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Two-Particle Cluster Theory for Biaxial Nematic Phase Based on a Recently Proposed Interaction Potential *

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Two-particle cluster theory is applied to study the biaxial nematic phase formed by biaxial molecules interacting with a simplified model proposed by Sonnet et al. [Phys. Rev. E 67 (2003) 061701]. For the temperature dependences of the internal energy per particle and of the order parameters, the two-particle theory yields an improved result compared with mean field theory. Concerning the phase diagram, the two-particle theory gives the numerical result in qualitative agreement with the mean field theory.

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Stable biaxial phase has been observed in lyotropic systems as early as 1980[1] and it has definitely been confirmed by deuterium nuclear magnetic resonance spectroscopy.[2] In 2004, firm evidence of this phase in the thermotropics was reported.[3,4] This fact received a great deal of attention[5] and might create a new area of research in the field of liquid crystals: for example, new liquid crystal states in porous media.[6] In the theoretical aspect, the biaxial nematic liquid crystal phase has been studied by two kinds of microscopic models, which represent liquid crystal molecules possessing D_{2h} symmetry. The one, consisting of appropriate continuous potentials, has been treated by molecular field (MF) theory[7−11] and by Monte Carlo (MC) simulation.[12−16] The other, consisting of hard core potentials, has been investigated by analytical study[17−19] and also by simulation.[20,21] Here we are interested in the former, which can be traced back to a general model proposed by Straley,[8]

$$\begin{aligned} V(\Omega_1,\Omega_2) &= V(\boldsymbol{u}_1,\boldsymbol{v}_1,\boldsymbol{w}_1;\boldsymbol{u}_2,\boldsymbol{v}_2,\boldsymbol{w}_2) \\ &= -\varepsilon\{P_2(\boldsymbol{w}_1\cdot\boldsymbol{w}_2) - \Gamma[P_2(\boldsymbol{u}_1\cdot\boldsymbol{u}_2) - P_2(\boldsymbol{v}_1\cdot\boldsymbol{v}_2)] \\ &\quad + \Lambda[2P_2(\boldsymbol{u}_1\cdot\boldsymbol{u}_2) + 2P_2(\boldsymbol{v}_1\cdot\boldsymbol{v}_2) - P_2(\boldsymbol{w}_1\cdot\boldsymbol{w}_2)]\}, \end{aligned} \tag{1}$$

where P_2 is the second order Legendre polynomial; ε denotes a positive quantity setting temperature and energy scales, i.e. $T^* = k_BT/\varepsilon$, and this scaled temperature is the same as that in Refs. [14,15] (it differs from its counterpart in Refs. [8,10] by a fact of 9). Here $\boldsymbol{u},\boldsymbol{v}$, and $\boldsymbol{w}$ are the three mutually orthogonal unit vectors set in the molecule frame and $\boldsymbol{w}$ is along the long axial of prolate molecules. Both Γ and Λ are the potential parameters. An important special case is $\Gamma = \Lambda^2$, and Eq. (1) reduces to the pair potential proposed by Luckhurst and Romano,[12] which can be interpreted within London's dispersion approximation. Recently, the admissible values of Γ and Λ were discussed by Sonnet *et al.*,[10] and another special case of Straley interaction, defined by $\Gamma = 0$, was explored by means of MF.[10,11]

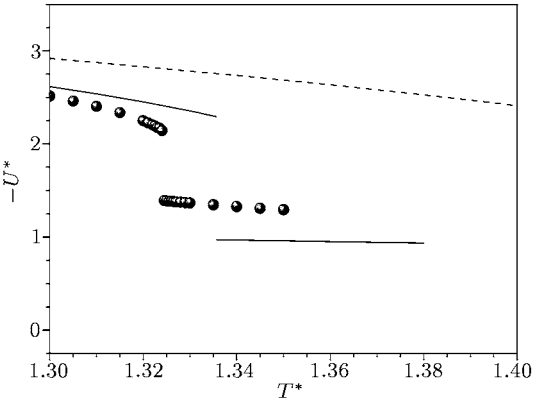

Fig. 1. Scaled internal energy as a function of scaled temperature. Solid line: the TPC theory; dashed line: the MF theory; circles: the MC simulation.[15]

