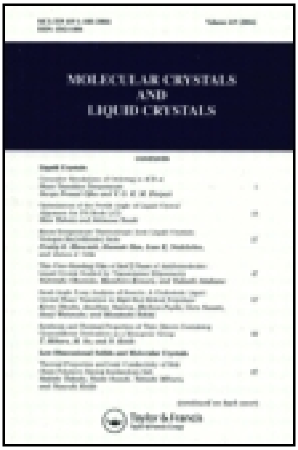

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MOLECULAR THEORETICAL CALCULATIONS FOR TEMPERATURE INDUCED PHASE TRANSITION AND HELIX INVERSION IN SINGLE COMPONENT CHOLESTERIC LIQUID CRYSTALS

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A chiral nematic phase of liquid crystals is studied using both the molecular field theory and the two-particle cluster theory. The interacting chiral molecules (as derived by van der Meer et al.) are placed at the sites of a three-dimensional, simple cubic lattice with orientations confined to two dimensions. The equilibrium pitch, internal energy, second- and fourth-rank order parameters as functions of temperature are calculated, and numerical results are compared with those predicted by the Monte Carlo computer simulation. The fourth-order terms in the interaction potential give rise to temperature-dependent pitch, and a helix inversion takes place in certain temperature. Both the molecular theories show a first order chiral nematic–isotropic phase transition when the fourth-order terms in the interaction potential are included. The two-partcile cluster theory, taking into account short-range correlations between molecules, yields improved values for the temperature dependence of the helical wavevector and of the scaled internal energy compared with the molecular field theory.

Keywords: cholesteric liquid crystal; phase transition; helix inversion; molecular statistical theory; short range correlation

INTRODUCTION

The cholesteric or chiral nematic phase of liquid crystals results in nematic packing of molecules in layers and possesses long-range orientational order with a superimposed twist, i.e., a spatial variation of the director leading to a helical structure. As a consequence, the structure has a screw axis normal to the preferred molecular direction. If we consider a series of planes

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perpendicular to the helix, there is in each plane an orientational order as in the nematic phase. However, the local direction of alignment of the molecules is slightly rotated in adjacent planes. If the director is twisted in a distance r perpendicular to the director through an angle θ, it is related to the helical pitch p by

$$\theta = \frac{2\pi r}{p} \equiv qr, \tag{1}$$

where q corresponds to the helical wavevector. Experimental investigations show that the pitch of a cholesteric varies with temperature. In particular, the phenomenon of a helix inversion induced by temperature variation has attracted much attention. It took place not only in varieties of mixtures [1–4] but also in single-component cholesteric liquid crystals [5–7].

Recently, Memmer and Janssen reported Monte Carlo computer simulation studies of the temperature dependence of the pitch, including the chiral nematic–isotropic phase transition [8] and the temperature-induced helix inversion [9]. The centers of the molecules are fixed on the sites of a three-dimensional simple cubic lattice. Molecular orientations are confined orthogonal to a selected axis chosen to be the Z axis. Only nearest neighbor interactions are taken into account, i.e., each particle interacts with four horizontal neighbors in a plane parallel to the X–Y plane and two vertical neighbors along the Z direction. The magnitude of the orientational order is uniform, but the twist causes the local director to vary linearly with the layer coordinate Z. To describe this variation, we make a helical transformation [10], i.e., the orientation of particle i on layer Z_i is written as

$$\phi_i = Z_i q + \psi_i, \tag{2}$$

Here ϕ_i and ψ_i denote the orientation of particle in the X–Y plane with respect to the laboratory frame and to the local director, respectively.

The pair potential is based up on the electric multipole expansion for cylindrically symmetric chiral molecules given by van der Meer et al. [11]. For particles i and j in the same layer, Z_i and Z_j are identical and the potential is given by

$$V^h(\psi_i, \psi_j) = -J\cos^2(\psi_i - \psi_j) - L\cos^4(\psi_i - \psi_j). \tag{3}$$

This is not so for particles in adjacent layers; for these, Z_i–Z_j is equal to $\pm a$, where a is the lattice constant. The potential is written as

$$\begin{aligned} V^{up}(\psi_i, \psi_j; q) = & -J\cos^2(\psi_i - \psi_j - qa) + K\cos(\psi_i - \psi_j - qa) \\ & \times \sin(\psi_i - \psi_j - qa) - L\cos^4(\psi_i - \psi_j - qa) \\ & + M\cos^3(\psi_i - \psi_j - qa)\sin(\psi_i - \psi_j - qa) \end{aligned} \tag{4}$$

for particle i and particle j in its up layer, and

$$\begin{aligned} V^{down}(\psi_i,\psi_j;q) = &-J\cos^2(\psi_i-\psi_j+qa)-K\cos(\psi_i-\psi_j+qa)\\ &\times\sin(\psi_i-\psi_j+qa)-L\cos^4(\psi_i-\psi_j+qa)\\ &-M\cos^3(\psi_i-\psi_j+qa)\sin(\psi_i-\psi_j+qa) \end{aligned} \tag{5}$$

for particle i and particle j in its down layer. In a molecular statistical calculation, the equilibrium value q_0 can be obtained by minimizing the free energy with respect to q.

