Vol 13 No 2, February 2004
1009-1963/2004/13(02)/0212-013

Chinese Physics

© 2004 Chin. Phys. Soc.
and IOP Publishing Ltd

The microscopic theory for BPI and BPII of the blue phase

Yang Guo-Chen(杨国琛)[a)†], Cui Ying-Min(崔英敏)[a)],
Liu Jian-Jun(刘建军)[a)b)], and Shen Man(沈 曼)[b)]

[a)] *Institute of Physics, Hebei University of Technology, Tianjin* 300130, *China*

[b)] *Department of Physics, Hebei Normal University, Shijiazhuang* 050016, *China*

(Received 23 January 2003; revised manuscript received 14 August 2003)

A statistical theory of the blue phase of chiral liquid crystal is proposed. The form of the interaction potential between molecules is assumed to be the same as that used in the theory for cholesteric phase. Using the cell model of the liquid statistical theory, we deduced the distribution function of single molecule. The free energy of the system obtained has the same form as that of the Ginzberg–Landau phenomenology theory. The order-parameter tensors of BPI and BPII phases we calculated can be compared with the experimental results.

Keywords: blue phase, order-parameter tensor, potential parameter
PACC: 6470

1. Introduction

During the recent three decades, the blue phase of liquid crystal has attracted much attention.[1−5] The physical nature of BPI (the first subphase of blue phase) and BPII (the second subphase of blue phase) has a space group symmetry.[2,6] As a liquid, the blue phase shows the three-dimensional space group symmetry, just like crystals, which has aroused the interest of researchers.

Up to now, studies about the theory of blue phase[3,7−9] have been carried out within the framework of the Ginzberg–Landau theory. In this framework, the forms of the order-parameter tensors for BPI and BPII were given according to the space symmetries of the blue phase determined by experimental results,[10] and then the free energy was proposed. Based on the free energy, the phase diagram could be obtained for the chiral liquid crystals among BPI, BPII, BPIII, cholesteric phase and isotropic phase. Then the order-parameter tensors of BPI and BPII were determined by using the experimental results, and thus the structure of BPI and BPII could be known. However, the phenomenology theory is not concerned with the microscopic mechanism of the formation of blue phase, i.e. it cannot tell what kind of molecular interactions may respond to the blue phase formation.

To clarify the microscopic mechanism of blue phase formation, a statistical theory is necessary. Above all, the interaction potential among liquid crystal molecules should be determined. In our opinion, both the blue phase and cholesteric phase are the macro-state of the chiral liquid crystals, so the interaction potential among molecules should be unified. We adopt the same interaction potential as used in the molecular theory for the cholesteric phase, and believe that it can lead to the mechanism of the blue phase formation.

As soon as the interaction potential of molecules is established, a proper statistical method should be adopted. Mean-field theory is a common method which has been used to discuss nematic phase, cholesteric phase and smectic phase,[11,12] but it is difficult to apply in the blue phase (maybe that is why a statistical theory of blue phase has not yet been established). In this paper, we take another statistical approach, the cell-model of liquid theory,[13] which has been used in studying the nematic phase, cholesteric phase and smectic phase.[14−17] (In Ref.[14], we pointed out that this statistical method could be used in studying the blue phase.) Using the cell-model method to discuss the BPI and BPII, we will see that the coupling between the degrees of freedom of the molecular centroid and the molecular orientation plays

†E-mail: yang_gc@hotmail.com

an important role in the blue phase formation.

We deduce the free energy for the blue phase first. Our expression obtained has the same form as that in the Ginzberg–Landau phenomenology theory.[7,8,18−20] Because the expression of the free energy is the essential predetermined parameter in a phenomenology theory, the phase diagram of chiral liquid crystals and then the structure of BPI, BPII can be determined by means of mathematical method and experiment data. Our results give a microscopic foundation to the above-mentioned theory.

In order to obtain the structure of BPI and BPII, we then calculate the order-parameter tensor for these phases by using the molecular interaction potential according to statistical theory. The results can be compared with the experimental values.

2. The order-parameter tensor

The order-parameter tensor describes the structure of the chiral liquid crystal.[21] In the statistical theory, the corresponding microscopic quantity of this tensor can be expressed as

$$\widehat{Q}_{\mu\nu} = \frac{3}{2}\widehat{\Omega}_\mu\widehat{\Omega}_\nu - \frac{1}{2}\delta_{\mu\nu}, \qquad (\mu,\nu = 1,2,3), \tag{1}$$

where $\widehat{\Omega}$ is molecular orientation, which points to the molecular long axis with unit length. The statistical average of Eq.(1) is the order-parameter tensor of the chiral liquid crystal, i.e.

$$Q_{\mu\nu} = <\widehat{Q}_{\mu\nu}> = \frac{3}{2} <\widehat{\Omega}_\mu\,\widehat{\Omega}_\nu> - \frac{1}{2}\delta_{\mu\nu}. \tag{2}$$

The order-parameter tensor for cholesteric phase can be expressed as [15]

$$Q_{\rm ch} = \sqrt{6}\lambda\cos\zeta \begin{pmatrix} -\frac{1}{6} & 0 & 0 \\ 0 & -\frac{1}{6} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} + \frac{\lambda\sin\zeta}{\sqrt{2}} \begin{pmatrix} c_{2z} & s_{2z} & 0 \\ s_{2z} & -c_{2z} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{3}$$

where λ and ζ are parameters of the order-parameter tensor.

The BPI phase has the symmetry of O^8 space group, whose order-parameter tensor is expressed as [22]

$$\begin{aligned}
(Q_{\rm BPI})_{\mu\nu} = {} & \varepsilon_{(200)} \begin{pmatrix} c_{2z}-c_{2y} & -s_{2z} & -s_{2y} \\ -s_{2z} & c_{2z} & -s_{2x} \\ -s_{2y} & -s_{2x} & c_{2y}-c_{2x} \end{pmatrix} + \varepsilon_{(110)} \begin{pmatrix} 2s_yc_z & -\sqrt{2}s_zs_y & -\sqrt{2}c_yc_z \\ -\sqrt{2}s_zs_y & -s_yc_z & c_ys_z \\ -\sqrt{2}c_yc_z & c_ys_z & -s_yc_z \end{pmatrix} \\
& + \varepsilon_{(110)} \begin{pmatrix} -s_xc_y & c_xs_y & -\sqrt{2}s_ys_x \\ c_xs_y & -s_xc_y & -\sqrt{2}c_xc_y \\ -\sqrt{2}s_ys_x & -\sqrt{2}c_xc_y & 2s_xc_y \end{pmatrix} + \varepsilon_{(110)} \begin{pmatrix} -c_xs_z & -\sqrt{2}c_zc_x & s_xc_z \\ -\sqrt{2}c_zc_x & 2c_xs_z & -\sqrt{2}s_xs_z \\ s_xc_z & -\sqrt{2}s_xs_z & -c_xs_z \end{pmatrix} \\
& - \frac{2\sqrt{6}}{3}\varepsilon_{(211)} \begin{pmatrix} 2(c_{2z}s_xc_y - c_{2y}s_zc_x) & -s_{2y}s_zs_x - s_{2x}c_yc_z & -s_{2x}s_ys_z - s_{2z}c_xc_y \\ -s_{2y}s_zs_x - s_{2x}c_yc_z & 2(c_{2x}s_yc_z - c_{2z}s_xc_y) & -s_{2z}s_xs_y - s_{2y}c_zc_x \\ -s_{2x}s_ys_z - s_{2x}c_xc_y & -s_{2z}s_xs_y - s_{2y}c_zc_x & 2(c_{2y}s_zc_x - c_{2x}s_yc_z) \end{pmatrix} \\
& - \frac{2}{3}\varepsilon_{(211)} \begin{pmatrix} -2s_{2x}c_ys_z & 2c_{2x}s_ys_z & -2c_{2x}c_yc_z \\ 2c_{2x}s_ys_z & s_{2x}c_ys_z & -5s_{2x}s_yc_z \\ -2c_{2x}c_yc_z & -5s_{2x}s_yc_z & s_{2x}c_ys_z \end{pmatrix} \\
& - \frac{2}{3}\varepsilon_{(211)} \begin{pmatrix} s_{2y}c_zs_x & -2c_{2y}c_zc_x & -5s_{2y}s_zc_x \\ -2c_{2y}c_zc_x & -2s_{2y}c_zs_x & 2c_{2y}s_zs_x \\ -5s_{2y}s_zc_x & 2c_{2y}s_zs_x & s_{2y}c_zs_x \end{pmatrix} \\
& - \frac{2}{3}\varepsilon_{(211)} \begin{pmatrix} s_{2z}c_xc_y & -5s_{2z}s_xc_y & 2c_{2z}s_xs_y \\ -5s_{2z}s_xc_y & s_{2z}c_xc_y & -2c_{2z}c_xc_y \\ 2c_{2z}s_xs_y & -2c_{2z}c_xc_y & -2s_{2z}c_xc_y \end{pmatrix}.
\end{aligned} \tag{4}$$

The BPII phase has the O^2 space group symmetry, whose order-parameter tensor is expressed as [22]

$$(Q_{\mathrm{BPII}})_{\mu\nu} = \varepsilon_{(100)} \begin{pmatrix} c_z - c_y & -s_z & -s_y \\ -s_z & c_x - c_z & -s_x \\ -s_y & -s_x & c_y - c_x \end{pmatrix} + \varepsilon_{(110)} \begin{pmatrix} 2c_y c_z & -\sqrt{2}s_z c_y & \sqrt{2}s_y c_z \\ -\sqrt{2}s_z c_y & -c_y c_z & -s_y s_z \\ \sqrt{2}s_y c_z & -s_y s_z & -c_y c_z \end{pmatrix}$$
$$+ \varepsilon_{(110)} \begin{pmatrix} -c_x c_y & -s_x s_y & -\sqrt{2}s_y c_x \\ -s_x s_y & -c_x c_y & \sqrt{2}s_x c_y \\ -\sqrt{2}s_y c_x & \sqrt{2}s_x c_y & 2c_x c_y \end{pmatrix}$$
$$+ \varepsilon_{(110)} \begin{pmatrix} -c_x c_z & \sqrt{2}s_z c_x & -s_x s_z \\ \sqrt{2}s_z c_x & 2c_x c_z & -\sqrt{2}s_x c_z \\ -s_x s_z & -\sqrt{2}s_x c_z & -c_x c_z \end{pmatrix}, \quad (5)$$

where $s_\tau = \sin q\tau$, $c_\tau = \cos q\tau (\tau = x, y, z)$, and $\dfrac{2\pi}{q}$ is the crystal constant.