We are interested in the fact that the London force model (i.e. $\Gamma = \Lambda^2$) gives a phase diagram with Landau bicritical point at $\Gamma = 1/\sqrt{6}$, predicted both by MF and MC,[13] while the simplified model (i.e. $\Gamma = 0$) shows a phase diagram exhibiting two tricritical points,[11] one being in the range $0 < \Lambda \leq 1/3$, the other in $1/3 < \Lambda < 1$. In the resulting phase diagram of MF (Fig. 4 in Ref. [10]), the biaxial to uniaxial transition is found to be second order for $0 < \Lambda \leq 0.20$, the first order for $0.20 < \Lambda \leq 0.22$, and finally a direct first-order transition between biaxial and isotropic phases occurs for $0.22 < \Lambda \leq 1/3$. In the subsequent MC simulations made by Romano,[15]

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the B1 model ($\Lambda = 0.24$) and the B2 model ($\Lambda = 0.3$) were studied in detail. The existence of the tricritical point has also been confirmed by an experimental study,[22] so that it is meaningful at present to investigate this subject by means of improved statistical theory beyond MF. In this Letter, we apply the two-particle cluster (TPC) theory[23,24] to the biaxial nematic model along the scheme proposed by Sonnet *et al.* and we only pay attention to $0 < \Lambda \leq 1/3$.

Let us consider a system formed by N liquid crystal molecules. The orientations of liquid crystal molecules are described by the Euler angles $\Omega = (\alpha, \beta, \gamma)$. Using the Euler angles, we give the Cartesian components of the three unite vectors in the pair potential.[25] Define one-body orientational distribution function $g(\Omega_1)$ and two-body orientational distribution function $g(\Omega_1, \Omega_2)$. They satisfy the normalization condition and the consistency condition

$$\int g(\Omega_1) d\Omega_1 = 1, \tag{2}$$

$$\int g(\Omega_1, \Omega_2) d\Omega_2 = g(\Omega_1), \tag{3}$$

where $d\Omega = d\alpha \sin\beta d\beta d\gamma$ and the angular integration is extended to the usual domains $0 \leq \alpha \leq 2\pi$, $0 \leq \beta \leq \pi$, $0 \leq \gamma \leq 2\pi$. According to the TPC approximation, the free energy of the system is expressed as[23]

$$F = \frac{1}{2} N \iint \{zV(\Omega_1, \Omega_2) + zkT \ln g(\Omega_1, \Omega_2) - (z-1)kT \ln g(\Omega_1) g(\Omega_2)\} g(\Omega_1, \Omega_2) d\Omega_1 d\Omega_2, \tag{4}$$

where z is the coordination number and we take $z = 6$, which corresponds to the simple cubic lattice, as in the MC simulation.[15] Making variation to the distribution under the constraints of Eqs. (2) and (3), we minimize the free energy, and then obtain the one-body distribution function:

$$g(\Omega_1) = \Big\{ \int [g(\Omega_2)]^{1-1/z} \cdot \exp\Big[-\frac{1}{kT} V(\Omega_1, \Omega_2) \Big] d\Omega_2 \Big\}^z \cdot \Big\{ \int \Big\{ \int [g(\Omega_2)]^{1-1/z} \cdot \exp\Big[-\frac{1}{kT} V(\Omega_1, \Omega_2) \Big] d\Omega_2 \Big\}^z d\Omega_1 \Big\}^{-1}. \tag{5}$$

This is the functional equation that the one-body distribution function should be satisfied. From Eqs. (4) and (5), we can obtain the free energy for an equilibrium state:

$$F = -\frac{1}{2} N z kT \ln \iint \{g(\Omega_1)\}^{1-1/z} \{g(\Omega_2)\}^{1-1/z} \cdot \exp\Big\{ -\frac{1}{kT} V(\Omega_1, \Omega_2) \Big\} d\Omega_1 d\Omega_2. \tag{6}$$