In a recent letter [12], we reported the result of this model system with K/J = L/J = M/J = 1, treating by means of the molecular field theory and the two-particle cluster theory. In agreement with the Monte Carlo simulation predictions [8], a temperature dependence of the pitch was obtained by taking into account fourth-order terms, and the chiral nematic–isotropic phase transition appeared to be the first order instead of the second order as in the case of L = M = 0 [10,13]. The aim of this article is to give the course of theoretical treatment in some detail and to deal with the model system with K/J = 2, L/J = 1, and M/J = –2.5, for which there was a temperature-induced helix inversion predicted by the Monte Carlo simulation [9].

MOLECULAR STATISTICAL THEORIES OF THE MODEL SYSTEM

The Molecular Field Approximation

In the molecular field approximation, the free energy of our model system of N molecules is written as [14]

$$\begin{aligned} \beta F = N\Bigg\{ &\int_0^{2\pi} \frac{1}{2}\beta\left[4V^h(\psi_i,\psi_j) + V^{up}(\psi_i,\psi_j;q) + V^{down}(\psi_i,\psi_j;q)\right]\\ &\times g(\psi_i,q)g(\psi_j,q)d\psi_i d\psi_j + \int_0^{2\pi} g(\psi_i,q)\ln g(\psi_i,q)d\psi_i \Bigg\}, \end{aligned} \tag{6}$$

where $\beta \equiv 1/k_B T$. One-body distribution function is given by

$$\begin{aligned} g(\psi_i,q) = \frac{1}{Z}\exp\Bigg\{ -\beta\int_0^{2\pi} &\left[4V^h(\psi_i,\psi_j) + V^{up}(\psi_i,\psi_j;q)\right.\\ &\left. + V^{down}(\psi_i,\psi_j;q)\right] g(\psi_j,q)d\psi_j \Bigg\}, \end{aligned} \tag{7}$$

$$Z = \int_0^{2\pi} \exp\left\{ -\beta \int_0^{2\pi} \left[4V^h(\psi_i, \psi_j) + V^{up}(\psi_i, \psi_j; q) \right.\right.$$
$$\left.\left. + V^{down}(\psi_i, \psi_j; q) \right] g(\psi_j, q) d\psi_j \right\} d\psi_i. \qquad (8)$$

In numerical calculations, the distribution function is determined by an iterative method [15] for a q fixed in advance, whereas the optimum helical wavevector q_0 is obtained by minimizing Eq. (6). Then the orientational order parameters and the internal energy per particle are calculated by

$$\langle P_2 \rangle = \int_0^{2\pi} P_2(\cos\psi_i) g(\psi_i, q_0) d\psi_i, \qquad (9)$$

$$\langle P_4 \rangle = \int_0^{2\pi} P_4(\cos\psi_i) g(\psi_i, q_0) d\psi, \qquad (10)$$

and

$$U/N = \frac{1}{2} \int_0^{2\pi} \left[4V^h(\psi_i, \psi_j) + V^{up}(\psi_i, \psi_j; q_0) + V^{down}(\psi_i, \psi_j; q_0) \right]$$
$$\times g(\psi_i, q_0) g(\psi_j, q_0) d\psi_i \psi_j, \qquad (11)$$

respectively. Here P_m is the Legendre polynomial of rank m.

The Two-particle Cluster Approximation

In the two-particle cluster theory [13], we obtain the equation for one-body distribution function for a given q,

$$g(\psi_j; q) = \frac{\prod_{j=1}^{z} \int_0^{2\pi} \left[g(\psi_j; q) \right]^{1-1/z} \exp[-\beta V^{[ij]}(\psi_i, \psi_j; q)]}{\int_0^{2\pi} \prod_{j=1}^{z} \int_0^{2\pi} \left[g(\psi_{;j}; q) \right]^{1-1/z} \exp[-\beta V^{[ij]}(\psi_i, \psi_j; q)]} \frac{d\psi_j}{d\psi_j d\psi_i}, \qquad (12)$$