In the statistical theory of cholesteric phase, either λ, ζ and q or scalar parameter s_{ch}, biaxiality Δ and pitch p can be equally figured out from the interaction potential.[23] In the same way, four parameter values $\varepsilon_{(200)}$, $\varepsilon_{(110)}$, $\varepsilon_{(211)}$ and q_{BPI} for BPI and three parameter values $\varepsilon_{(100)}$, $\varepsilon_{(110)}$ and q_{BPII} for BPII, can be calculated based on the molecules' potential.

3. The distribution function

Suppose that the chiral liquid crystal contains N molecules in volume V. Molecular configurations are expressed as $\boldsymbol{X} = (\boldsymbol{r}, \widehat{\Omega})$, where $\boldsymbol{r}$ is the molecular centroid positional vector and $\widehat{\Omega}$ is the unit molecular orientation. We suppose that the interaction potential between the molecules i and j is [24]

$$\begin{aligned} V(i,j) =& V(\boldsymbol{X}_i, \boldsymbol{X}_j) \\ =& V_0(r_{ij}) + V_N(r_{ij}) P_2(\widehat{\Omega}_i \cdot \widehat{\Omega}_j) \\ &+ V_X(r_{ij})(\widehat{\Omega}_i \cdot \widehat{\Omega}_j)(\boldsymbol{r_{ij}} \cdot \widehat{\Omega}_i \times \widehat{\Omega}_j). \end{aligned} \quad (6)$$

The third term of Eq.(6) is the chiral potential which only exists in the chiral molecules and plays an important role in the helix structure of the cholesteric phase, as well as for the space groups of the BPI and BPII.

Using the cell-model,[13,25] notation of Ref.[14] and the single body approximation, we express the distribution function of a single molecule as

$$P(\boldsymbol{X}_i) = \frac{1}{Z} \exp[-\beta V(i)], \quad (7)$$

with

$$\begin{aligned} V(i) =& V(\boldsymbol{R}_i, \boldsymbol{\rho}_i, \widehat{\Omega}_j) \\ =& \sum_j{}' \int^{\Delta_j} V(i,j) P(\boldsymbol{X}_j) \mathrm{d}\boldsymbol{X}_j, \end{aligned} \quad (8)$$

where $\boldsymbol{r}_i$ is expressed as $\boldsymbol{r}_i = \boldsymbol{R}_i + \boldsymbol{\rho_i}$; $\boldsymbol{R}_i$ represents the positional vector of the centre of the ith cell, $\boldsymbol{\rho_i}$ represents the positional vector of the molecule relative to the ith cell centre, and $\mathrm{d}\boldsymbol{X}_j \equiv \mathrm{d}\boldsymbol{r_j}\mathrm{d}\widehat{\Omega}_j = \mathrm{d}\boldsymbol{\rho_j}\mathrm{d}\widehat{\Omega}_j$. The integration region Δ_j means integration for $\boldsymbol{r_j}$ in the whole volume of a cell. The integration region for $\widehat{\Omega}_j$ is the steric angle 4π. Hereafter $< V(i,j) >_j$ represents the integration appearing in Eq.(8): namely, the statistical average of $V(i,j)$ for molecule j. In the following discussions, this sign is used for all the statistical average. Furthermore, a nearest neighbour approximation is adopted: the sum of j is limited to the neighbours of molecule i, notated as $\sum'$.

As seen from Eqs.(6) and (7), there is a certain coupling between the degree of freedom of the molecular centre of mass at $\boldsymbol{r}$ and the orientation $\widehat{\Omega}$ (hereafter, we call it the coupling of degrees of freedom between translation and rotation). In the statistical theory for the cholesteric phase,[14] we took the approximation of separating variables, and the distribution function of a single molecule is expressed as

$$P_0(\boldsymbol{X}_i) = f(\boldsymbol{R}_i, \boldsymbol{\rho_i}) g(\boldsymbol{R}_i, \widehat{\Omega}_i), \quad (9)$$

where $f(\boldsymbol{R}_i, \boldsymbol{\rho_i})$ represents the distribution function of the molecular centre of mass at $\boldsymbol{\rho_i}$, and $g(\boldsymbol{R}_i, \widehat{\Omega}_i)$ is the distribution of Ω_i. We will see, in the next section, that the coupling of the two degrees of freedom is important for the blue phase. Thus, we take Eq.(9) as the primary approximation and use the sign $P_0(\boldsymbol{X}_i)$. Then we deduce the first approximation and sign $P(\boldsymbol{X}_i)$, and the mathematic process is as follows.

Starting from the primary approximation and substituting Eq.(9) into Eq.(8) yields

$$\begin{aligned} V(i) = &\sum_j{}' < V_0(r_{ij}) >_j \\ &+ \sum_j{}' < V_N(r_{ij}) >_j < P_2(\widehat{\Omega}_i \cdot \widehat{\Omega}_j) >_j \\ &+ \sum_j{}' < V_X(r_{ij}) >_j \\ &\times < (\widehat{\Omega}_i \cdot \widehat{\Omega}_j)(\boldsymbol{R_{ij}} \cdot \widehat{\Omega}_i \times \widehat{\Omega}_j) >_j, \end{aligned} \tag{10}$$

where an approximation is used in the third term,

$$\boldsymbol{r_{ij}} = \boldsymbol{R_{ij}} + (\boldsymbol{\rho}_j - \boldsymbol{\rho}_i) \approx \boldsymbol{R_{ij}}.$$

When we make a statistical average of $\boldsymbol{r_j}$ on Eq.(10); the distribution function used is $f(\boldsymbol{R}_i, \boldsymbol{\rho_i})$. As to $\widehat{\Omega}_j$, the distribution function used is $g(\boldsymbol{R}_i, \widehat{\Omega}_i)$. We noticed that $< V_\tau(r_{ij}) >_j$ $(\tau = 0, N, X)$ should be related to $\boldsymbol{R_{ij}}$. If we assume that $|\boldsymbol{R_{ij}}|$ is constant a and the distribution of the molecules j relative to i is central symmetrical, then $< V_\tau(r_{ij}) >_j$ is only related to $\boldsymbol{\rho_i}$. Therefore, we can define the function as follows:

$$v_0(i) \equiv v_0(\boldsymbol{\rho_i}) = z < V_0(r_{ij}) >_j, \tag{11}$$

$$v_N(i) \equiv v_N(\boldsymbol{\rho_i}) = < V_N(r_{ij}) >_j, \tag{12}$$

$$v_X(i) \equiv v_X(\boldsymbol{\rho_i}) = < V_X(r_{ij}) >_j, \tag{13}$$

$$\omega_N(i) \equiv \omega_N(\boldsymbol{R}_i, \widehat{\Omega}_i) = \sum_j{}' < P_2(\widehat{\Omega}_i \cdot \widehat{\Omega}_j) >_j, \tag{14}$$

$$\begin{aligned} \omega_X(i) &\equiv \omega_X(\boldsymbol{R}_i, \widehat{\Omega}_i) \\ &= \sum_j{}' < (\widehat{\Omega}_i \cdot \widehat{\Omega}_j)(\boldsymbol{R_{ij}} \cdot \widehat{\Omega}_i \times \widehat{\Omega}_j) > . \end{aligned} \tag{15}$$

Substituting Eq.(10) into Eqs.(11)–(15), we obtain

$$V(i) = v_0(i) + v_N(i)\omega_N(i) + v_X(i)\omega_X(i), \tag{16}$$

and Eq.(16) can be taken as the approximation of Eq.(8).

