Volume 6, Number 9
1004-423X/97/06090671-06

ACTA PHYSICA SINICA
(Overseas Edition)

September, 1997
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A TWO-PARTICLE CLUSTER THEORY FOR UNIAXIAL NEMATIC LIQUID CRYSTALS FORMED BY BIAXIAL MOLECULES

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(Received 3 March 1997)

A two-particle cluster theory is presented to study uniaxial nematic liquid crystals formed by biaxial molecules, which interact with each other via dispersion forces. The equation for the molecular orientational distribution functions in two-particle cluster approximation is obtained and is solved by an iterative method. The temperature dependences of the order parameter and of the internal energy per particle are calculated, and the values of the relevant quantities at the nematic-isotropic phase transition are given. The present theory, by taking into account the short range correlations between molecules, yields improved results compared with the mean field theory.

PACC: 1240E; 6470M

I. INTRODUCTION

Maier and Saupe[1] constructed the mean field theory of nematic liquid crystals based upon anisotropic dispersion forces. They assumed that the constituent molecules possess cylindrical symmetry. Such an assumption is attractive because it simplifies both the experimental analysis and the theoretical treatment. Of course, the molecules forming nematics do not possess $D_{\infty h}$ symmetry, thus the assumption actually means that the effective orientational pair potential is cylindrically symmetric. However, the experiments for nematics show that the pair potential does not possess such a high symmetry[2,3] and Luckhurst *et al*.[4] have presented a mean field theory for the system of biaxial particles interacting with each other via the dispersion forces. The above two theories[1,4] and new developments of the molecular statistical theories[5,6] for biaxial molecules are known to neglect the short range correlations between molecular orientations.

The importance of the short range correlations in nematic liquid crystals has been demonstrated by experimental data and computer simulations.[7] There have been a few molecular theories published on the subject of the short range correlations, including the Bethe method[8], the cluster variation theory[9] and the constant coupling theory.[10] But these theories mainly studied the effects of the short range correlations on the Maier-Saupe theory, in all of which empirical expansions for the effective potential felt by a molecule are used and the expansions are truncated approximately. When the pair potential is complicated, for example, the pair potential contains terms which represent the molecular biaxiality, it is difficult to carry out a reliable calculation.

In a previous paper[11], we took into account the molecular short range correlations in nematics on the basis of the cluster variation method.[12] We have obtained an equation for the molecular orientational distribution functions in the two-particle cluster approximation.

Now this theory is applied to the study of the system of biaxial molecules, and our attention is focused on the uniaxial nematic liquid crystals. In order to solve the equation for the distribution functions, we develop an iterative method. We do not use any functional expansions for the distribution functions, but we can obtain accurate orientational distributions. Then various physical quantities can be calculated and accurate numerical results of the order parameter at the nematic-isotropic phase transition and the entropy change *etc*. could be obtained.

II. THE MOLECULAR ORIENTATIONAL DISTRIBUTIONS

In this section, we outline the molecular orientational distributions in the two-particle cluster theory and give the numerical method of calculation.

Let us consider a system of N liquid crystal molecules. The orientation of a molecule is described by three Euler angles α, β and γ. Denote $\Omega \equiv (\alpha, \beta, \gamma)$. Assume that one-body and two-body orientational distribution functions are $g(\Omega_1)$ and $g(\Omega_1, \Omega_2)$, respectively, where $g(\Omega_1)$ is the probability density of molecule 1 in orientation Ω_1; $g(\Omega_1, \Omega_2)$ is the probability density of molecule 1 in orientation Ω_1 and molecule 2 in Ω_2. They satisfy the normalization condition and the consistency condition

$$\int g(\Omega_1)\mathrm{d}\Omega_1 = 1, \tag{1}$$

$$\int g(\Omega_1, \Omega_2)\mathrm{d}\Omega_2 = g(\Omega_1), \tag{2}$$

where $\mathrm{d}\Omega = \mathrm{d}\alpha \sin\beta \mathrm{d}\beta \mathrm{d}\gamma$ and the angular integration is extended to the usual domains $0 \leqslant \alpha \leqslant 2\pi, 0 \leqslant \beta \leqslant \pi, 0 \leqslant \gamma \leqslant 2\pi$. Within the two-particle cluster approximation, the free energy of the system is expressed as[11-13]