where the product $\prod$ ranges over z neighbors of the molecule i. The neighboring molecules are allowed to have different pair potentials $V^{[ij]}(\psi_i, \psi_j; q)$, and it has three forms given by Equations (3), (4), and (5). The free energy depending on the helical wavevector q is given by

$$\begin{aligned}\beta F &= \frac{1}{2} N \ln A \\ &= -\frac{1}{2} N \ln\left\{ \prod_{j=1}^{z} \int_{0}^{2\pi}\int_{0}^{2\pi} \left[g(\psi_i;q)g(\psi_j;q)\right]^{1-1/z} \right. \\ &\qquad \left. \times \exp\left[-\beta V^{[ij]}(\psi_i,\psi_j;q)\right] \; d\psi_i d\psi_j \right\}. \end{aligned} \tag{13}$$

The functional equation of Equation (12) is solved by the iterative method, and the equilibrium value of q is determined by minimizing Equation (13). The order parameters are then calculated by Equations (9) and (10) and the internal energy by the expression based upon $U = \partial(\beta F)/\partial\beta$.

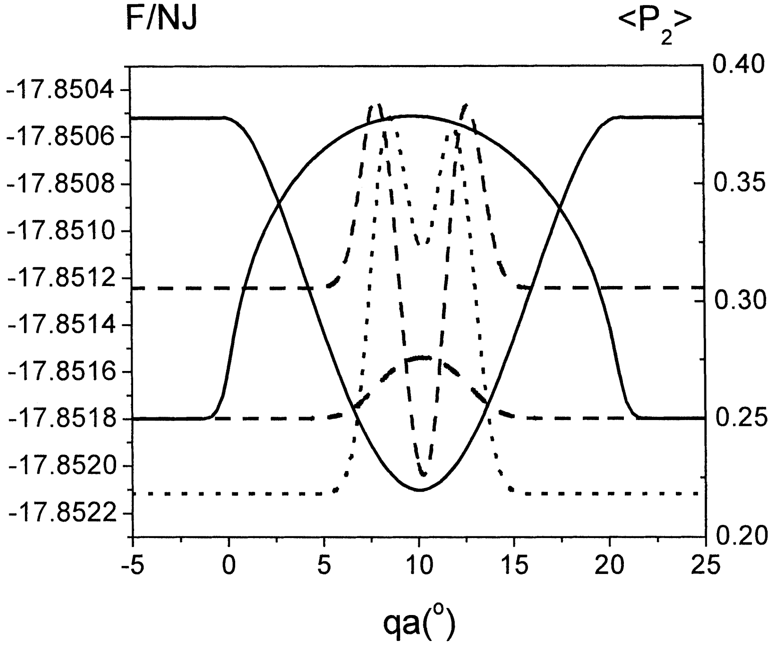

FIGURE 1 Numerical results of molecular field theory: the scaled free energy per particle and the second-rank order parameter as functions of qa, where q is the helical wavevector and a is the lattice constant. Solid line, t = 3.0; dashed line, t = 3.066, which is lower than the transition temperature; dot line, t = 3.068, which is higher than the transition temperature.

NUMERICAL RESULTS

In numerical calculations based upon both the molecular field approximation and the two-particle cluster approximation, we define one-body distribution function g(ψ;q) on the n discrete points which are limited to the domain $0 \leq \psi \leq 2\pi$. In order to link up with integral calculations, we choose the Gaussian point order

$$h(1 - 1/\sqrt{3} + 2k),\ h(1 + 1/\sqrt{3} + 2k)$$

where k = 0, 1, 2, …, n/2 − 1; h = 2π/n, and n = 160 in calculations.

To illustrate our theoretical calculations, we give some results for the molecular field approximation in detail. For a typical value of the scaled temperature t = 3.0 ($t \equiv k_B$ T/J), we calculate q-dependent one-body distribution function g(ψ;q) from Equations (7) and (8), and then we give the scaled free energy per particle and the second-rank order parameter as functions of qa. Results are shown by the solid line in Figure 1. The free energy takes minimum at qa = 10.0°, which is the value representing the equilibrium state of the system, and the order parameter takes the value

