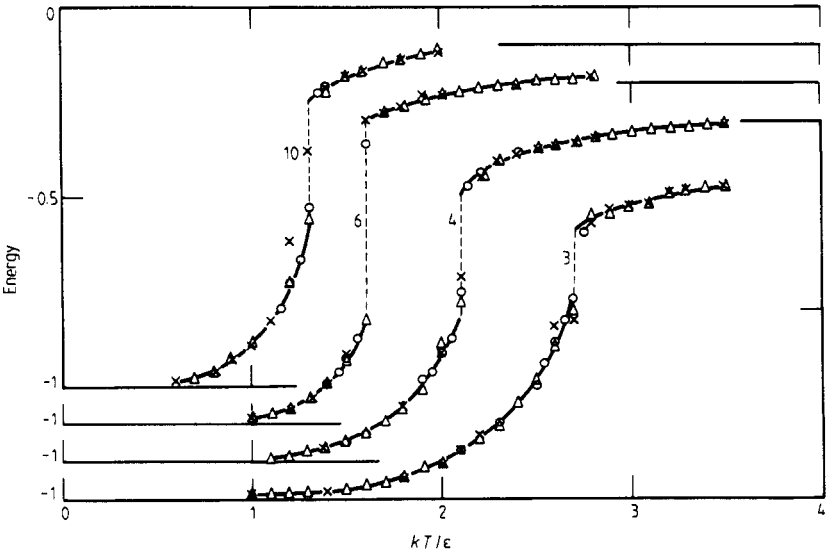


Figure 3. The temperature dependence of energy estimated from Monte Carlo simulations. All symbols are the same as in figure 2.

to be equal. Thus the order parameter can be given by

$$\xi = \lambda_1 - (1/2)(\lambda_2 + \lambda_3) = (3\lambda_1 - 1)/2, \quad (3.4)$$

where we used the relation $\lambda_1 + \lambda_2 + \lambda_3 = 1$.

Our Monte Carlo data for the order parameter and energy are shown in figures 2 and 3, respectively. At the specified temperature, the average covers 200 successive MCS ignoring the first 100 steps. We found some hysteresis between lowering and raising temperatures near the transition temperature. In this region another 2000 MCS are carried out. Recently Blöte and Swendsen (1979) found the small hysteresis in energy through Monte Carlo simulations performed on the three-states Potts model on the sc lattice. Steep changes in the order parameter and energy strongly suggest a first-order phase transition for all the restricted orientational models. The estimated transition temperatures together with the jump of order parameter and energy at this temperature are listed in table 1. The error of the transition temperature is thought to be probably within 2%.

Table 1. Spinodal temperatures T_0 . Transition temperatures T_c and jump of order parameter ξ and energy E at T_c for the cases of 3-, 4-, 6-, and 10-direction. (a) pair-approximation; (b) Monte Carlo simulations.

		3	4	6	10
kT_0/ϵ	(a)	2.680	1.9236	1.3097	0.7050
kT_c/ϵ	(a)	2.819	2.164	1.639	1.332
	(b)	2.71	2.11	1.60	1.30
$\Delta\xi$	(a)	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{1}{2}$	0.653
	(b)	0.55	0.67	0.81	0.66
$\Delta E/\epsilon$	(a)	0.185	0.346	0.526	0.335
	(b)	0.18	0.34	0.53	0.36

Jensen and Mouritsen (1979) and Lasher (1972) have performed similar Monte Carlo calculations on the 3-state Potts model on 30^3 sites and 6-site direction model on 10^3 sites respectively. They found that $kT/\epsilon = 2.73$ and 1.60 for the 3- and 6-direction models respectively. In spite of our small lattice the estimated values for the transition temperatures are found to be in rather good agreement with them.

The transition temperature becomes lower as the restricted number of orientation is increased. This is probably because of the decrease of excitation energy gap from the ground state and also the increase of available numbers of these states. The jumps of the order parameter at the transition temperature increase except for the case of the 10-directional model.