Then we consider the second approximation of the distribution function. Substituting Eq.(16) into Eq.(7), the distribution function becomes

$$\begin{aligned} P(\boldsymbol{X}_i) = &\frac{1}{Z} \exp\{-\beta[v_0(i) \\ &+ v_N(i)\omega_N(i) + v_X(i)\omega_X(i)]\}. \end{aligned} \tag{17}$$

On the other hand, $P_0(\boldsymbol{X}_i)$ can be obtained by using the method in Ref.[14]. Adopting the notation in Eq.(16), we obtain

$$\begin{aligned} P_0(\boldsymbol{X}_i) = &\frac{1}{Z_0} \exp\{-\beta[v_0(i) + v_N(i) < \omega_N(i) > \\ &+ v_X(i) < \omega_X(i) >]\} \\ &\times \exp\{-\beta[< v_N(i) > \omega_N(i) \\ &+ < v_X(i) > \omega_X(i)]\} \\ = &f(\boldsymbol{R}_i, \boldsymbol{\rho}_i) g(\boldsymbol{R}_i, \widehat{\Omega}_i), \end{aligned} \tag{18}$$

where

$$\begin{aligned} f(\boldsymbol{R}_i, \boldsymbol{\rho}_i) = &\frac{1}{Z_r} \exp\{-\beta[v_0 + v_N < \omega_N > \\ &+ v_X < \omega_X >]\}, \end{aligned} \tag{19}$$

$$g(\boldsymbol{R}_i, \widehat{\Omega}_i) = \frac{1}{Z_\Omega} \exp\{-\beta[< v_N > \omega_N + < v_X > \omega_X]\}. \tag{20}$$

Here $< \omega_N >$, $< \omega_X >$, $< v_N >$ and $< v_X >$ are statistical averages for molecule i. f and g are both normalized as

$$\int^{\Delta_i} f(\boldsymbol{R}_i, \boldsymbol{\rho_i}) \mathrm{d}\boldsymbol{\rho_i} = 1,$$

$$\int^{\Delta_i} g(\boldsymbol{R}_i, \widehat{\Omega}_i) \mathrm{d}\widehat{\Omega}_i = 1.$$

Moreover, we have

$$Z_0 = Z_r Z_\Omega. \tag{21}$$

Now, we discuss the relationship between $P(\boldsymbol{X}_i)$ and $P_0(\boldsymbol{X}_i)$. Considering that in

$$\begin{aligned} &v_0 + v_N\omega_N + v_X\omega_X \\ &= \{v_0 + v_N < \omega_N > + v_X < \omega_X >\} \\ &\quad + \{< v_N > \omega_N + < v_X > \omega_X\} \\ &\quad + \{(v_N - < v_N >)(\omega_N - < \omega_N >) \\ &\quad + (v_X - < v_X >)(\omega_X - < \omega_X >)\} \\ &\quad - \{< v_N >< \omega_N > + < v_X >< \omega_X >\}, \end{aligned}$$

the last term in the right-hand side of the above equation is constant, we obtain

$$\begin{aligned} P(\boldsymbol{X}_i) = &\frac{1}{Z'} \exp\{-\beta[v_0(i) + v_N(i) < \omega_N(i) > \\ &+ v_X(i) < \omega_X(i) >]\} \\ &\times \exp\{-\beta[< v_N(i) > \omega_N(i) + < v_X(i) > \omega_X(i)]\} \\ &\times \exp\{(v_N(i) - < v_N(i) >)(\omega_N(i) - < \omega_N(i) >) \\ &+ (v_X(i) - < v_X(i) >)(\omega_X(i) - < \omega_X(i) >)\}, \end{aligned}$$

where

$$Z' = Z \exp\{-\beta[< v_N >< \omega_N > + < v_X >< \omega_X >]\}.$$

Supposing

$$-\beta\{(v_N-<v_N>)(\omega_N-<\omega_N>)+(v_X-<v_X>)(\omega_X-<\omega_X>)\}$$

is a small quantity, we can express $P(\boldsymbol{X}_i)$ as

$$P(\boldsymbol{X}_i)=P_0(\boldsymbol{X}_i)\{1-\beta[(v_N-<v_N>)(\omega_N-<\omega_N>)+(v_X-<v_X>)(\omega_X-<\omega_X>)]\}. \quad (22)$$

Equation (22) is the distribution function for a single molecule we proposed, and can be described as $P(\boldsymbol{R}_i,\boldsymbol{\rho}_i,\widehat{\Omega}_i)$. Its normalization form is

$$\int^{\Delta_i} P(\boldsymbol{R}_i,\boldsymbol{\rho}_i,\widehat{\Omega}_i)\mathrm{d}\boldsymbol{\rho}_i\mathrm{d}\widehat{\Omega}_i=1. \quad (23)$$

4. The free energy

The free energy can be expressed as [14]

$$F=U-TS, \quad (24)$$

where

$$U=\frac{1}{2}\sum_{i\neq j}^{N}\int^{\Delta_i}\int^{\Delta_j}V(\boldsymbol{X}_i,\boldsymbol{X}_j)P(\boldsymbol{X}_j)P(\boldsymbol{X}_i)\mathrm{d}\boldsymbol{X}_j\mathrm{d}\boldsymbol{X}_i$$
$$=\frac{1}{2}D\int_V\mathrm{d}\boldsymbol{R}\int^{\Delta}V(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})P(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})\mathrm{d}\boldsymbol{\rho}\mathrm{d}\widehat{\Omega}, \quad (25)$$

$$S=-Dk_{\mathrm{B}}\int_V\mathrm{d}\boldsymbol{R}\int^{\Delta}P(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})\ln P(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})\mathrm{d}\boldsymbol{\rho}\mathrm{d}\widehat{\Omega}. \quad (26)$$

Equation (25) is obtained by using the definition of the single body potential Eq.(8), and D is the molecular number density. In this section, we derive the expression of the free energy which is similar to the expression used in Ginzberg–Landau's phenomenology theory.[22]

From Eq.(25), the energy density u can be denoted as

$$u(\boldsymbol{R})=\frac{D}{2}\int^{\Delta}V(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})P(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})\mathrm{d}\boldsymbol{\rho}\mathrm{d}\widehat{\Omega}, \quad (27)$$

where $P(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})$ can be rewritten by using Eq.(18) as

$$P(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})=P_0(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})(1-\beta\Gamma), \quad (28)$$

where

$$\Gamma=(v_N-<v_N>)(\omega_N-<\omega_N>)+(v_X-<v_X>)(\omega_X-<\omega_X>); \quad (29)$$

the distribution function used by those statistical average $<\cdots>$ above is $P_0(\boldsymbol{R},\boldsymbol{\rho},\widehat{\Omega})$ (as in the following). Substituting Eq.(16) into Eq.(27), we obtain

$$u(\boldsymbol{R})=u^{(0)}(\boldsymbol{R})+u'(\boldsymbol{R}), \quad (30)$$

where

$$u^{(0)}(\boldsymbol{R})=\frac{D}{2}\{<v_0>+<v_N><\omega_N>+<v_X><\omega_X>\}, \quad (31)$$

$$u'(\boldsymbol{R})=\frac{D}{2}\{-\beta<\Gamma^2>\}, \quad (32)$$

$$<\Gamma^2>=(<v_N^2>-<v_N>^2)(<\omega_N^2>-<\omega_N>^2)+(<v_X^2>-<v_X>^2)(<\omega_X^2>-<\omega_X>^2)+2(<v_Nv_X>-<v_N><v_X>)\times(<\omega_N\omega_X>-<\omega_N><\omega_X>). \quad (33)$$

Next, we take S into account. From Eq.(26), the density of entropy is

$$s(\boldsymbol{R})=-Dk_{\mathrm{B}}\int^{\Delta}P(\boldsymbol{R},\boldsymbol{P},\widehat{\Omega})\ln P(\boldsymbol{R},\boldsymbol{P},\widehat{\Omega})\mathrm{d}\boldsymbol{\rho}\mathrm{d}\widehat{\Omega}. \quad (34)$$

Substituting Eq.(28) into Eq.(34), we obtain

$$s(\boldsymbol{R})\approx s^{(0)}(\boldsymbol{R})+s'(\boldsymbol{R}), \quad (35)$$

where

$$s^{(0)}(\boldsymbol{R})=-Dk_{\mathrm{B}}\int^{\Delta}P_0\ln P_0\mathrm{d}\boldsymbol{\rho}\mathrm{d}\widehat{\Omega},$$
$$s'(\boldsymbol{R})=-Dk_{\mathrm{B}}<\Gamma^2>.$$

In deriving Eq.(35), an approximation is made:

$$\ln P=\ln P_0+\ln(1-\beta\Gamma)\approx\ln P_0-\beta\Gamma.$$

In this way, the density of free energy $\mathcal{F}$ is obtained

$$\mathcal{F}(\boldsymbol{R})=\mathcal{F}^{(0)}(\boldsymbol{R})+\mathcal{F}'(\boldsymbol{R}), \quad (36)$$

where

$$\mathcal{F}^{(0)}(\boldsymbol{R})=u^{(0)}(\boldsymbol{R})-Ts^{(0)}(\boldsymbol{R}),$$
$$\mathcal{F}'(\boldsymbol{R})=\frac{1}{2}k_{\mathrm{B}}TD<\Gamma^2>.$$

We divide $\mathcal{F}(\boldsymbol{R})$ into two parts to make the physical meaning clear. When the coupling between the translation and rotation is weak, $\mathcal{F}^{(0)}(\boldsymbol{R})$ represents the result that the distribution function for a single molecule can be separated into variables $\boldsymbol{r}$ and $\widehat{\Omega}$. $\mathcal{F}'(\boldsymbol{R})$ represents the revision by considering this coupling further.