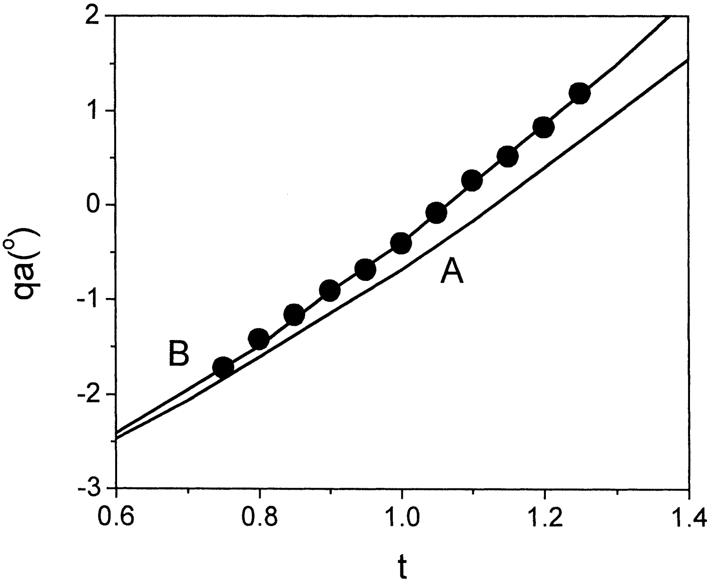

FIGURE 2 The helical wavevector qa as a function of the scale temperature: A, the molecular field theory: B, the two-particle cluster theory; ●, the Monte Carlo simulation [9] for the lattice size 16 × 16 × 16.

$\langle P_2 \rangle = 0.378$ at that point of qa when $g(\psi;q) = 1/2\pi$, i.e., for the isotropic phase of the system, $\langle P_2 \rangle = 1/4$ [8]. For t = 3.066, the free energy takes an absolute minimum at qa = 10.3° (shown by dash line): The system is in the chiral nematic phase. But for t = 3.068, the free energy takes a local minimum that is higher than the value of the isotropic phase (shown by dot line): The system is in the isotropic phase. At this temperature, the curve for the order parameter cannot be distinguished with that at t = 3.066, and it is omitted. A first-order chiral nematic–isotropic phase transition takes place at $t_C = 3.067$ and the order parameter at the transition is $\langle P_2 \rangle_C = 0.273$.

The two-particle cluster approximation leads to the same qualitative behavior for the chiral nematic–isotropic phase transition. The transition temperature predicted by the two-particle cluster theory is at $t_C = 2.527$. For comparison, the value predicted by the Monte Carlo simulation [9] is about 2.20. The order parameter at the transition predicted by the two-particle cluster theory is $\langle P_2 \rangle_C = 0.278$, but this is not estimated in the Monte Carlo simulations [8,9].

The most important characteristic of the chiral nematic phase is the helical wavevector as functions of the scaled temperature. The numerical

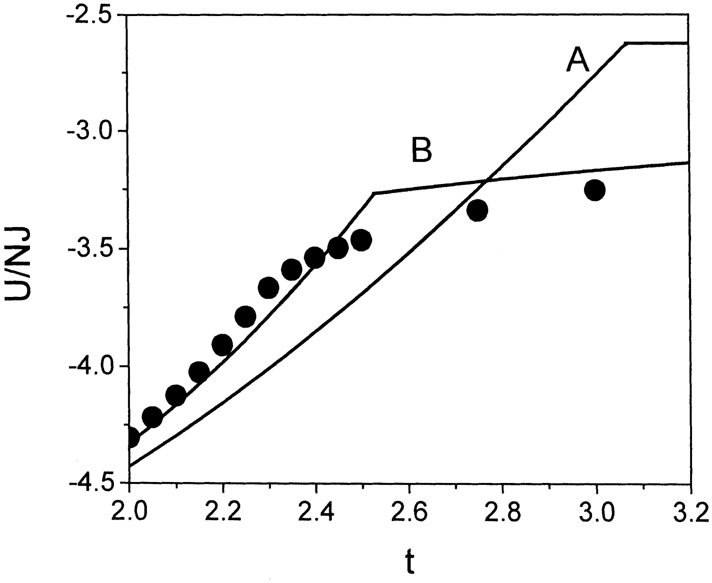

FIGURE 3 The scaled internal energy per particle as a function of the scale temperature: A, the molecular field theory; B, the two-particle cluster theory; ●, the Monte Carlo simulation [9] for the lattice size 16 × 16 × 16.

results neighboring the helix inversion temperature are shown in Figure 2. On the increasing of the temperature, qa increases continuously to zero and changes its sign at a temperature. This temperature was estimated to be t = 1.05 by the Monte Carlo simulation [9]. For comparison, the value predicted by the molecular field theory is t = 1.130, whereas that predicted by the two-particle cluster theory is t = 1.065. The other characteristic quantities of the chiral nematic phase as functions of the scaled temperature, including the scaled internal energy per particle U/NJ, the second- and fourth-rank order parameters are also calculated, and the numerical results are shown in Figures 3–5, respectively.