4. Analytic studies on phase transition

In this section we will deal theoretically with the phase transition of the restricted orientational model by the pair approximation method.

As mentioned in § 2 the 3-, 4- and 6-direction models are completely equivalent to 3-, 4-, and 6-state Potts models. The 10-directional model, on the other hand, is no

longer equivalent to any Potts model because they are allowed to have three different values of pair energy as $-\varepsilon$, $-\varepsilon/3$, and $\varepsilon/3$ so we will treat them separately in the following subsections.

4.1. The 3-, 4- and 6-direction models

The Hamiltonian for the corresponding r -state Potts model can be written as

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \delta(\sigma_i, \sigma_j)$$

$$\delta(\sigma_i, \sigma_j) = \begin{cases} 1 & \text{for } \sigma_i = \sigma_j \\ 0 & \text{for } \sigma_i \neq \sigma_j \end{cases} \quad (4.1)$$

where σ_i specifies the state on the i th lattice site by taking values 1 to r , and the interaction parameter J stands for $\frac{2}{3}\varepsilon$, $\frac{4}{3}\varepsilon$, or $\frac{6}{3}\varepsilon$ for the 3-, 4- or 6-direction models, respectively. A constant part of the Hamiltonian was ignored here.

4.1.1. Isotropic phase. The number of molecules occupying the state α is represented by $[\alpha]$ and the number of nearest neighbouring molecule pairs occupying the pair states α and β by $[\alpha, \beta]$. In an isotropic phase all states are assumed to be equally occupied, so we have

$$[\alpha] = Np = N/r \quad (\alpha = 1, 2, \dots, r). \quad (4.2)$$

Similarly we have

$$[\alpha, \alpha] = \frac{1}{2}NZ\lambda, \quad (4.3a)$$

$$[\alpha, \beta] = \frac{1}{2}NZ\mu \quad \text{for } \alpha \neq \beta \quad (4.3b)$$

where z is the number of the nearest neighbour sites and N the number of sites. We have subsidiary relations to which single and pair distribution functions should be submitted

$$2[\alpha, \alpha] + \sum_{\beta \neq \alpha} [\alpha, \beta] = z[\alpha] \quad (\alpha = 1, 2, \dots, r) \quad (4.4)$$

thus follows the relations between the probabilities

$$\lambda + (r-1)\mu/2 = 1/r. \quad (4.5)$$

The energy and entropy for these distributions can be written within the pair approximation (Takagi 1941, 1942, 1944)

$$E = -J \sum_{\alpha} [\alpha, \alpha] \quad (4.6)$$

$$S/k = - \sum_{\alpha} [\alpha, \alpha] \ln \left\{ \frac{[\alpha, \alpha]}{(Nz/2)} \right\} - \sum_{\alpha \neq \beta} [\alpha, \beta] \ln \left\{ \frac{[\alpha, \beta]}{2(Nz/2)} \right\}$$

$$+ (z-1) \sum_{\alpha} [\alpha] \ln \left(\frac{[\alpha]}{N} \right). \quad (4.7)$$

By use of (4.2), (4.3), and (4.5), these expressions reduced to

$$E_0 = -(\frac{1}{2}NzJ)r\lambda \quad (4.8)$$

$$S_0/k = -(\frac{1}{2}Nz) \left\{ \lambda r \ln \lambda + (1-r\lambda) \ln \left[\frac{1-r\lambda}{r(r-1)} \right] \right\} + N(z-1) \ln r. \quad (4.9)$$

Minimising free energy $F_0 = E_0 - TS_0$ with respect to λ , we have explicitly

$$\begin{aligned}\lambda &= \frac{e^K}{r(e^K + r - 1)} \\ \mu &= \frac{2}{r(e^K + r - 1)}\end{aligned}\quad (4.10)$$

with $K = J/kT$.