Substituting Eq.(6) into the above equation, $\mathcal{F}^{(0)}(\boldsymbol{R})$ can be expressed as

$$\mathcal{F}^{(0)}(\boldsymbol{R}) = \frac{D}{2}\{<v_0> + <v_N><\omega_N> + <v_X><\omega_X> - Ts^{(0)}\}, \quad (37)$$

where the statistical average can be written out by using Eqs.(11)–(15), such as

$$<v_0> = z \ll V_0 \gg,$$
$$<v_N> = \ll V_N \gg,$$
$$<v_X> = \ll V_X \gg, \quad (38)$$

where $\ll \cdots \gg$ represents twice the statistical averages of molecules i and j.

Now we use the order-parameter tensor $Q_{\mu\nu}$ to express $<\omega_N>$ and $<\omega_X>$. From Eq.(2), we have

$$\widehat{\Omega}(i)_\mu \widehat{\Omega}(i)_\nu = \frac{2}{3}\widehat{Q}_{\mu\nu}(i) + \frac{1}{3}\delta_{\mu\nu},$$

we denote $\widehat{\Omega}_i$ (the orientation of molecule i) as $\widehat{\Omega}(i)$ (as in the following), and take into account $<\omega_N>$ and $<\omega_X>$ respectively. For $<\omega_N>$, we have

$$P_2[\widehat{\Omega}(i)\cdot\widehat{\Omega}(j)] = \frac{3}{2}\sum_{\mu\nu}\widehat{\Omega}(i)_\mu\widehat{\Omega}(j)_\mu\widehat{\Omega}(i)_\nu\widehat{\Omega}(j)_\nu = \frac{2}{3}\sum_{\mu\nu}\widehat{Q}(i)_{\mu\nu}\widehat{Q}(j)_{\mu\nu}.$$

From the above equations and Eq.(14), we obtain

$$\omega_N(\boldsymbol{R}_i, \widehat{\Omega}_i) = \frac{2}{3}\sum_j{}' \sum_{\mu\nu}\widehat{Q}(i)_{\mu\nu}Q(j)_{\mu\nu}. \quad (39)$$

For $<\omega_X>$, we have

$$\widehat{\Omega}(i)\cdot\widehat{\Omega}(j)[\boldsymbol{R_{ij}}\cdot\widehat{\Omega}(i)\times\widehat{\Omega}(j)] = \frac{4}{9}\sum_{\substack{\mu\\ \alpha\beta\gamma}}\varepsilon_{\alpha\beta\gamma}R_{ij,\alpha}\widehat{Q}(i)_{\mu\beta}\widehat{Q}(j)_{\mu\gamma},$$

where

$$\varepsilon_{\alpha\beta\gamma} = \begin{cases} 1, & \text{when } (\alpha\beta\gamma) = (123),(231),(312), \\ -1, & \text{when } (\alpha\beta\gamma) = (132),(213),(321), \\ 0, & \text{otherwise,} \end{cases}$$

so

$$\omega_x(\boldsymbol{R}, \hat{\Omega}_i) = \frac{4}{9}\sum_j{}' \sum_{\substack{\mu\\ \alpha\beta\gamma}}\varepsilon_{\alpha\beta\gamma}R_{ij,\alpha}\widehat{Q}(i)_{\mu\beta}\widehat{Q}(j)_{\mu\gamma}. \quad (40)$$

Here $Q(j)_{\mu\nu}$ is the function of $\boldsymbol{R}_j$, which can be expanded in the Taylor series about $\boldsymbol{R}_j$ (hereafter, we use the symbol $\boldsymbol{R}$),

$$Q(j)_{\mu\nu} = Q(i)_{\mu\nu} + \sum_\alpha \left.\frac{\partial Q_{\mu\nu}}{\partial R_\alpha}\right|_i R_\alpha + \frac{1}{2}\sum_{\alpha\beta}\left.\frac{\partial^2 Q_{\mu\nu}}{\partial R_\alpha \partial R_\beta}\right|_i R_\alpha R_\beta + \cdots \quad (41)$$

We substitute Eq.(41) into Eqs.(39), (40), and assume that the distribution of cell j is centrosymmetrical to cell i, and that the distance between the centres of the two cells is a (a is small), then, to $O(a^2)$, we obtain

$$<\omega_N> = \frac{2}{3}zQ(i)_{\mu\nu}Q(i)_{\mu\nu} + \frac{1}{9}za^2Q_{\mu\nu}(i)\nabla_R^2Q_{\mu\nu}(i), \quad (42)$$

$$<\omega_X> = \frac{4}{27}za^2\sum_{\substack{\mu\\ \alpha\beta\gamma}}\varepsilon_{\alpha\beta\gamma}Q(i)_{\mu\beta}\frac{\partial}{\partial R_\alpha}Q_{\mu\gamma}(i), \quad (43)$$

hence, we can express $<\omega_N>$ and $<\omega_X>$ in $\mathcal{F}^{(0)}$ with the order-parameter tensor.

The last term in Eq.(37) is $Ts^{(0)}$. One can prove that $s^{(0)}$ is unrelated to $Q_{\mu\nu}$ (see Appendix A). This means that if the coupling between the degrees of freedom of translation and rotation is considered insufficiently, there would be only one term $\mathcal{F}^{(0)}$ in the free energy density, and the latent heat of phase transitions among the BPI, BPII, BPIII and cholesteric phases would be zero. Experiments proved that these phase transitions are first-order, in other words, the latent heat does exist, therefore $\mathcal{F}'$ must be taken into consideration.

According to Eq.(37), using Eqs.(38)–(43), we obtain

$$\mathcal{F}^{(0)} = \frac{1}{2}D\Big\{z \ll V_0 \gg + \frac{2}{3}z \ll V_N \gg \sum_{\mu\nu}Q_{\mu\nu}Q_{\mu\nu} + \frac{1}{9}za^2 \ll V_N \gg \sum_{\mu\nu}Q_{\mu\nu}\nabla_R^2Q_{\mu\nu} + \frac{4}{27}za^2 \ll V_X \gg \times \sum_{\substack{\mu\\ \alpha\beta\gamma}}\varepsilon_{\alpha\beta\gamma}Q_{\mu\beta}\frac{\partial}{\partial R_\alpha}Q_{\mu\gamma}\Big\} - Ts^{(0)}. \quad (44)$$

$\mathcal{F}'(\boldsymbol{R})$, the revised term of the free energy density, can be calculated using Eq.(36). When calculating $<\Gamma^2>$, the items $<\omega_N^2>$, $<\omega_X^2>$ and $<\omega_N\omega_X>$ should be calculated respectively (see Eq.(33)). Using Eqs.(39) and (40), we obtain

$$\mathcal{F}'(\boldsymbol{R}) = \frac{1}{2}D\{H\mathrm{Tr}[Q^2] + J\mathrm{Tr}[Q^3] + K\mathrm{Tr}[Q^2]^2\}, \quad (45)$$

where

$$H = -\frac{2}{15}z^2(\ll V_N^2 \gg - \ll V_N \gg^2) - \frac{4}{135}za^2(\ll V_X^2 \gg - \ll V_X \gg^2),$$
$$J = -\frac{8}{21}za^2(\ll V_N^2 \gg - \ll V_N \gg^2) - \frac{8}{189}za^2(\ll V_X^2 \gg - \ll V_X \gg^2),$$
$$K = \frac{4}{9}z^2(\ll V_N^2 \gg - \ll V_N \gg^2). \qquad (46)$$

The free energy density $\mathcal{F}^{(0)} + \mathcal{F}'$ obtained is consistent with that adopted in the phenomenology theory of Ginzberg-Landau.[7−10] The only difference is that the parameters are statistical averages obtained by using the molecular theory, and they are relevant to temperature in principle, such as $\ll V_N \gg$ and $\ll V_X \gg$ etc. Yet the changes are very small in the temperature range of 1 K. Thus, using the molecular theory, we deduce the free energy of the blue phase.

5. Order-parameter tensor and self-consistent equations for BPI and BPII

Now we calculate the parameters of the order-parameter tensor according to the interaction potential among molecules, i.e. figure out $\varepsilon_{(200)}$, $\varepsilon_{(110)}$, $\varepsilon_{(211)}$ and q for BPI and $\varepsilon_{(100)}$, $\varepsilon_{(110)}$ and q for BPII. The method (the basic principle) for calculating the above parameters is similar to the one used in nematic phase theory, in which the scalar order-parameter S ($S =< P_2(\cos\theta) >$) is figured out. We call it the self-consistent method and explain it as follows.