Now, the problem is how to solve the functional equation (5). If the function is known, we can then calculate the four order parameters:[13]

$$R_{00}^2 = \int P_2(\cos\beta) g(\Omega) d\Omega, \tag{7a}$$

$$R_{02}^2 = \sqrt{3/8} \int \sin^2\beta \cos(2\gamma) g(\Omega) d\Omega, \tag{7b}$$

$$R_{20}^2 = \sqrt{3/8} \int \sin^2\beta \cos(2\alpha) g(\Omega) d\Omega, \tag{7c}$$

$$R_{22}^2 = \int \Big[\frac{1}{4} (\cos^2\beta + 1) \cos(2\alpha) \cos(2\gamma) - \frac{1}{2} \cos\beta \sin(2\alpha) \sin(2\gamma) \Big] g(\Omega) d\Omega; \tag{7d}$$

the fourth rank order parameter

$$R_{00}^4 = \int P_4(\cos\beta) g(\Omega), \tag{8}$$

and the internal energy $\bar{U} = \partial(\bar{\beta}F)/(\partial\bar{\beta})$ (here $\bar{\beta} \equiv 1/k_B T$). R_{20}^2 and R_{22}^2 are the order parameters for the biaxial nematic phase, i.e. at least one of them is non-zero in this phase.

Here we use an iterative method to solve the functional equation (5). We know that $g(\Omega)$ depends on the Euler angles α, β, γ, so we can define $g(\Omega)$ on $n \times n \times n$ discrete points, the values of the corresponding points are limited as follows:

$$0 \leq \alpha \leq 2\pi, \quad 0 \leq \cos\beta \leq 1, \quad 0 \leq \gamma \leq 2\pi.$$

Here we choose the Gaussian point order:

$$h_\alpha(1 - 1/\sqrt{3} + 2k), \quad h_\alpha(1 + 1/\sqrt{3} + 2k) \quad \text{for the value of } \alpha,$$

$$h_\beta(1 - 1/\sqrt{3} + 2k), \quad h_\beta(1 + 1/\sqrt{3} + 2k) \quad \text{for the value of } \cos\beta,$$

$$h_\gamma(1 - 1/\sqrt{3} + 2k), \quad h_\gamma(1 + 1/\sqrt{3} + 2k) \quad \text{for the value of } \gamma,$$

where $k = 0, 1, 2, \cdots, \frac{n}{2} - 1$; $h_\alpha = 2\pi/n$, $h_\beta = 1/n$, $h_\gamma = 2\pi/n$.

Let us define a six-dimensional matrix

$$M(i_1, j_1, k_1; i_2, j_2, k_2) = \exp\Big[-\frac{1}{kT} V(\Omega_1, \Omega_2) \Big] \quad (i_1, j_1, k_1; i_2, j_2, k_2 = 1, 2, \cdots n). \tag{9}$$

Using the iterative method and the above matrix, Eq. (5) can be rewritten as

$$g_{m+1}(\alpha_{i_1}, \cos\beta_{j_1}, \gamma_{k_1}) = \Big\{ h_\alpha h_\beta h_\gamma \sum_{i_2 j_2 k_2} M(i_1, j_1, k_1; i_2, j_2, k_2)$$

$$\cdot [g_m(\alpha_{i_2}, \cos\beta_{j_2}, \gamma_{k_2})]^{1-1/z} \Big\}^z$$
$$\cdot \Big\{ h_\alpha h_\beta h_\gamma \sum_{i_1 j_1 k_1} \Big\{ h_\alpha h_\beta h_\gamma \sum_{i_2 j_2 k_2} M(i_1, j_1, k_1; i_2, j_2, k_2)$$
$$\cdot [g_m(\alpha_{i_2}, \cos\beta_{j_2}, \gamma_{k_2})]^{1-1/z} \Big\}^z \Big\}^{-1}. \quad (10)$$

If the iterative converges, i.e. $g_{l+1}(\alpha, \cos\beta, \gamma) = g_l(\alpha, \cos\beta, \gamma)$ for $l \geq m$, then $g_m(\alpha, \cos\beta, \gamma)$ is a solution to Eq. (5).

In order to compare our numerical results with those by the MC simulation[15] and by the MF theory,[10] we have made calculations for the B1 and B2 models as mentioned above. We take $n = 20$, and it may be the maximum value available for the six-dimensional matrix given by Eq. (9), when performing our calculations on supercomputer NK stars in Nankai Institute of Scientific Computing, Nankai University, China. Numerical results obtained successfully are reasonable.

Firstly, for the B1 model, we find a direct first-order transition between biaxial and isotropic phases at $T^* = 1.2294$, so that the result is consistent with the prediction of MF, but in contradiction with that of MC. We know that MC predicts that for the B1 model, there is a biaxial to uniaxial transition at $T^* = 1.20$, closely followed by a uniaxial to isotropic transition at $T^* = 1.22$.