4.1.2. Ordered phase. Below a certain temperature the distribution of molecular axes may bias uniaxially because of interaction, called a nematic phase. In the Potts models this phase corresponds to dominating distribution for one state, say state '1', than any other states. So the distributions of the states are supposed to be

$$\begin{aligned}[1] &= Np \\ [\alpha] &= Nq \quad \text{for } \alpha = 2, 3, \dots, r\end{aligned}\quad (4.11)$$

where p and q represent the probability of occurrence of that state, thus

$$p + (r - 1)q = 1. \quad (4.12)$$

The order parameter ξ defined in (3.1) is reduced to

$$\xi = p - q = \frac{rp - 1}{r - 1}. \quad (4.13)$$

Here we used the relation $\cos^2 \theta = 1$ for the '1' state and $\cos^2 \theta = 0$ ($\frac{1}{2}, \frac{1}{2}$) for all other states in the 3- (4-, 6-) direction model. When the anisotropic distribution is assumed, the pair-distribution functions should be discriminated between state '1' and other states:

$$\begin{aligned}[1, 1] &= Nz\lambda_1/2 & [\alpha, \alpha] &= Nz\lambda_2/2 \\ [1, \alpha] &= Nz\mu_1/2 & [\alpha, \beta] &= Nz\mu_2/2\end{aligned}\quad (4.14)$$

where $2 < \alpha \leq \beta \leq r$.

From (4.6) and (4.7) we have the expressions of the energy and entropy within the pair approximation

$$E = -(NzJ/2) [\lambda_1 + (r - 1)\lambda_2] \quad (4.15a)$$

$$\begin{aligned}S/k &= -(\frac{1}{2}Nz) [\lambda_1 \ln \lambda_1 + (r - 1) \lambda_2 \ln \lambda_2 \\ &\quad + (r - 1)\mu_1 \ln(\mu_1/2) + \frac{1}{2}(r - 1)(r - 2)\mu_2 \ln(\mu_2/2)] \\ &\quad + N(z - 1) [p \ln p + (r - 1)q \ln q].\end{aligned}\quad (4.15b)$$

The subsidiary conditions in (4.4) yield

$$\lambda_1 + (r - 1)\mu_1/2 = p \quad (4.16a)$$

$$\lambda_2 + \mu_1/2 + (r - 2)\mu_2/2 = q. \quad (4.16b)$$

Minimising the free energy $F = E - TS$ with respect to $p, q, \lambda_1, \lambda_2, \mu_1$, and μ_2 we have

self-consistent coupled equations for these variables:

$$\left. \begin{aligned} p &= e^{K'(A-B)} & q &= e^{K'(A-C)} \\ \lambda_1 &= e^{-K(B-1)} & \lambda_2 &= e^{-K(C-1)} \\ \mu_1 &= 2e^{-K(B+C)/2} & \mu_2 &= 2e^{-KC} \end{aligned} \right\} \quad (4.17)$$

where $K = J/kT$, $K' = (J/2kT)[z/(z-1)]$, and A , B , and C are arbitrary constants to be determined by (4.16).

The Landau expansion of the self-consistent equations for the order parameter ξ is given, eliminating other unknown parameters as λ and μ , by

$$f_2\xi + f_3\xi^2 + f_4\xi^3 + \dots = 0 \quad (4.18)$$

where coefficients f are explicitly given by

$$f_2(K) = r \left[\frac{z-2}{z} e^K + \frac{z-1}{z} (r-2) - (r-1) \right], \quad (4.19)$$

$$\begin{aligned} f_3(K) = \frac{2(z-1)}{z} & \left[\frac{(z-2)r}{2z} e^K + (2r-3) \right. \\ & \left. + (r-2) \left(\frac{1-r}{2} + \frac{2z-5}{4z} \right) \right] \end{aligned} \quad (4.20)$$

where $K = J/kT$. Thus free energy in terms of ξ should be proportional to

$$F(\xi) \propto f_0 + \frac{1}{2}f_2\xi^2 + \frac{1}{6}f_3\xi^3 + \dots \quad (4.21)$$