From Eq.(2)

$$Q_{\mu\nu} = \frac{3}{2} < \widehat{\Omega}_\mu \widehat{\Omega}_\nu > -\frac{1}{2}\delta_{\mu\nu}, \qquad (47)$$

where $\widehat{\Omega}_\mu$ is the molecular orientation and $< \cdots >$ represents the statistical average. We should use the distribution function $P(\boldsymbol{X})$ to calculate the statistical average in Eq.(47). However, since

$$\int^{\Delta} (\widehat{\Omega}_\mu \widehat{\Omega}_\nu) \Gamma P_0(\boldsymbol{X}) \mathrm{d}\boldsymbol{\rho} \mathrm{d}\widehat{\Omega} = 0,$$

(see Eqs.(28) and (29)) one can use $P_0(\boldsymbol{X})$, whose variables can be separated and denoted as in Eq.(18). So the actual distribution function is $g(\boldsymbol{R}, \widehat{\Omega})$; however, Eq.(20) shows that $g(\boldsymbol{R}, \widehat{\Omega})$ is relevant to $Q_{\mu\nu}$, thus Eq.(47) can determine the self-consistent equations of $Q_{\mu\nu}$. We know that $Q_{\mu\nu}$ is a function of $\boldsymbol{R}$, and $\varepsilon_{(200)}$ and $\varepsilon_{(110)}$ are constants and unrelated to $\boldsymbol{R}$. As a result, it is reasonable to choose a special $\boldsymbol{R}$ without affecting the result. The self-consistent equation of $Q_{\mu\nu}$ is

$$Q_{\mu\nu} = \int \left(\frac{3}{2}\widehat{\Omega}_\mu \widehat{\Omega}_\nu - \frac{1}{2}\delta_{\mu\nu}\right) g(\boldsymbol{R}_i, \widehat{\Omega}_i) \mathrm{d}\widehat{\Omega}_i, \qquad (48)$$

where $\boldsymbol{R}$, the local self-consistent equations, has a special value.

The local self-consistent equations of the order-parameter tensors for BPI and BPII are as follows. For convenience, we discuss BPII first.

5.1. The order-parameter tensor for BPII

From Eq.(5), we know that the values of $\varepsilon_{(100)}$, $\varepsilon_{(110)}$ and q determine the order-parameter tensor. As these parameters are independent of $\boldsymbol{R}$ (just as we have discussed above), some special point can be selected to deduce the relationship between these parameters and molecular interaction potential. For simplicity, we choose point A where $\boldsymbol{R_A}$ satisfies the equation $q\boldsymbol{R_A} = \left(\frac{\pi}{2}, 0, 0\right)$. The order-parameter tensor at point A is

$$Q_{\mathrm{BPII}}\Big|_A = \begin{pmatrix} 2\varepsilon_{(110)} & 0 & 0 \\ 0 & -\varepsilon_{(110)} - \varepsilon_{(100)} & 0 \\ 0 & 0 & \varepsilon_{(100)} - \varepsilon_{(110)} \end{pmatrix}. \qquad (49)$$

Similarly, the distribution functions $f(\boldsymbol{R_A}, \boldsymbol{\rho})$ and $g(\boldsymbol{R_A}, \widehat{\Omega})$ at point A are obtained. Substituting Eq.(5) into Eqs.(42), (43) and letting $\boldsymbol{R} = \boldsymbol{R_A}$, we obtain the expressions of $< \omega_N >$ and $< \omega_X >$ at point A. Then substituting them into Eq.(19), we have

$$f(\boldsymbol{R_A}, \boldsymbol{\rho}) = \frac{1}{Z_r}\exp\left\{-\beta\left[z < V_0 > + < V_N > \left(\frac{2}{3}z(4\varepsilon_{(100)}^2 + 6\varepsilon_{(110)}^2) - \frac{1}{9}za^2(51076\varepsilon_{(100)}^2 + 153230\varepsilon_{(110)}^2)\right) - < V_X > \left(\frac{4}{27}za^2q(4\varepsilon_{(100)}^2 + 6\sqrt{2}\varepsilon_{(110)}^2)\right)\right]\right\}, \qquad (50)$$

and

$$g(\boldsymbol{R}_{\boldsymbol{A}},\widehat{\Omega}) = \frac{1}{Z_\Omega}\exp\Bigg\{-\beta\Bigg[\ll V_N\gg\Bigg(\frac{2}{3}z\Bigg(3\varepsilon_{(110)}\widehat{\Omega}_x^2-\frac{3}{2}\widehat{\Omega}_y^2(\varepsilon_{(100)}+\varepsilon_{(110)})-3\varepsilon_{(100)}\widehat{\Omega}_y\widehat{\Omega}_z$$
$$+\frac{3}{2}\Omega_z^2(\varepsilon_{(100)}-\varepsilon_{(110)})\Bigg)+\frac{1}{9}za^2(-76614\varepsilon_{(110)}\widehat{\Omega}_x^2+19154(2\varepsilon_{(110)}+\varepsilon_{(100)})\widehat{\Omega}_y^2$$
$$+38307\varepsilon_{(100)}\widehat{\Omega}_y\widehat{\Omega}_z+19154(2\varepsilon_{(110)}-\varepsilon_{(100)})\widehat{\Omega}_z^2)\Bigg)$$
$$+\ll V_X>>\frac{4}{27}za^2q\Bigg(\frac{3}{2}\widehat{\Omega}_y^2(\varepsilon_{(100)}+\sqrt{2}\varepsilon_{(110)})-3\sqrt{2}\varepsilon_{(110)}\widehat{\Omega}_x^2+3\varepsilon_{(100)}\widehat{\Omega}_y\widehat{\Omega}_z$$
$$+\frac{3}{2}(\sqrt{2}\varepsilon_{(110)}-\varepsilon_{(100)})\widehat{\Omega}_z^2\Bigg)\Bigg]\Bigg\}. \tag{51}$$

In addition, q can be obtained from minimizing the free energy. Supposing q can minimize $\mathcal{F}^{(0)}$ (the same method as in the phenomenology theory of Ginzberg–Landau [8]), we substitute Eq.(5) into Eq.(44) and obtain

$$q_{\mathrm{BPII}} = -\frac{2}{3}\frac{(\varepsilon_{(100)}^2+2\sqrt{2}\varepsilon_{(110)}^2)}{(\varepsilon_{(100)}^2+4\varepsilon_{(110)}^2)}\frac{\ll V_X\gg}{\ll V_N\gg}. \tag{52}$$

Using Eqs.(2) and (49) (the expression for BPII at point A), we obtain

$$-\varepsilon_{(100)}-\varepsilon_{(110)} = \int_{4\pi}\left[\left(\frac{3}{2}\widehat{\Omega}_y^2-\frac{1}{2}\right)g(\boldsymbol{R}_{\boldsymbol{A}},\widehat{\Omega})\right]\mathrm{d}\widehat{\Omega},$$
$$\varepsilon_{(100)}-\varepsilon_{(110)} = \int_{4\pi}\left[\left(\frac{3}{2}\widehat{\Omega}_z^2-\frac{1}{2}\right)g(\boldsymbol{R}_{\boldsymbol{A}},\widehat{\Omega})\right]\mathrm{d}\widehat{\Omega}. \tag{53}$$

We have deduced three self-consistent equations including $\varepsilon_{(100)}$, $\varepsilon_{(110)}$ and q (see Eqs.(52) and (53)), which determine the order-parameter tensor's parameters for BPII.

5.2. The order-parameter tensor for BPI

From Eq.(4), we can find that the order-parameter tensor is determined by four parameters $\varepsilon_{(200)}$, $\varepsilon_{(110)}$, $\varepsilon_{(211)}$ and q. Using the same method as the above, and selecting a special point B where $\boldsymbol{R}_{\mathrm{B}}$ satisfies equation $q\boldsymbol{R}_{\mathrm{B}} = \left(\frac{\pi}{2},0,0\right)$ (as q for BPI may be different from q for BPII, we name it point B), we obtain

$$Q_{\mathrm{BPI}}\Big|_{\mathrm{B}} = \begin{pmatrix} -\varepsilon_{(110)}-\frac{4}{3}\sqrt{6}\varepsilon_{(211)} & 0 & -\varepsilon_{(110)}(\sqrt{2}-1)-\frac{4}{3}\varepsilon_{(211)} \\ 0 & -2\varepsilon_{(200)}-\varepsilon_{(110)}+\frac{4}{3}\sqrt{6}\varepsilon_{(211)} & 0 \\ -\varepsilon_{(110)}(\sqrt{2}-1)-\frac{4}{3}\varepsilon_{(211)} & 0 & 2\varepsilon_{(200)}+2\varepsilon_{(110)} \end{pmatrix}, \tag{54}$$

$$f(\boldsymbol{R}_{\mathrm{B}},\boldsymbol{\rho}) = \frac{1}{Z_r}\exp\Bigg\{-\beta\Bigg[z<V_0>+<V_N>\Bigg(\frac{2}{3}z(24.9\varepsilon_{(211)}^2+6.344\varepsilon_{(110)}^2+8\varepsilon_{(200)}^2$$
$$+12\varepsilon_{(200)}\varepsilon_{(110)}-13.064\varepsilon_{(200)}\varepsilon_{(211)}+2.208\varepsilon_{(110)}\varepsilon_{(211)})+\frac{1}{9}za^2(408608\varepsilon_{(200)}^2$$
$$-161991\varepsilon_{(110)}^2-1906800\varepsilon_{(211)}^2+834067.5873\varepsilon_{(200)}\varepsilon_{(211)}-459684\varepsilon_{(200)}\varepsilon_{(110)}$$
$$-112840.5832\varepsilon_{(110)}\varepsilon_{(211)})\Bigg)+<V_X>\frac{4}{27}za^2q(-1.6569\varepsilon_{(110)}^2+8.7092\varepsilon_{(211)}^2$$
$$-7.6751\varepsilon_{(110)}\varepsilon_{(211)})\Bigg]\Bigg\}, \tag{55}$$