$$\begin{aligned} F = \frac{1}{2} N \iint \{ & zV(\Omega_1, \Omega_2) + zkT\ln g(\Omega_1, \Omega_2) \\ & - (z-1)kT\ln g(\Omega_1) g(\Omega_2) \} g(\Omega_1, \Omega_2)\mathrm{d}\Omega_1 \mathrm{d}\Omega_2, \end{aligned} \tag{3}$$

where z is the coordination number; $V(\Omega_1, \Omega_2)$ is the orientational pair potential.

Following Luckhurst and Romano[14], we take the pair potential as

$$\begin{aligned} V(\Omega_1, \Omega_2) &= V(u_1, v_1, w_1; u_2, v_2, w_2) \\ &= -\varepsilon \{ [3(w_1 \cdot w_2)^2 - 1]/2 + \lambda \sqrt{6} [(u_1 \cdot u_2)^2 - (v_1 \cdot v_2)^2] \\ &\quad + \lambda^2 [(u_1 \cdot u_2)^2 + (v_1 \cdot v_2)^2 - (u_1 \cdot v_2)^2 - (v_1 \cdot u_2)^2] \}, \end{aligned} \tag{4}$$

where the three mutually orthogonal unit vectors u, v and w are set in the mirror planes of a molecule and w is along the long molecular axis. We can write the Cartesian components of the three unit vectors[15],

$$\begin{aligned} u &= (-\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma, -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma, \sin\beta\sin\gamma), \\ v &= (\cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma, \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma, -\sin\beta\cos\gamma), \\ w &= (\cos\alpha\sin\beta, \sin\alpha\sin\beta, \cos\beta), \end{aligned}$$

the pair potential is thus expressed by the Euler angles. Equation (4) represents the system of biaxial molecules interacting with each other via dispersion forces and it is truncated at the second rank terms. The potential parameter ε can be merged into the effective temperature; λ is a measure of the molecular biaxiality.

Minimizing the free energy with respect to the variation of the distribution func-

tions under the constraints of Eqs. (1) and (2), we obtain the equation for equilibrium distribution,

$$zV(\Omega_1,\Omega_2) + zkT\ln g(\Omega_1,\Omega_2) - (z-1)kT\ln g(\Omega_1)g(\Omega_2) - \eta = 0, \tag{5}$$

where η is the variational parameter. This result can be rewritten as

$$g(\Omega_1,\Omega_2) = A\{g(\Omega_1)\}^{1-1/z}\{g(\Omega_2)\}^{1-1/z}\exp\left|-\frac{1}{kT}V(\Omega_1,\Omega_2)\right|, \tag{6}$$

with

$$A = \exp\left(\frac{\eta}{zkT}\right).$$

From Eqs. (1), (2) and (6), we obtain the equation for one-body distribution function

$$g(\Omega_1) = \frac{\left\{\int[g(\Omega_2)]^{1-1/z}\exp\left[-\frac{1}{kT}V(\Omega_1,\Omega_2)\right]d\Omega_2\right\}^z}{\int\left\{\int[g(\Omega_2)]^{1-1/z}\exp\left[-\frac{1}{kT}V(\Omega_1,\Omega_2)\right]d\Omega_2\right\}^z d\Omega_1}. \tag{7}$$

Substituting Eq. (6) into Eq. (3) yields the free energy for the equilibrium distribution

$$\begin{aligned} F &= \frac{1}{2}NzkT\ln A \\ &= -\frac{1}{2}NzkT\ln\iint\{g(\Omega_1)\}^{1-1/z}\{g(\Omega_2)\}^{1-1/z}\exp\left|-\frac{1}{kT}V(\Omega_1,\Omega_2)\right|d\Omega_1 d\Omega_2. \end{aligned} \tag{8}$$