The spinodal temperature K_0 below which the solution $\xi = 0$ for (4.21) becomes unstable can be given from $f_2(K_0) = 0$ or

$$K_0 = \frac{J}{kT_0} = \ln \left(\frac{z-2+r}{z-2} \right). \quad (4.22)$$

This result perfectly coincides with the temperature at which the susceptibility becomes divergent for the r -state Potts model on the Bethe lattice due to Wang and Wu (1976). If this phase transition is supposed to be of second order, the third coefficient f_3 should vanish at least at the critical temperature. But explicit expression of f_3 at K_0 becomes $f_3(K_0) = (2-r)(1+3r/8)$. So f_3 does not vanish except for $r = 2$. The r -state Potts model is shown to undergo first-order phase transition, if r is more than 2, within the pair approximation.

We found the first-order transition at the temperature which is described by

$$\begin{aligned} K_c &\equiv \frac{J}{kT_c} = \ln[(r-2)/(r'-1)] \\ r' &= (r-1)^{(z-2)/z}. \end{aligned} \quad (4.23)$$

The order parameter jumps from 0 to

$$\xi(T_c) = \Delta\xi = (r-2)/(r-1). \quad (4.24)$$

At this temperature, one can find the coincidence of free energy at T_c between the disordered and ordered phases. The explicit expression for the free-energy at T_c is given by

$$F(T_c, \xi_c) = F_0(T_c) = -\frac{z}{2} + \frac{z}{2} \frac{1}{K_c} \ln \left[\frac{r-2}{r'(r-1)-1} \right] + \frac{1}{K_c} \frac{z-2}{z} \ln r. \quad (4.25)$$

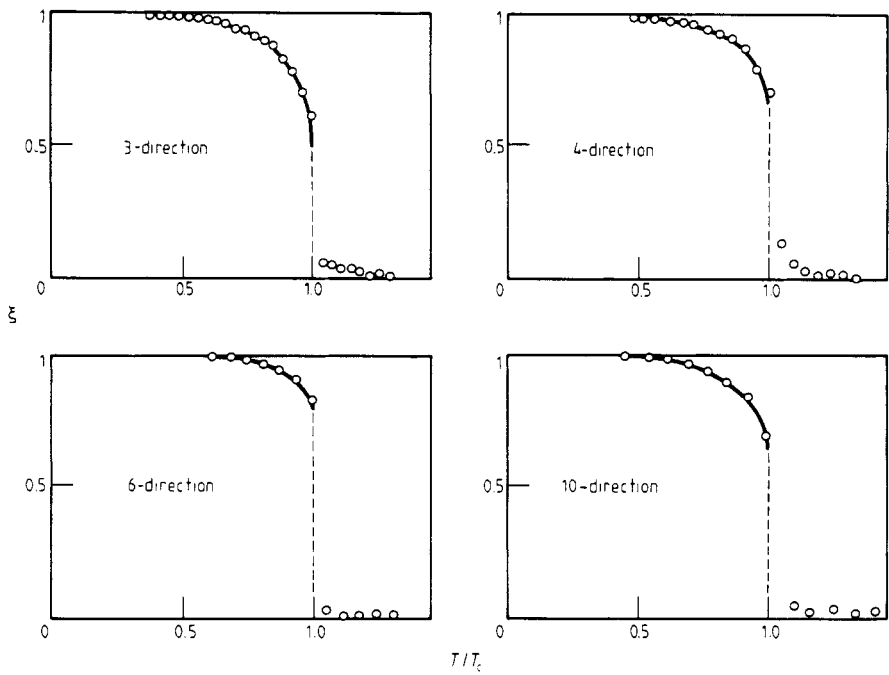


Figure 4. Temperature dependence of order parameter ξ . Full curves are obtained from the present pair approximation and open circles indicate the Monte Carlo calculation for comparison. Temperature is normalised by the phase transition temperature T_c estimated from each method.