$$g(\boldsymbol{R}_{\rm B},\widehat{\Omega}) = \frac{1}{Z_\Omega}\exp\Bigg\{-\beta\Bigg[\ll V_N\gg\left(\frac{2}{3}z((-3\sqrt{2}\varepsilon_{(110)}\widehat{\Omega}_y - 3\sqrt{2}\varepsilon_{(110)}\widehat{\Omega}_z + 4\varepsilon_{(211)}\widehat{\Omega}_y + 4\varepsilon_{(211)}\widehat{\Omega}_z)\widehat{\Omega}_x - 3\sqrt{2}\varepsilon_{(110)}\widehat{\Omega}_y\widehat{\Omega}_z + 4\varepsilon_{(211)}\widehat{\Omega}_y\widehat{\Omega}_z) + \frac{1}{9}za^2((38307\varepsilon_{(110)} + 153228\sqrt{6}\varepsilon_{(211)})\widehat{\Omega}_x^2 + (38307\varepsilon_{(110)} - 153228\sqrt{6}\varepsilon_{(211)} + 153228\varepsilon_{(200)}^2)\widehat{\Omega}_y^2 - (153228\varepsilon_{(200)} + 76614\varepsilon_{(110)})\widehat{\Omega}_z^2 + (-76614\varepsilon_{(110)} + 306456\varepsilon_{(211)} + 76614\sqrt{2}\varepsilon_{(110)})\widehat{\Omega}_z\widehat{\Omega}_x)\right) + \ll V_X\gg\frac{4}{27}za^2q\left(\left(\frac{3}{2}\sqrt{2}\varepsilon_{(110)} + 12\varepsilon_{(211)}\right)\widehat{\Omega}_x^2 + \left(3\varepsilon_{(200)} + \frac{3}{2}\sqrt{2}\varepsilon_{(110)} - 12\varepsilon_{(211)}\right)\widehat{\Omega}_y^2 - (6\varepsilon_{(200)} + 3\sqrt{2}\varepsilon_{(110)})\widehat{\Omega}_z^2 + (4\sqrt{6}\varepsilon_{(211)} + (6-3\sqrt{2})\varepsilon_{(110)})\widehat{\Omega}_x\widehat{\Omega}_z + \varepsilon_{(200)}\right)\Bigg]\Bigg\}, \tag{56}$$

$$q_{\rm BPI} = -\frac{1}{3}\frac{\left(10\varepsilon_{(200)}^2 + 11\sqrt{2}\varepsilon_{(110)}^2 + \frac{70}{3}\sqrt{6}\varepsilon_{(211)}^2\right)}{(10\varepsilon_{(200)}^2 + 11\varepsilon_{(110)}^2 + 72\varepsilon_{(211)}^2)}\frac{\ll V_X\gg}{\ll V_N\gg}, \tag{57}$$

$$\begin{aligned} -2\varepsilon_{(200)} - \varepsilon_{(110)} + \frac{4}{3}\sqrt{6}\varepsilon_{(211)} &= \int_{4\pi}\left[\left(\frac{3}{2}\widehat{\Omega}_y^2 - \frac{1}{2}\right)g(B,\widehat{\Omega})\right]{\rm d}\widehat{\Omega}, \\ 2\varepsilon_{(200)} + 2\varepsilon_{(110)} &= \int_{4\pi}\left[\left(\frac{3}{2}\widehat{\Omega}_z^2 - \frac{1}{2}\right)g(B,\widehat{\Omega})\right]{\rm d}\widehat{\Omega}, \\ -\varepsilon_{(110)}(\sqrt{2}-1) - \frac{4}{3}\varepsilon_{(211)} &= \int_{4\pi}\left[\left(\frac{3}{2}\widehat{\Omega}_x\widehat{\Omega}_z\right)g(B,\widehat{\Omega})\right]{\rm d}\widehat{\Omega}. \end{aligned} \tag{58}$$

Four self-consistent equations determine four parameters $\varepsilon_{(200)}$, $\varepsilon_{(110)}$, $\varepsilon_{(211)}$ and $q_{\rm BPI}$ (see Eqs.(57) and (58)).

6. Calculated results

When we use numerical methods to solve the self-consistent Eqs.(52), (53) for BPII and Eqs.(57), (58) for BPI, the interaction potential between molecules (see Eq.(6)) adopted is consistent with that in Refs.[21] and [26–30]:

$$V_0(r_{ij}) = \mu_0\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{59}$$

$$V_N(r_{ij}) = -\mu_N\left(\frac{\sigma}{r_{ij}}\right)^{6}, \tag{60}$$

$$V_X(r_{ij}) = -\frac{\mu_X}{r_{ij}}\left(\frac{\sigma}{r_{ij}}\right)^{7}, \tag{61}$$

where σ, μ_0, μ_N and μ_X are all constants, called potential parameters. When we find the parameters of the order-parameter tensor using the self-consistent equations, the first statistical average $<V_\tau>$ $(\tau = 0, N, X)$ should be calculated first. In the cell model of an ordinary liquid, the Lennard-Jones and Devonshire (LJD) theory [31] is a good approximation. We use the smearing-average method of LJD liquid theory,[31] and obtain

$$\begin{aligned} <V_0> &= \mu_0\left[\left(\frac{\sigma}{a}\right)^{12} l\left(\frac{\rho^2}{a^2}\right) - \left(\frac{\sigma}{a}\right)^{6} m\left(\frac{\rho^2}{a^2}\right)\right], \\ <V_N> &= -\mu_N\left(\frac{\sigma}{a}\right)^{6} m\left(\frac{\rho^2}{a^2}\right), \\ <V_X> &= -\mu_X\frac{\sigma^7}{a^8} n\left(\frac{\rho^2}{a^2}\right), \end{aligned} \tag{62}$$

where the expressions of $l(x)$, $n(x)$ and $m(x)$ are

$$\begin{aligned} l(x) &= (1 + 12x + 25.2x^2 + 12x^3 + x^4)(1-x)^{-10} - 1, \\ m(x) &= (1+x)(1-x)^{-4} - 1, \\ n(x) &= \left(1 + \frac{10}{3}x + x^2\right)(1-x)^{-6} - 1. \end{aligned} \tag{63}$$

As soon as $<V_\tau>$ is figured out, the mass centre distribution functions for BPII $f(\boldsymbol{R_A}, \boldsymbol{\rho})$ and for BPI $f(\boldsymbol{R_B}, \boldsymbol{\rho})$ are obtained. Using $f(\boldsymbol{R_A}, \boldsymbol{\rho})$ and $f(\boldsymbol{R_B}, \boldsymbol{\rho})$, we calculate the second average $\ll V_\tau \gg$ (the first average is $<V_\tau>$ $(\tau = 0, N, X)$), and obtain the orientation distribution functions $g(\boldsymbol{R_A}, \widehat{\Omega})$ and $g(\boldsymbol{R_B}, \widehat{\Omega})$, which are functions of $\varepsilon_{(100)}$, $\varepsilon_{(110)}$, $q_{\rm BPII}$ for BPII and of $\varepsilon_{(200)}$, $\varepsilon_{(110)}$, $\varepsilon_{(211)}$, $q_{\rm BPI}$ for BPI.

As we solve the self-consistent equations (see Eqs.(52), (53) and (57), (58)), for $\widehat{\Omega}$ we adopt the spherical coordinates

$$\begin{aligned}\widehat{\Omega}_x &= \sin\theta\cos\varphi,\\ \widehat{\Omega}_y &= \sin\theta\sin\varphi,\\ \widehat{\Omega}_z &= \cos\theta,\\ \mathrm{d}\widehat{\Omega} &= \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi.\end{aligned} \tag{64}$$

We define a reduced temperature τ as

$$\tau = \frac{1}{\beta\mu_0} = \frac{k_{\mathrm{B}}T}{\mu_0}. \tag{65}$$

The results are obtained as follows.

1) The numerical values of parameters for the order-parameter tensor for BPII

From Figs.1 and 2, it can be seen that $\varepsilon_{(100)}$ and $\varepsilon_{(110)}$, the two parameters of Q_{BPII}, increase with the increase of τ, and that $\varepsilon_{(110)}$ has a rapid increase as compared with $\varepsilon_{(100)}$. In order to find the relationship between $\varepsilon_{(110)}$, $\varepsilon_{(100)}$ and the potential parameters μ_N/μ_0, μ_X/μ_N, we have tried different values of μ_N/μ_0 and μ_X/μ_N and found that the figures are little sensitive to μ_X/μ_N. Thus, we select different μ_N/μ_0 values while keeping μ_X/μ_N invariant. As seen from Fig.2, with the decrease of μ_N/μ_0, the values of $\varepsilon_{(100)}$ and $\varepsilon_{(110)}$ increase at a certain τ. However, we do not find these potential parameters have much effect on the whole figures of the curves $\varepsilon_{(100)}$ and $\varepsilon_{(110)}$. It seems that these figures have just a little excursion towards the left when μ_N/μ_0 decreases.

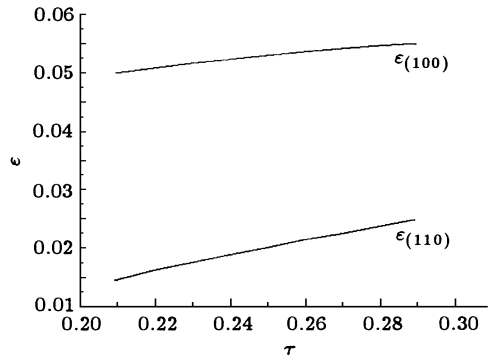


Fig.1. Numerical values of the parameters $\varepsilon_{(100)}$ and $\varepsilon_{(110)}$ for Q_{BPII} versus the reduced temperature τ. The values of potential parameters adopted are: μ_N/μ_0=0.5, μ_X/μ_N=0.63, $\sigma/a = 1.0$.