The crux of the above theory is to solve the functional equation (7) to determine the orientational distribution function $g(\Omega)$. If the function is known, we can then calculate the order parameter

$$S = \int P_2(\cos\beta)g(\Omega)d\Omega \tag{9}$$

and the internal energy

$$\begin{aligned} \bar{U} &= \frac{\partial(\bar{\beta}F)}{\partial(\bar{\beta})} \\ &= \frac{1}{2}Nz\,\frac{\iint V(\Omega_1,\Omega_2)\{g(\Omega_1)\}^{1-1/z}\{g(\Omega_2)\}^{1-1/z}\exp\left|-\frac{1}{kT}V(\Omega_1,\Omega_2)\right|d\Omega_1 d\Omega_2}{\iint\{g(\Omega_1)\}^{1-1/z}\{g(\Omega_2)\}^{1-1/z}\exp\left|-\frac{1}{kT}V(\Omega_1,\Omega_2)\right|d\Omega_1 d\Omega_2}, \end{aligned} \tag{10}$$

where $\bar{\beta}\equiv 1/kT$.

We use an iterative method to solve the functional equation (7). For the uniaxial nematic phase, the distribution function $g(\Omega)$ depends only on β (through $\cos\beta$) and γ. We can define $g(\Omega)$ on the $n\times n$ discrete points which can be limited to the domains $0\leqslant\cos\beta\leqslant 1$ and $0\leqslant\gamma\leqslant\pi$ for the symmetry in the pair potential. In order to link up with integral calculations, we choose the Gaussian point order

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

for the values of $\cos\beta$, and

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

for the values of γ, where $k=0,1,2,\cdots,n/2-1$; $h_\beta=1/n$ and $h_\gamma=\pi/n$.

Define a four-dimensional matrix

$$K(i_1,j_1;i_2,j_2)=\int_0^{2\pi}\exp\Big[-\frac{1}{kT}V(\Omega_1,\Omega_2)\Big]\,d\alpha_2 \qquad (i_1,j_1,i_2,j_2=1,2,\cdots,n). \tag{11}$$

Here $V(\Omega_1,\Omega_2)$ is given by Eq. (4); i_1, j_1, i_2 and j_2 are integers which specify the i_1th, j_1th, i_2th and j_2th elements out of n total elements in $\cos\beta_1$, γ_1, $\cos\beta_2$ and γ_2, respectively. Moreover, α_1 is set to be zero without the loss of generality.

Expressing the integral over $\cos\beta$ and γ in Eq. (7) by summation (because of the symmetry, the integration over $\cos\beta$ can be restricted to $[0,1]$ and γ to $[0,\pi]$) and noting the molecules 1 and 2 have the same orientational distribution, we have the iterative solution

$$g_{m+1}(\cos\beta_{i_1},\gamma_{j_1})=\frac{\Big|h_\beta h_\gamma\sum_{i_2j_2}K(i_1,j_1;i_2,j_2)\big[g_m(\cos\beta_{i_2},\gamma_{j_2})\big]^{1-1/\varepsilon}\Big|^{\varepsilon}}{h_\beta h_\gamma\sum_{i_1j_1}\Big|h_\beta h_\gamma\sum_{i_2j_2}K(i_1,j_1;i_2,j_2)\big[g_m(\cos\beta_{i_2},\gamma_{j_2})\big]^{1-1/\varepsilon}\Big|^{\varepsilon}}. \tag{12}$$

If the iteration converges, *i. e.*, $g_{l+1}(\cos\beta,\gamma)=g_l(\cos\beta,\gamma)$ for $l\geqslant m$, then $g_m(\cos\beta,\gamma)$ is a solution of Eq. (7).

Inserting $g_m(\cos\beta,\gamma)$ into Eq. (9), we can calculate the order parameter. By the following matrix

$$KU(i_1,j_1;i_2,j_2)=\int_0^{2\pi}V(\Omega_1,\Omega_2)\exp\Big[-\frac{1}{kT}V(\Omega_1,\Omega_2)\Big]\,d\alpha_2 \tag{13}$$

and Eq. (10), the internal energy is determined. The free energy for the equilibrium distribution can also be calculated easily.