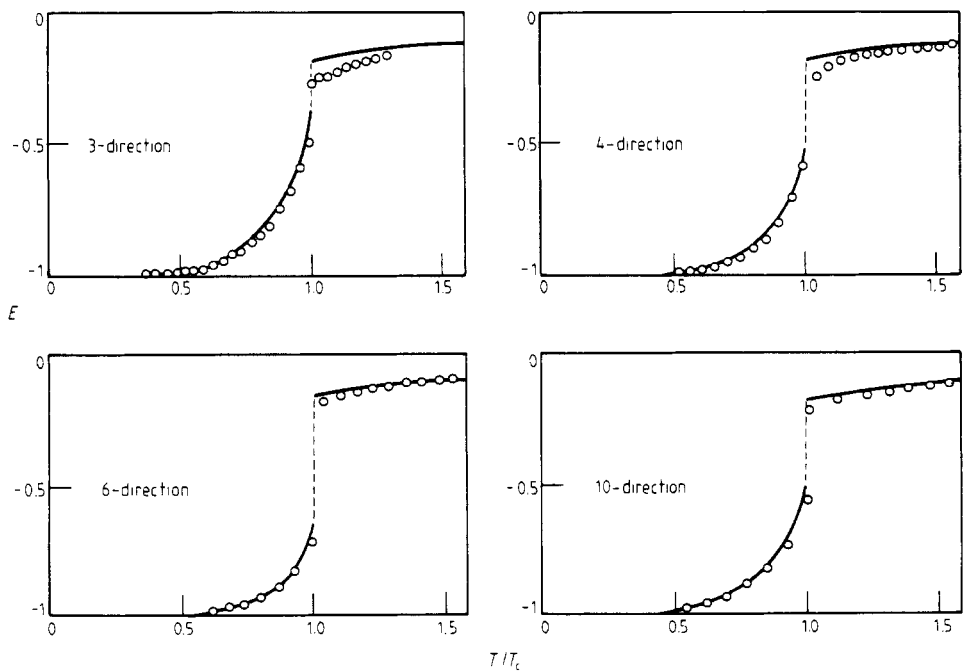


Figure 5. Temperature dependence of energy normalised between -1 and 0 . All symbols are the same as in figure 4.

In table 1 the transition temperatures and the jumps of the order parameters and energy at the transition temperature are comparatively shown. Figures 4 and 5 illustrate the temperature dependence of the order parameter and energy obtained by analytic and Monte Carlo methods, where the temperature is normalised by the transition temperature.

4.2. 10-direction model

The pair approximation similarly to the previous subsection is applicable to this 10-direction model. As mentioned above, the mutual angles between the axes of the molecules allow three different angles. If the axis of molecules occupying the '1' state is assigned to the symmetry axis of the nematic phase, the other states may be divided into two groups, say α and β groups, as according to angles of molecular axis referred to the symmetry axis. The probabilities of appearing of states which belong to the identical groups are assumed to be same. Thus we have

$$\begin{aligned} [1] &= Np \\ [\alpha] &= Nq \quad \text{for } 2 \leq \alpha \leq 4 \\ [\beta] &= Nr \quad \text{for } 5 \leq \beta \leq 10 \end{aligned} \quad (4.26)$$

where naming of the state is indicated in Appendix 1 and these probabilities should be submitted to

$$p + 3q + 6r = 1. \quad (4.27)$$

With the aid of $\cos^2 \theta = 1, \frac{5}{9}$ or $\frac{1}{9}$ for the '1', α or β group, respectively. The order parameter is reduced to

