Two-Particle Cluster Approximation for Biaxial Nematic Phase of Liquid Crystals

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Abstract

The two-particle cluster theory is applied to study the biaxial nematic phase formed by biaxial molecules interacting with a second-rank anisotropic potential. The one-body orientational distribution function is obtained at a certain reduced temperature by an iterative method and all the second-rank order parameters are calculated. By numerical calculation for the molecular biaxiality \( \lambda = 0.40825 \), we reached the conclusion that the short range correlation between molecules was as important in the biaxial nematic phase as in the uniaxial nematic phase.

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1. INTRODUCTION

With the finds of biaxial nematic phase in the lyotropic liquid crystals\(^1\) and the firm indications of this phase in the thermotropics\(^2-3\), the biaxial nematic liquid crystal phase receives a great deal of attention\(^4\). In theoretical aspect, the biaxial nematic phase has been studied by a number of methods; e.g., mean field theory\(^5\), counting methods\(^6\), density functional theory\(^7\), Monte Carlo simulation\(^8\), etc. Among all the mentioned above, the Monte Carlo simulation made by F. Biscarini et al.\(^8\) is in an outstanding position. Their work is based on a second-rank attractive pair potential within London’s dispersion forces approximation, and gives the phase diagram under the full set of biaxiality parameter \( \lambda \), using both the Monte Carlo simulation and the mean field theory. Afterwards, the simulation
results of the full set of order parameters for molecule biaxiality $\lambda = 0.40825$ were published$^9$. Although a general pair potential form for the biaxial nematic phase has been built up by Straly$^{10}$ as early as 1974, his pair potential form represents the general nematic interaction between molecules with frequency-dependent biaxiality and the dependence of two biaxiality parameter’s relationship on the frequency dispersion is very complex$^{11}$. A special case of Straly’s form is London’s dispersion forces approximation, and then two biaxiality parameters reduce to one$^{12}$ (i.e. biaxiality parameter $\lambda$). Since the biaxial nematic systems with $\lambda > 1/\sqrt{6}$ (plates) can be related to systems with $\lambda < 1/\sqrt{6}$ (rods) by a relabeling of the axes$^8$, $\lambda = 0.40825 \approx 1/\sqrt{6}$ gives nearly the maximum molecular biaxiality. In fact, experimentalists have been looking for the thermotropic biaxial nematic phase by designing of mesogenic molecules with sufficient biaxiality$^{13}$.

It is well known that in the uniaxial nematic phase formed by either uniaxial molecules$^{14,15}$ or biaxial molecules$^{16}$, the short range correlation between molecules plays an important role. In both cases, the two-particle cluster theory$^{15,16}$ obtained better results than the mean field theory, by taking into account the short range correlation. In this letter, we will apply the two-particle cluster theory to the biaxial nematic phase formed by biaxial molecules interacting with the anisotropic potential as used in Refs 8 and 9. Numerical results will be compared with those of both the Monte Carlo simulation and the mean field theory and some useful discussions will be given.

2. THE MOLECULES ORIENTATIONAL DISTRIBUTION

We consider a system formed by $N$ liquid crystal molecules. Introduce the three Euler angles $\alpha$, $\beta$ and $\gamma$. Denote $\Omega = (\alpha, \beta, \gamma)$, which is used to describe the orientation of a liquid crystal molecule, and $\Omega_1, \Omega_2$ are for the orientation of molecule 1 and molecule 2, respectively. We define one-body and two-body orientational distribution functions, $g(\Omega_1)$ and $g(\Omega_1, \Omega_2)$, which satisfy conditions:

$$\int g(\Omega_1) d\Omega_1 = 1,$$

(1)
Two-particle cluster approximation

\[ \int g(\Omega_1, \Omega_2) d\Omega_2 = g(\Omega_1), \quad (2) \]

where \( d\Omega = d\alpha \sin \beta d\beta d\gamma \) and the integration domains are:

\[
0 \leq \alpha \leq 2\pi, \quad 0 \leq \beta \leq \pi, \quad 0 \leq \gamma \leq 2\pi.
\]

According to Luckhurst and Romano\textsuperscript{[16]}, we take the pair potential as the following form:

\[
V(\Omega_1, \Omega_2) = V(u_1, v_1, w_1; u_2, v_2, w_2) = -\varepsilon \left[ \frac{1}{2} + \lambda \sqrt{6} \left[ \frac{1}{2} - (v_1 \cdot v_2)^2 - \frac{1}{2} (u_1 \cdot u_2)^2 \right] \right]
\]

\[
+ \lambda \left[ (u_1 \cdot u_2)^2 + (v_1 \cdot v_2)^2 - (u_1 \cdot v_1)^2 - (u_2 \cdot v_2)^2 \right],
\]