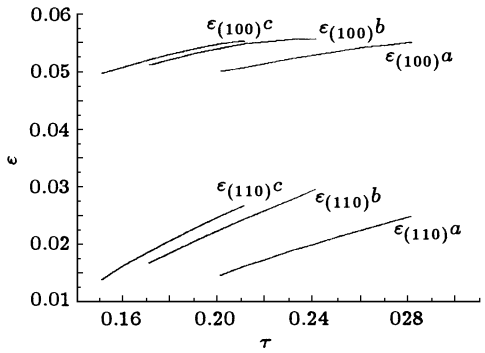


Fig.2. Numerical values of the parameters $\varepsilon_{(100)}$ and $\varepsilon_{(110)}$ for Q_{BPII} versus the reduced temperature τ. The values of potential parameters adopted are: curve a: $\mu_N/\mu_0 = 0.5, \mu_X/\mu_N = 0.63, \sigma/a = 1.0$; curve b: $\mu_N/\mu_0 = 0.33, \mu_X/\mu_N = 0.63, \sigma/a = 1.0$; curve c: $\mu_N/\mu_0 = 0.29$, $\mu_X/\mu_N = 0.63, \sigma/a = 1.0$.

2) The numerical values of parameters for the order-parameter tensor for BPI

The numerical values of q, $\varepsilon_{(110)}$, $\varepsilon_{(200)}$ and $\varepsilon_{(211)}$ versus τ for Q_{BPI} can be seen from Figs.3, 4 and 5. One can see that the curves of $\varepsilon_{(200)}$, $\varepsilon_{(110)}$ and $\varepsilon_{(211)}$ are almost horizontal lines for lower reduced temperatures τ, i.e. there are minor changes with the increase of lower τ. Moreover, the value of $\varepsilon_{(110)}$ is very close to the value of $\varepsilon_{(200)}$. However, for larger values of τ and beyond a certain value τ_{c}, the values of $\varepsilon_{(200)}$ and $\varepsilon_{(211)}$ become smaller and change rapidly; therefore, the lines of $\varepsilon_{(200)}$ and $\varepsilon_{(211)}$ drop beyond a certain point. These results mentioned above are relevant to the values of molecular-potential parameters.

As examples, we adopt the values of μ_N/μ_0 in Figs.3, 4 and 5 as 0.5, 0.33 and 0.29 respectively, and the calculated values of τ_{c} are 0.75, 0.60 and 0.55 in Figs.3, 4 and 5 respectively. So the value of molecular-potential parameter μ_N/μ_0 decreases when the value of τ_{c} decreases.

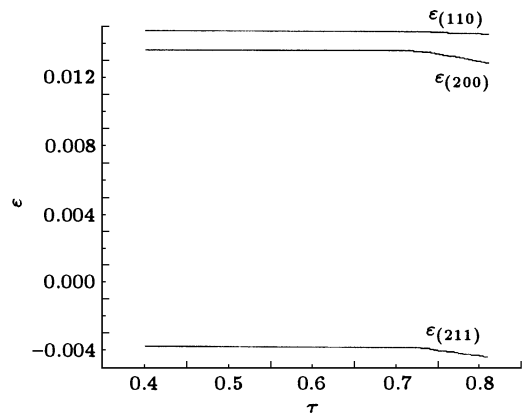


Fig.3. Numerical values of the parameters $\varepsilon_{(110)}$, $\varepsilon_{(200)}$ and $\varepsilon_{(211)}$ for Q_{BPI} versus the reduced temperature τ. The values of potential parameters adopted are: $\mu_N/\mu_0 = 0.5, \mu_X/\mu_N = 0.63, \sigma/a = 1.0$.

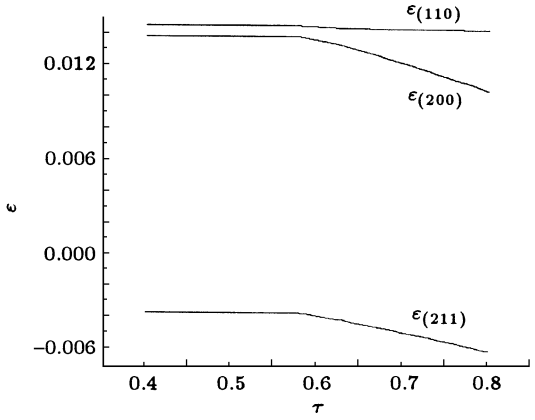


Fig.4. Numerical values of the parameters $\varepsilon_{(110)}$, $\varepsilon_{(200)}$ and $\varepsilon_{(211)}$ for $Q_{\rm BPI}$ versus the reduced temperature τ. The values of potential parameters adopted are: $\mu_N/\mu_0 = 0.33, \mu_X/\mu_N$ =0.63, $\sigma/a = 1.0$.

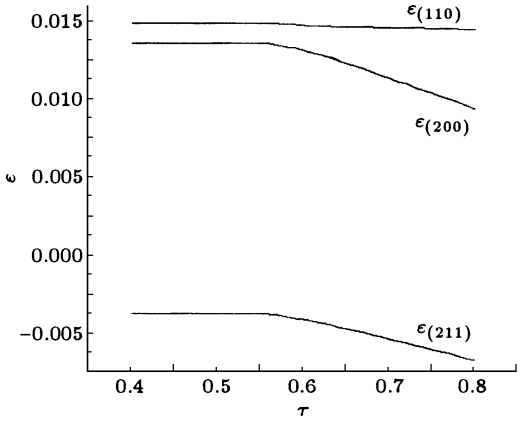


Fig.5. Numerical values of the parameters $\varepsilon_{(110)}$, $\varepsilon_{(200)}$ and $\varepsilon_{(211)}$ for $Q_{\rm BPI}$ versus the reduced temperature τ. The values of potential parameters adopted are: $\mu_N/\mu_0 = 0.29, \mu_X/\mu_N = 0.63, \sigma/a = 1.0$.

3) The values of q for BPII and BPI

In Fig.6, the curve of $q_{\rm BPII}$ increases slowly at first and looks like a horizontal line, however, when $\tau \geq 0.55$, it increases sharply, and when $\tau \geq 0.65$, it again becomes horizontal. Curve $q_{\rm BPI}$ increases slowly at first, but it begins to increase steadily when $\tau \geq 0.65$.

Note that all the calculated results described in 1), 2) and 3) are not sensitive to a variance of the value of potential parameter μ_X/μ_N, so we adopt $\mu_X/\mu_N = 0.63$ for all calculations.

Now we compare our calculated results with the experimental data.

a) The parameters for the order-parameter tensor

For a number of mixtures of cholesteryl nonanoate and cholesteryl chloride, experimental results [32,33] give the ratios of parameters of order-parameter tensors are on the average

$$|\varepsilon_{(100)}| : |\varepsilon_{(110)}| \approx 2.5 : 1, \quad \text{for BPII,}$$

and

$$|\varepsilon_{(110)}| : |\varepsilon_{(200)}| : |\varepsilon_{(211)}| \approx 1 : 1 : 0.33, \quad \text{for BPI.}$$

One can find from Figs.1–5 that our calculated results are in agreement with these experimental results.

b) The crystal constant $\dfrac{2\pi}{q}$

The experimental values of parameter q for BPII and BPI, i.e. $q_{\rm BPII}$ and $q_{\rm BPI}$, have the relations [33,34] $q_{\rm BPII} : q_{\rm BPI} \approx 1.13 : 1.3$ at lower temperatures and $q_{\rm BPII} : q_{\rm BPI} \approx 1.2 : 1.4$ at higher temperatures.

One can see also from Fig.5 that our calculated results are close to the experimental data.

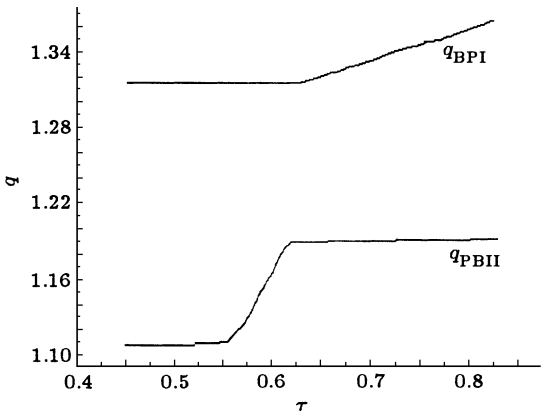


Fig.6. Values $q_{\rm BPII}$ and $q_{\rm BPI}$ versus the reduced temperature τ, The values of potential parameters adopted are: $\mu_N/\mu_0 = 0.5, \mu_X/\mu_N = 0.63, \sigma/a = 1.0$.

7. Discussion

Now, we discuss two problems as follows:

1) In this paper, we have calculated the parameters for the order-parameter tensors for BPI and BPII based on the expression Q (see Eqs.(4) and (5)). Equations (4) and (5) are reliable as in the following statements:

i) Their validity have been testified by experiments.

ii) Q can be obtained according to the expression of the free energy in phenomenology theory,[8] and the expression of the free energy has been obtained by using the microscopic theory in this paper. However, it is necessary to prove this form of Q theoretically.