$$\xi = p + q - 2r. \quad (4.28)$$

The pair distribution function $[\alpha, \beta]$, on the other hand, should be dependent on the angles referred to the symmetry axis as well as the mutual angles. The ten distinct kinds of pair distribution functions are obtained as shown in Appendix 2. In the isotropic phase these ten types are reduced to three categories, say A, B, and C, which depend on only the mutual angles. The energy and entropy are given by

$$\begin{aligned} E &= -\left(\frac{Nz\varepsilon}{2}\right) (\lambda_1 + 3\lambda_2 + 6\lambda_3 + \mu_1 + 2\mu_2 + 2\mu_3 - 2\nu_1 - \nu_2 - 4\nu_3 - 3\nu_4) \\ S/k &= \left(\frac{Nz}{2}\right) [\lambda_1 \ln \lambda_1 + 3\lambda_2 \ln \lambda_2 + 6\lambda_3 + 3\mu_1 \ln(\mu_1/2) + 6\mu_2 \ln(\mu_2/2) + 6\mu_3 \ln(\mu_3/2) \\ &\quad + 6\nu_1 \ln(\nu_1/2) + 3\nu_2 \ln(\nu_2/2) + 12\nu_3 \ln(\nu_3/2) + 9\nu_4 \ln(\nu_4/2)]. \end{aligned} \quad (4.29)$$

The subsidiary condition (4.4) reduced to the following set of equations

$$\begin{aligned} 2\lambda_1 + 3\mu_1 + 6\nu_1 &= 2p \\ 2\lambda_2 + \mu_1 + 2\mu_2 + 2\nu_2 + 4\nu_3 &= 2q \\ 2\lambda_3 + \mu_2 + 2\mu_3 + \nu_1 + 2\nu_3 + 3\nu_4 &= 2r. \end{aligned} \quad (4.30)$$

Minimising the free-energy $F = E - TS$ with respect to variables λ , μ and ν , we have the self-consistent equations.

In the isotropic phase the condition $p = q = r = \frac{1}{10}$, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_0$, $\mu_1 = \mu_2 =$

$\mu_3 = \mu_0$ and $\nu_1 = \nu_2 = \nu_3 = \nu_4 = \nu_0$ follows the explicit expression for pair distributions

$$\lambda_0 = \frac{1}{10z_0} e^{4\epsilon/3kT} \quad \mu_0 = \frac{2}{10z_0} e^{2\epsilon/2kT} \quad \nu_0 = \frac{2}{10z_0} \quad (4.31)$$

where $z_0 = e^{4\epsilon/3kT} + 3e^{2\epsilon/3kT} + 6$.

The spinodal temperature for the isotropic phase is given by

$$\epsilon/kT_0 = \frac{2}{3} \ln\left(\frac{8}{3}\right). \quad (4.32)$$

By use of the natural iteration method (Kikuchi 1974) we found out the order parameter from the self-consistent equations. The transition temperatures are determined numerically from the temperature at which the free energies between both phases coincide with each other. The evaluated value $kT_c/\epsilon = 1.332$ should be compared with 1.30 from Monte Carlo simulations. As shown in table 1, the analytically estimated transition temperature is in satisfactory agreement with the Monte Carlo results in this case.

The temperature dependence of the order parameter and energy are shown in figures 4(d) and 5(d). The coincidence is also satisfactory like the Potts models.

Transition temperatures obtained are plotted against the inverse exponent of 1.5 of the number of restricted orientation in figure 6. A linear extrapolation to the infinite division will meet at $kT_c/\epsilon = 1.03$. On the other hand the Monte Carlo simulations for the continuous models due to Lebwohl and Lasher (1972), and Jansen *et al* (1977) gave $kT_c/\epsilon = 1.12$. Thus our prediction is not quite successful.

The differences between the spinodal and the first-order transition temperature increase according to the increase in the number of division as shown in figure 6.