where \( \varepsilon \) describes the strength of the interaction, and \( \lambda \) is the molecular biaxiality parameter. Equation (3) is just the second-rank attractive pair potential within London’s dispersion forces approximation and has been used in Refs 8 and 9. The parameter \( \lambda \) varies from 0 to \( 1/\sqrt{6} \) for a system of prolate and \( \lambda > 1/\sqrt{6} \) for oblate molecules. Thus, \( \lambda = 1/\sqrt{6} \) marks Landau bicritical point\textsuperscript{[8]}. \( u, v, w \) are the three mutually orthogonal unit vectors set in the molecule frame and \( w \) is along the long axial of prolate molecules. Using the Euler angles, we give the Cartesian components of the three vectors as follow,

\[
u_x = \cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma, \]

\[
u_y = -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma, \]

\[
u_z = \sin \beta \sin \gamma; \]

\[
w_x = \cos \alpha \sin \beta, \]

\[
w_y = \sin \alpha \sin \beta, \]

\[
w_z = \cos \beta. \]

According to the two-particle cluster theory, the free energy of the system is expressed as\textsuperscript{[14,15]}. 
\[ F = \frac{1}{2} N \iint \{ zV(\Omega_1, \Omega_2) + zkT \ln g(\Omega_1, \Omega_2) - (z-1)kT \ln g(\Omega_1)g(\Omega_2) \} d\Omega_1 d\Omega_2. \] (4)

Making variation to the distribution under the constraints of (1) and (2), we minimize the free energy, and then obtain the equation for equilibrium distribution:

\[ zV(\Omega_1, \Omega_2) + zkT \ln g(\Omega_1, \Omega_2) - (z-1)kT \ln g(\Omega_1)g(\Omega_2) - \eta = 0, \] (5)

where \( \eta \) is the variational parameter. Equation (5) can be rewritten as:

\[ g(\Omega_1, \Omega_2) = A \exp \left\{ \frac{-1}{kT} V(\Omega_1, \Omega_2) \right\} \] (6)

where \( A = \exp \left( \frac{-\eta}{zkT} \right) \). Eq. (6) gives the two-body distribution function, and then we can get the one-body distribution function by using Eqs. (1) and (2):

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

This is the functional equation that the one-body distribution function should satisfy. From Eqs. (4) and (7), we can obtain the free energy for an equilibrium state:

\[ F = \frac{1}{2} NzkT \ln A \]

and then

\[ F = -\frac{1}{2} NzkT \ln \iint \{ [g(\Omega_1)]^{\frac{1}{1-z}} [g(\Omega_2)]^{\frac{1}{1-z}} \exp \left\{ \frac{-1}{kT} V(\Omega_1, \Omega_2) \right\} \} d\Omega_1 d\Omega_2. \] (8)

Now, the problem is how to solve the functional equation (7). Here we use an iterative method\(^\text{[16]}\). We know that \( g(\Omega) \) depends on the Euler angles \( \alpha, \beta, \gamma \), so we can define \( g(\Omega) \) on the \( n \times n \times n \) (three dimensional) discrete points. The values of the corresponding points are limited as following:

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

Here, we choose the Gaussian point order,

\[ h_\alpha (1 - 1/\sqrt{3} + 2k), \quad h_\alpha (1 + 1/\sqrt{3} + 2k) \] for the value of \( \alpha \),
Two-particle cluster approximation

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

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

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

By defining a six-dimensional matrix:

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

Eq. (7) can be rewritten as:

$$g_{mw}(\alpha, \cos \beta, \gamma) = \frac{\{h_{\alpha}h_{\beta}h_{\gamma} \sum_{i_1,j_1,k_1} K(i_1, j_1, k_1; i_2, j_2, k_2)[g_{m(w)}(\alpha, \cos \beta, \gamma)]\}^{1-\frac{1}{2}}}{h_{\alpha}h_{\beta}h_{\gamma} \sum_{i_1,j_1,k_1} [g_{m(w)}(\alpha, \cos \beta, \gamma)]^{1-\frac{1}{2}}} \quad (10)$$

If the iterative converges, \( i.e., g_{m(w)}(\alpha, \cos \beta, \gamma) = g_{l}(\alpha, \cos \beta, \gamma) \) for \( l \geq m \), then

$$g_{m}(\alpha, \cos \beta, \gamma) \quad \text{is a solution of Eq. (7).}$$

The two rank order parameters are defined as\([8,9]\)

$$<P_2> = \frac{3}{2} <\cos^2 \beta > - \frac{1}{2},$$

$$<R_{02}^2> = \sqrt{\frac{3}{8}} <\sin^2 \beta \cos 2\gamma >,$$

$$<R_{20}^2> = \sqrt{\frac{3}{8}} <\sin^2 \beta \cos 2\alpha >,$$

$$<R_{22}^2> = \frac{1}{4} (\cos^2 \beta + 1)\cos 2\alpha \cos 2\gamma - \frac{1}{2} \cos \beta \sin 2\alpha \sin 2\gamma >.$$

Inserting the one body distribution function \( g_m(\alpha, \cos \beta, \gamma) \) into the Eq. (11), then we can calculate the order parameters at a certain temperature. The results will be given in the following part of this letter.