2) As for the three subphases (BPI, BPII and BPIII), we have only discussed BPI and BPII, and BPIII is not concerned.

The above question is to be discussed in subsequent papers. We hope that the space group symmetries of BPI and BPII can be obtained by using the

first principle, and that the structure of BPIII and the mechanism of its formation can be clarified.

Appendix A: Entropy $S^{(0)}$ independent of $Q_{\mu\nu}$

The entropy expression $S^{(0)}$ is

$$S^{(0)} = \int_V s^{(0)} \mathrm{d}\boldsymbol{R}, \tag{A1}$$

$$s^{(0)}(\boldsymbol{R}) = -Dk_{\mathrm{B}} \int^{\Delta} P_0 \ln P_0 \mathrm{d}\boldsymbol{\rho} \mathrm{d}\widehat{\Omega}. \tag{A2}$$

Using Eqs.(9), (19) and (20), we obtain

$$s^{(0)}(\boldsymbol{R}) = -Dk_{\mathrm{B}}\{-\beta[<\nu_0> + 2<\nu_N><\omega_N> + 2<\nu_X><\omega_X>] - \ln Z_r - \ln Z_\Omega\}, \tag{A3}$$

where

$$Z_r = \int_\Delta \mathrm{d}\boldsymbol{\rho}_i \exp\{-\beta[v_0(i) + v_N <\omega_N> + v_X <\omega_X>]\}, \tag{A4}$$

$$Z_\Omega = \int_{4\pi} \mathrm{d}\widehat{\Omega}_i \exp\{-\beta[<\nu_N>\omega_N + <\nu_X>\omega_X]\}. \tag{A5}$$

Equations (A1), (A2) show that $S^{(0)}$ is a function of $Q_{\mu\nu}(\boldsymbol{R})$. In order to prove that $S^{(0)}$ is independent of $Q_{\mu\nu}(\boldsymbol{R})$, we need first to prove that the variation of $S^{(0)}$ with $Q_{\mu\nu}(\boldsymbol{R})$ is zero, i.e. $S^{(0)}(\boldsymbol{R})$ satisfies the Lagrange–Euler equation.

Considering $\dfrac{\partial s^{(0)}}{\partial Q_{\mu\nu}}$, we compute the derivative of $Q_{\mu\nu}$ in Eq.(A3),

$$\frac{\partial s^{(0)}}{\partial Q_{\mu\nu}} = -Dk_{\mathrm{B}}\left\{-\beta\left[\frac{\partial <\nu_0>}{\partial Q_{\mu\nu}} + 2\frac{\partial <\nu_N>}{\partial Q_{\mu\nu}} <\omega_N> + 2<\nu_N> \frac{\partial <\omega_N>}{\partial Q_{\mu\nu}} + 2\frac{\partial <\nu_X>}{\partial Q_{\mu\nu}} <\omega_X> + 2<\nu_X> \frac{\partial <\omega_X>}{\partial Q_{\mu\nu}}\right] - \frac{1}{Z_r}\frac{\partial Z_r}{\partial Q_{\mu\nu}} - \frac{1}{Z_\Omega}\frac{\partial Z_\Omega}{\partial Q_{\mu\nu}}\right\}, \tag{A6}$$

From Eqs.(A4), (A5), we have

$$\frac{1}{Z_r}\frac{\partial Z_r}{\partial Q_{\mu\nu}} = -\beta\left[\frac{\partial <\nu_0>}{\partial Q_{\mu\nu}} + \frac{\partial <\nu_N>}{\partial Q_{\mu\nu}} <\omega_N> + <\nu_N> \frac{\partial <\omega_N>}{\partial Q_{\mu\nu}} + \frac{\partial <\nu_X>}{\partial Q_{\mu\nu}} <\omega_X> + <\nu_X> \frac{\partial <\omega_X>}{\partial Q_{\mu\nu}}\right], \tag{A7}$$

$$\frac{1}{Z_\Omega}\frac{\partial Z_\Omega}{\partial Q_{\mu\nu}} = -\beta\left[\frac{\partial <\nu_N>}{\partial Q_{\mu\nu}} <\omega_N> + <\nu_N> \frac{\partial <\omega_N>}{\partial Q_{\mu\nu}} + \frac{\partial <\nu_X>}{\partial Q_{\mu\nu}} <\omega_X> + <\nu_X> \frac{\partial <\omega_X>}{\partial Q_{\mu\nu}}\right]. \tag{A8}$$

Equations (39) and (40) are used to express ω_N and ω_X when Eq.(A5) is obtained. We expand $Q(j)_{\mu\nu}$ at $\boldsymbol{R}_i$ using Taylor expansion, and substitute Eqs.(A7) and (A8) into Eq.(A6), and obtain

$$\frac{\partial s^{(0)}}{\partial Q_{\mu\nu}} = 0.$$

Using the same process, we obtain

$$\frac{\partial s^{(0)}}{\partial\left(\dfrac{\partial Q_{\mu\nu}}{\partial R_a}\right)} = 0,$$

thus, $s^{(0)}(\boldsymbol{R})$ satisfies the Lagrange–Euler equation, and we finally prove that entropy $S^{(0)}$ is independent of $Q_{\mu\nu}$.

References

[1] Belyakov V A and Dmitrienko V E 1985 *Sov. Phys. Usp.* **28** 535

[2] Wright D C and Mermin N D 1989 *Rev. Mod. Phys.* **61** 385

[3] Hornreich R M and Shtrkman S 1980 *J. Phys.* (Paris) **41** 335

[4] Armitage A and Price F P 1975 *J. Phys.* (Paris) **36** C133
Armitage A and Price F P 1977 *J. Chem. Phys.* **66** 3414

[5] Kleiman R N, Pindak D J and Taborek P 1984 *Phys. Rev. Lett.* **53** 2137
Thoen J 1987 *Phys. Rev.* A **37** 1754

[6] Crooker P P 1989 *Liq. Cryst.* **5** 751

[7] Grebel H, Hornreich R M and Shtrkman S 1984 *Phys. Rev.* A **30** 3264

[8] De Gennes P G 1971 *Mol. Cryst. Liq. Cryst.* **12** 193

[9] Longa L, Fink W and Trebin H R 1994 *Phys. Rev.* E **50** 3841

[10] Flack J H, Crooker P P and Svoboda R C 1982 *Phys. Rev.* A **26** 723

[11] Xie Y Z 1988 *The Physics of Liquid Crystal* (Beijing: Science Press) pp401–507 (in Chinese)

[12] Luckhurst G R and Gray G W 1979 *The Molecular Physics of Liquid Crystals* (London: Academic)

[13] Wu H S and Yang G C 1960 *Acta Phys. Sin.* **16** 143 (in Chinese)

[14] Yang G C, Zhang Z D and Zhao T J 1995 *Acta Phys. Sin.* **44** 513 (in Chinese)
[15] Wright D C and Mermin N D 1989 *Rev. Mod. Phys.* **61** 385
[16] Yang G C and Qian X Z 1993 *Acta Phys. Sin.* **42** 551 (in Chinese)
[17] Yang G C and Zhang Z D 1988 *Acta Phys. Sin.* **37** 635 (in Chinese)
[18] Brazovskii S A and Filev V M 1978 *Sov. Phys. JETP* **48** 573
[19] Hornreich R M, Kugler M and Shtrkman S 1982 *Phys. Rev. Lett.* **48** 3246
[20] Meiboom S, Sethna J P and Brinkman W F 1983 *Phys. Rev.* A **27** 438
[21] Luckhurst G R and Gray G W 1979 *The Molecular Physics of Liquid Crystals* (London: Academic) Chap 2
[22] Belyakov V A and Dmitrienko V E 1985 *Sov. Phys. Usp.* **28** 545
[23] Lin Liu Y R and Lee M A 1983 *Phys. Rev.* A **28** 2580
[24] Lin Liu Y R, Shih Y M, Woo C W and Tan H T 1976 *Phys. Rev.* A **14** 445
[25] Kirkwood J G 1950 *J. Chem. Phys.* **18** 380
[26] Rajan V T and Woo C W 1987 *Phys. Rev.* A **17** 382
[27] Nakagawa M and Akhane T 1982 *Mol. Cryst. Liq. Cryst.* **90** 53
[28] Van der Meer B W, Votogen G, Dekker A J and Yama G J 1976 *J. Chem. Phys.* **65** 3935
[29] Tao R, Shen P and Lin Z F 1993 *Phys. Rev. Lett.* **70** 1271
[30] Luckhurst G R and Zannonic C 1977 *Nature* **267** 412
[31] Lennard-Jones J E and Deoonshire A F 1937 *Proc. R. Soc.* (London) A **163** 53
Lennard-Jones J E and Devonshire A F 1938 *Proc. R. Soc.* (London) A **165** 1
[32] Kizel' V A and Prokhorov V V 1984 *Zh. Eksp. Teor. Fiz.* **87** 450
[33] Meiboom S and Sammon M 1980 *Phys. Rev. Lett.* **44** 882
Meiboom S and Sammon M 1981 *Phys. Rev.* A **24** 468
[34] Johnson D L, Flack J H and Crooker P P 1980 *Phys. Rev. Lett.* **45** 641
Johnson D L, Flack J H and Crooker P P 1981 *Phys. Lett.* A **82** 247