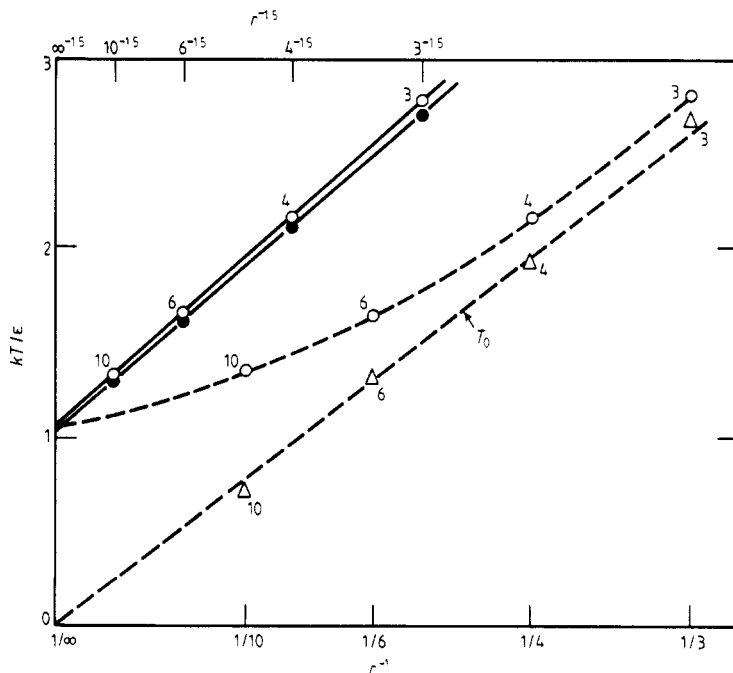


Figure 6. Variations of the phase transition temperatures from Monte Carlo simulation (\bullet) and from the pair-approximation (\circ) and spinodal temperatures (\triangle) against the number of the restricted orientation r . Transition temperatures seem to be proportional to $r^{-1.5}$. Extrapolation to infinite r suggests $kT_c/J = 1.03$ for the continuous rotation model (see text).

5. Conclusions and discussions

We have systematically performed Monte Carlo and analytic calculations on the restricted orientational models on the sc lattice for liquid crystals. When the interaction is of type $P_2(\cos \theta_{ij})$, the phase transition between isotropic and nematic phase was shown to be of first order.

It is clearly seen from table 1 that the pair approximation gives quantitatively good results, not only for the transition temperatures, but also for the temperature dependence of the order parameter and energy even if the temperature were modified a little.

The 3-, 4-, and 6-directional models are shown to be equivalent to 3-, 4-, and 6-state Potts models. The obtained analytic expressions for the first-order transition temperatures and for the jump of order parameter would be within the pair approximation for the first time though.

Wang and Wu (1976), and Southern and Thorpe (1979) found that the susceptibility became divergent at a certain temperature for the Potts model on the Bethe lattice. They assumed a continuous phase transition at that temperature. According to the present pair approximation, on the other hand, this temperature should be identified as a spinodal point and the first-order phase transition occurs at another higher temperature. Since the pair approximation leads to results identical to those obtained from the Bethe lattice in the case of the Ising model, their prediction for the Potts model should be reconsidered.

In the case of a face-centred cubic lattice, the type of phase transition has not yet been determined definitely. Levy and Sudano (1978) have studied the 3-state Potts model by the cluster variation method and concluded that it underwent a first-order phase transition. On the other hand, Yamashita (1979) has predicted the continuous phase transition by use of high-temperature expansions, although each order terms led to first-order phase transitions.