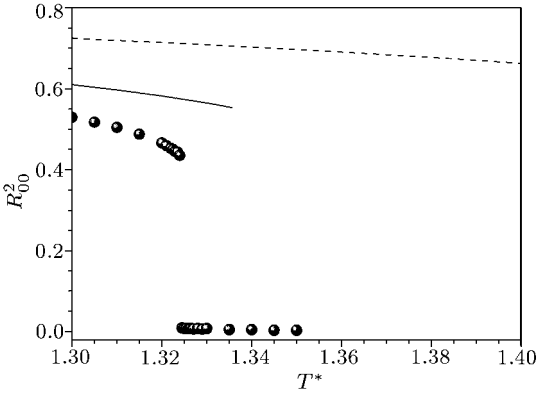

Fig. 2. Order parameter R^2_{00} as a function of scaled temperature. Solid line: the TPC theory; dashed line: the MF theory; circles: the MC simulation.[15]

For the B2 model, there is a direct first-order transition between biaxial and isotropic phases, predicted by TPC, MF and MC; i.e. the order parameters are non-zero at the phase transition and the phase transition is determined by the free energy. We can quantitatively compare numerical results of our TPC theory with those of MF and MC. In Figs. 1–4, the solid line represents the results of TPC; the dashed line is the theoretical predictions of MF and the pluses are the results obtained by MC. Figure 1 shows the scaled internal energy per particle $U^*(= \bar{U}/N\varepsilon)$ as a function of the scaled temperature T^*. We can see that TPC predicts that the non-zero internal energy will occur in the isotropic phase, which is expected and consistent with the simulation. The difficulty of MF in the wrong prediction that the isotropic phase has the zero internal energy is thus overcome.[23,24]

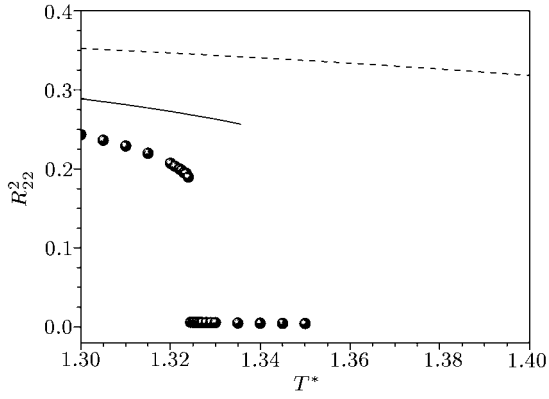

Fig. 3. Order parameter R^2_{22} as a function of scaled temperature. Solid line: the TPC theory; dashed line: the MF theory; circles: the MC simulation.[15]

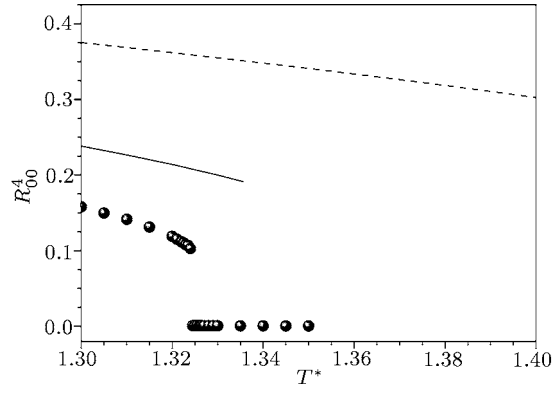

Fig. 4. Order parameter R^4_{00} as a function of scaled temperature. Solid line: the TPC theory; dashed line: the MF theory; circles: the MC simulation.[15]

In Figs. 2–4, we give the order parameters R^2_{00}, R^2_{22} and R^4_{00}, and we have paid attention to the fact that both R^2_{02} and R^2_{20} are smaller than 0.01 for all the calculated temperatures (and for the whole simplified model, i.e. $\Gamma = 0$ and $0 \leq \Lambda \leq 1/3$), which is in agreement with the result of MF and that of MC. The biaxial–isotropic phase transition occurs at the scaled temperature 1.3356, predicted by TPC. In Table 1, we list the relevant properties at the phase transition given by our theory and compare with the MC simulation[15] and the MF theory.[10] We can see that taking the result of MC as the criterion TPC yields an improved result compared with MF. As we know that MF overestimates the strength of the first-order uniaxial nematic–isotropic phase transition,[25] it stands to reason that overestimating occurs for MF to represent the biaxial nematic–isotropic phase transition.