III. NUMERICAL RESULTS AND DISCUSSION

In order to compare our results with those by the Monte Carlo simulation[14], we have made numerical calculations for the potential parameter $\lambda=0.2$ and the coordination number $z=12$, which corresponds to the face-centred-cubic lattice as adopted in the simulation.[14] In calculation, we took $n=30$, which gave an accuracy of 1 part in 10^4 or better in performing all our integral calculations.

Figure 1 shows the order parameter S as a function of reduced temperature kT/ϵ ($\equiv T^*$). The solid line represents the result obtained using the two-particle cluster theory in this paper. The dashed line is the theoretical prediction of the mean field theory[4] and the pluses are the Monte Carlo simulation results.[14] We can see that the result of the two-particle cluster theory is improved considerably compared with the mean field theory.

In Fig. 2, the temperature dependence of the reduced internal energy per particle $\bar{U}/N\epsilon$ ($\equiv U^*$) is shown by the solid line. For comparison, the result of the mean field theory[4] (the dashed line) and those of the simulation[14] (the pluses) are also given. In contrast with the mean field theory, the two-particle cluster theory predicts that the non-zero internal energy will occur in the isotropic phase, which is expected[10,11] and consistent with the simula-

tion.

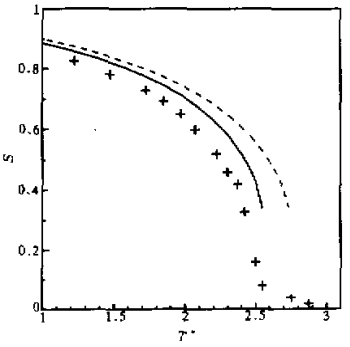

Fig.1. The order parameter as a function of reduced temperature. Solid line: the two-particle cluster theory; dashed line: the mean field theory; pluses: the Monte Carlo simulation.

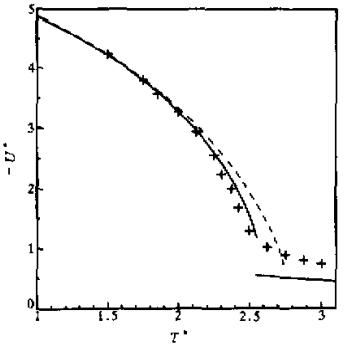

Fig.2. The reduced internal energy as a function of reduced temperature. Solid line: the two-particle cluster theory; dashed line: the mean field theory; pluses: the Monte Carlo simulation.

Table 1. Comparison of the predictions of the two-particle cluster theory with the results of the mean field theory and those of the simulation.

	T^*_{NI}	S_{NI}	$\Delta S/R$
Two-particle theory	2.552	0.337	0.249
Mean field theory[4]	2.736	0.341	0.275
Monte Carlo[14]	2.44 ± 0.03	0.31 ± 0.01	0.08 ± 0.01

In Figs. 1 and 2, the nematic-isotropic phase transition occurs at the reduced temperature 2.552, predicted by the two-particle cluster theory. The relevant properties at the phase transition given by our theory are listed in Table 1, where the entropy change $\Delta S/R$ is obtained from the change in the internal energy at the phase transition. The results of the mean field theory[4] and those of the Monte Carlo simulation[14] are also listed. Compared with the mean field theory, the two-particle cluster theory yields improved values for all quantities investigated by the simulation.[14] We have noted that adopting a face-centred-cubic lattice($z = 12$) instead of a simple cubic lattice($z = 6$) did not give fully play to the advantages of the two-particle cluster theory. The smaller the number of nearest neighbours, the more important the short range correlations between molecules.[9-11] In addition, the two-particle cluster theory only takes into account the correlations between a pair of neighbouring molecules, the incomplete quantitative agreement between the theory and the simulation is therefore expected.

IV. CONCLUSION

In this work a two-particle cluster theory of uniaxial nematic liquid crystals formed by biaxial molecules was presented. After solving the equation for the equilibrium distribution by an iterative method, the relevant orientational quantities were calculated. The present theo-

ry, taking into account the short range correlations between molecules, yields improved results compared with the mean field theory.

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