3. NUMERICAL CALCULATIONS

Our numerical calculations are made with the molecular biaxiality parameter \( \lambda = 0.40825 \approx 1/\sqrt{6} \) so that numerical results can be compared with those of the Monte Carlo simulation published in Ref. 9. Take \( z = 6 \), which corresponds to the simple cubic lattice, as in the Monte Carlo simulation. We take \( n = 20 \), and it
may be the maximum value being 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 successively are reasonable.

In Figs.1-4, we show that the order parameters vary with the reduced temperature $T^* = kT / \varepsilon$. In those figures, the solid line represents the result obtained using the two-particle cluster theory, the dash line is the theoretical prediction of the mean field theory and the square symbols are the Monte Carlo simulation results\(^9\).

![Graph](image)

Fig.1. The second-rank nematic order parameter $\langle P_2 \rangle$ vs the reduced temperature $T^*$. Solid line: two-particle cluster theory; dash line: mean field theory; squares: Monte Carlo simulation\(^9\) with the size $L=40$. 
Fig. 2 The biaxial second-rank nematic order parameter $<R_{20}^2>$ vs the reduced temperature $T^*$. Solid line: two-particle cluster theory; dash line: mean field theory; squares: Monte Carlo simulation\cite{9} with the size $L=40$.

Fig. 3 The second-rank nematic order parameter $<R_{02}^2>$ vs the reduced temperature $T^*$. Solid line: two-particle cluster theory; dash line: mean field theory; squares: Monte Carlo simulation\cite{9} with the size $L=40$. 
At the calculated point $\lambda = 0.40825$, the uniaxial nematic-isotropic phase transition and the transition from the biaxial nematic phase to the uniaxial nematic phase are very close\cite{8,9}. The transition occurs at $T^* = 1.16$ and $T^* = 1.09$, predicted by the two-particle cluster theory and Monte Carlo simulation, respectively. Some properties at the transition point are given in the Table 1. The present theory, taking into account the short range correlations between molecules, yields improved results compared with the mean field theory.

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.

<table>
<thead>
<tr>
<th></th>
<th>$T^*_\text{NI}$</th>
<th>$&lt;P_2&gt;_{NI}$</th>
<th>$&lt;R_{22}^2&gt;_{NI}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-particle theory</td>
<td>1.29</td>
<td>0.060</td>
<td>0.024</td>
</tr>
<tr>
<td>Mean field theory</td>
<td>1.60</td>
<td>0.012</td>
<td>0.0048</td>
</tr>
<tr>
<td>Monte Carlo Simulation</td>
<td>1.09</td>
<td>0.22</td>
<td>0.069</td>
</tr>
</tbody>
</table>

Fig.4 The biaxial second-rank nematic order parameter $<R_{22}^2>$ vs the reduced temperature $T^*$. Solid line: two-particle cluster theory; dash line: mean field theory; squares: Monte Carlo simulation\cite{9} with the size $L=40$. 
4. CONCLUSION AND DISCUSSIONS

In this letter, we presented a two-particle cluster theory for the biaxial nematic phase of biaxial molecules interacting with a second-rank anisotropic potential. After solving the equation for the equilibrium distribution by an iterative method, the one-body orientational distribution function was obtained at a certain reduced temperature and all the second-rank order parameters were calculated. Taking the Monte Carlo simulation as the criterion, the two-particle cluster theory yields improved results compared with the mean field theory, and the short range correlation between molecules is as important in the biaxial nematic phase as in the uniaxial nematic phase. As the search for thermotropic biaxial liquid crystals has recently received a fresh impetus from the new evidence\cite{2,3}, our theoretical results may be useful for new areas opened up in the experimental studies. Firstly, the pair potential given by Eq. (3) is very attractive, because it is meaningful in respect of physics, i. e. it is based upon London’s dispersion forces approximation and it has only one biaxiality parameter. This pair potential gives the phase diagram with Landau bicritical point at $\lambda = 1/\sqrt{6}$, predicting by the two-particle cluster theory, as well as the mean field theory and the Monte Carlo simulation. Since a tricritical point in a phase diagram has also been confirmed by an experimental study\cite{18} and can only be explained beyond London’s dispersion forces approximation\cite{11}, the discovery will certainly stimulate the search for other examples of which phase diagrams correspond to London’s dispersion forces approximation. Secondly, the effects of the short range correlation between molecules appeared in Figs. 1-4 for the second-rank order parameters, need to be finally confirmed by experimental studies, as those in uniaxial nematic liquid crystals\cite{19}. Our quantitative prediction is a likely candidate for understanding fundamental behavior of the biaxial nematics.

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REFERENCES


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