Table 1. Comparison of the prediction of the TPC theory with the results of the MF theory and of the MC simulation.

Method	T^*_{NI}	ΔU^*	R^2_{00}	R^2_{22}	R^4_{00}
TPC	1.3356	1.3204	0.5534	0.2567	0.1912
MF	1.4652	1.9221	0.5967	0.2812	0.2395
MC[15]	1.324+0.001	0.75+0.04	0.435+0.016	0.19+0.01	0.103+0.008

In conclusion, TPC achieves success for the B2 model by taking into account molecular short-range correlations and MF overestimates the first-order character of the transition, as is well known for the Lebwohl–Lasher model[26] (set $\Gamma = 0$, $\Lambda = 0$ in Eq. (1)). As far as we know, we firstly give a molecular statistical theory for the biaxial nematic liquid crystals beyond MF. Concerning the phase diagram, TPC seems to be closer to MF than to MC, since TPC deals only with two-body correlations among two-body correlations, three-body correlations, four-body correlations, etc.[27] Besides the B1 model, this viewpoint is supported by choosing $\Gamma = 0$, $\Lambda = 0.21$, and TPC giving the numerical result in qualitative agreement with MF (i.e. there is a biaxial-to-uniaxial transition, closely followed by a uniaxial-to-isotropic transition). Further investigation on the full range of the potential parameter Λ is in progress.

References

[1] Yu L J and Saupe A 1980 *Phys. Rev. Lett.* **45** 1000
[2] Luckhurst G R 2001 *Thin Solid Films* **393** 40
[3] Madsen L A, Dingemans T J, Nakata M and Samulski E T 2004 *Phys. Rev. Lett.* **92** 145505
[4] Acharya B R, Primak A and Kumar S 2004 *Phys. Rev. Lett.* **92** 145506
[5] Luckhurst G R 2004 *Nature* **430** 413
[6] Yue W Z, Tao G and Zhu K Q 2004 *Chin. Phys. Lett.* **21** 2059
[7] Freiser M J 1970 *Phys. Rev. Lett.* **24** 1041
[8] Straley J P 1974 *Phys. Rev.* A **10** 1881
[9] Luckhurst G R, Zannoni C, Nordio P L and Segre U 1975 *Mol. Phys.* **30** 1345
[10] Sonnet A M, Virga E G and Durand G E 2003 *Phys. Rev.* E **67** 061701
[11] De Matteis G and Virga E G 2005 *Phys. Rev.* E **71** 061703
[12] Luckhurst G R and Romano S 1980 *Mol. Phys.* **40** 129
[13] Biscarini F, Chiccoli C, Pasini P, Semeria F and Zannoni C 1995 *Phys. Rev. Lett.* **75** 1803
[14] Romano S 2004 *Phys. Lett.* A **333** 110
[15] Romano S 2004 *Physica* A **337** 505
[16] De Matteis G, Romano S and Virga E G 2005 *Phys. Rev.* E **72** 041706
[17] Shih C and Alben R 1972 *J. Chem. Phys.* **57** 3057
[18] Mulder B 1989 *Phys. Rev.* A **39** 360
[19] Zakhlevnkh A N and Sosnin P A 1997 *Mol. Cryst. Liq. Cryst.* **293** 135
[20] Allen M P 1990 *Liq. Cryst.* **8** 499
[21] Camp P J, Allen M P and Masters A J 1999 *J. Chem. Phys.* **111** 9871
[22] Merkel K, Kocot A, Vij J K, Korlacki R, Mehl G H and Meyer T 2004 *Phys. Rev. Lett.* **93** 237801
[23] Zhang Z D Zhang D X and Sun Y B 2000 *Chin. Phys. Lett.* **17** 749
[24] Zhang Z D, Liu J W and Zhang W 2000 *Int. J. Mod. Phys.* B **14** 475
[25] Zhang Z D and Huang X M 1997 *Acta Phys. Sin.* **6** 671
[26] Lebwohl P A and Lasher G 1972 *Phys. Rev.* A **6** 426
[27] Van der Haegen R, Debruyne J, Luyckx R and Lekkerkerker H N W 1980 *J. Chem. Phys.* **73** 2469