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Appendix 1. Directional cosines of restricted orientations

3-directional model

$$(1) (0, 0, 1) \quad (2) (1, 0, 0) \quad (3) (0, 1, 0).$$

4-directional model

$$(1) (0, 0, 1) \quad (2) (\frac{1}{3}\sqrt{8}, 0, \frac{1}{3}) \\ (3) (-\frac{1}{3}\sqrt{2}, \sqrt{\frac{2}{3}}, \frac{1}{3}) \quad (4) (-\frac{1}{3}\sqrt{2}, -\sqrt{\frac{2}{3}}, \frac{1}{3}).$$

6-directional model

- (1) $(0, 0, 1)$ (2) $(2/\sqrt{5}, 0, 1/\sqrt{5})$
(3) $(\frac{1}{2}(1 - 1/\sqrt{5}), \sqrt{\frac{1}{2}(1 + 1/\sqrt{5})}, 1/\sqrt{5})$
(4) $(-\frac{1}{2}(1 + 1/\sqrt{5}), \sqrt{\frac{1}{2}(1 - 1/\sqrt{5})}, 1/\sqrt{5})$
(5) $(-\frac{1}{2}(1 + 1/\sqrt{5}), -\sqrt{\frac{1}{2}(1 - 1/\sqrt{5})}, 1/\sqrt{5})$
(6) $(\frac{1}{2}(1 - 1/\sqrt{5}), -\sqrt{\frac{1}{2}(1 + 1/\sqrt{5})}, 1/\sqrt{5})$.

10-directional model

- (1) $(0, 0, 1)$ (2) $\frac{1}{3}(2, 0, \sqrt{5})$
(3) $(-1, \sqrt{3}, \sqrt{5})$ (4) $(-1, -\sqrt{3}, \sqrt{5})$
(5) $\frac{1}{3}(\sqrt{5}, \sqrt{3}, 1)$ (6) $(-\frac{1}{6}\sqrt{5} + \frac{1}{2}, \frac{1}{6}(\sqrt{15} + \sqrt{3}), \frac{1}{3})$
(7) $(-\frac{1}{6}\sqrt{5} - \frac{1}{2}, (\frac{1}{6}\sqrt{15} + \sqrt{3}), \frac{1}{3})$ (8) $(-\frac{1}{6}\sqrt{5} - \frac{1}{2}, \frac{1}{6}(-\sqrt{15} + \sqrt{3}), \frac{1}{3})$
(9) $(-\frac{1}{6}\sqrt{5} + \frac{1}{2}, +\frac{1}{6}(\sqrt{15} + \sqrt{3}), \frac{1}{3})$ (10) $\frac{1}{3}(\sqrt{5}, -\sqrt{3}, 1)$.

Appendix 2. Pair distribution functions of 10-dimensional model

Groups $\cos^2 \theta_{ij}$	Typical pairs	Pair distribution function	Probability of occurring
A 1	$(1, 1)$	$[1, 1]$	λ_1
	(α, α)	$[2, 2] [3, 3] [4, 4]$	λ_2
	(β, β)	$\{ [5, 5] [6, 6] [7, 7] [8, 8] [9, 9] [10, 10] \}$	λ_3
B $\frac{2}{3}$	$(1, \alpha)$	$[1, 2] [1, 3] [1, 4]$	μ_1
	(α, β)	$\{ [2, 5] [2, 10] [3, 6] [3, 7] [4, 8] [4, 9] \}$	μ_2
	(β, β')	$\{ [5, 6] [7, 8] [9, 10] [5, 8] [6, 9] [7, 10] \}$	μ_3
C $\frac{1}{3}$	$(1, \beta)$	$\{ [1, 5] [1, 6] [1, 7] [1, 8] [1, 9] [1, 10] \}$	ν_1
	(α, α')	$[2, 3] [2, 4] [3, 4]$	ν_2
	(α, β)	$\{ [2, 6] [2, 7] [2, 8] [2, 9] [3, 5] [3, 8] [3, 9] [3, 10] [4, 5] [4, 6] [4, 7] [4, 10] \}$	ν_3
	(β, β')	$\{ [5, 7] [5, 9] [5, 10] [6, 7] [6, 8] [6, 10] [7, 9] [8, 9] [8, 10] \}$	ν_4

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