CONCLUSIONS

In conclusion, we have made an investigation on a lattice model for a chiral nematic phase using both the molecular field theory and the two-particle cluster theory. The interacting chiral molecules (as derived by van der Meer et al.) are placed at the sites of a three-dimensional, simple

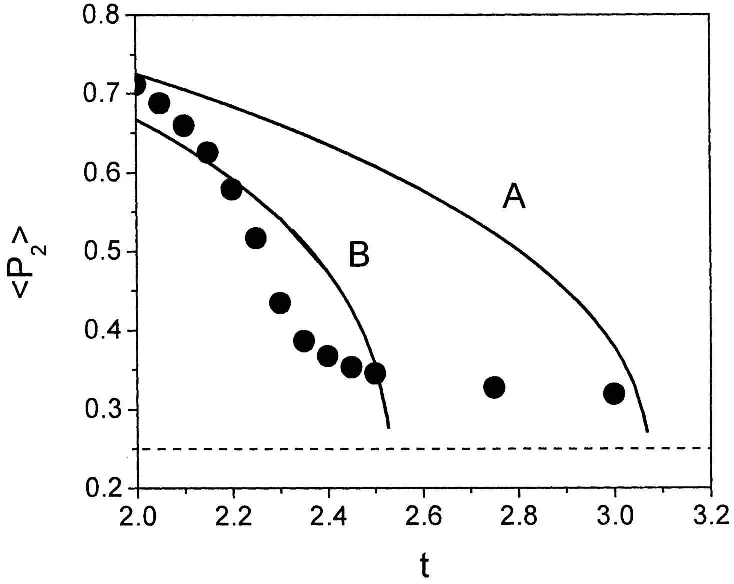

FIGURE 4 The second-rank order parameter as a function of the scale temperature: A, the molecular field theory; B, the two-particle cluster theory; ●, the Monte Carlo simulation [9] for the lattice size 16 × 16 × 16. The dash line gives the value $\langle P_2 \rangle = 1/4$, representing the isotropic phase.

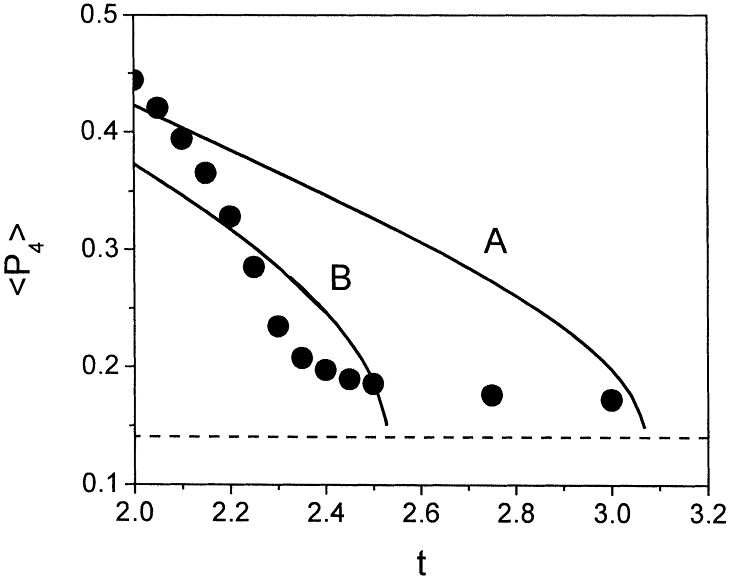

FIGURE 5 The fourth-rank order parameter as a function of the scale temperature: A, the molecular field theory; B, the two-particle cluster theory; ●, the Monte Carlo simulation [9] for the lattice size 16 × 16 × 16. The dash line gives the value $\langle P_4 \rangle = 9/64$, representing the isotropic phase.

cubic lattice with orientations confined to two dimensions. In agreement with the predictions in the Monte Carlo computer simulation, the fourth-order terms in the interaction potential give rise to temperature-dependent pitch, and a helix inversion takes place in certain temperature. Both the molecular field theory and the two-particle cluster theory show a first-order chrial nematic–isotropic phase transition when the fourth-order terms in the interaction potential are included. This phase transition was instead second-order in the system with $L = M = 0$ (i.e., without the higher order interaction terms), for which the temperature-independent pitch of the cholesteric phase was given [10,13]. Finally, the two-particle cluster theory, taking into account short-range correlations between molecules, yields improved values for the temperature dependence of the helical wavevector and of the scaled internal energy compared with the molecular field theory (See Figures 2 and 3). But for the second- and fourth-rank order parameters in the low temperature range, there were obvious discrepancies between the Monte Carlo data and those of both the molecular theories (See Figures 4 and 5). Such discrepancies did not appear in the nematic system [16,17] and a problem was given for further study.

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