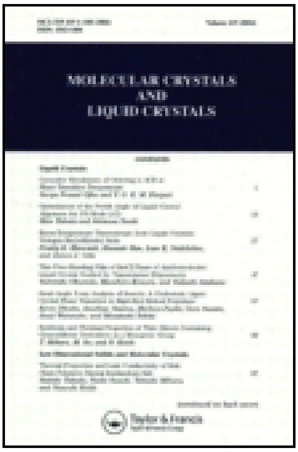

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Microscopic Approach to Theory of Biaxial Nematic Liquid Crystals

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MICROSCOPIC APPROACH TO THEORY OF BIAXIAL NEMATIC LIQUID CRYSTALS

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Abstract Microscopic description of biaxial nematic liquid crystals based on theory of invariants is presented. Full set of basic functions relevant to biaxial nematics is given. Soft potential of Lennard-Jones type is applied for description of intermolecular interactions. The isotropic-symmetry-breaking bifurcations are studied. Detailed computations for a simple model are presented.

1. INTRODUCTION

The existing models describing properties of biaxial nematics liquid crystals (BNLC) are generalizations of the Onsager theory with new kinds of intermolecular potential and with new order parameters. In paper by Straley[1] a potential was quadratic in the relative directions cosines and the four order parameters were ensemble averages of the four functions with the distribution function. In the work of Mulder[2] the detailed calculations for hard spheroplatelet fluid were presented and the pair-excluded volume at fixed relative orientation was used as an effective interaction. The set of symmetry-adapted functions was introduced as well.

The present paper provides a more complete description of BNLC by taking into account the complete set of basic functions. Earlier papers omitted some of them. The reason is that an inversion (which is symmetry element of biaxial molecules) is not properly adapted to the formalism of rotation matrix elements.

In this paper the intermolecular interactions are described by pair interaction potential more realistic in the comparison to models which have been used in the earlier papers. Soft potential of the Lennard-Jones type is used, in which a dependence on relative orientations and direction of the vector between centres of molecules is included.

Our main result is the formalism which allows description of BNLC starting from the microscopic potential and getting predictions of the existence of different phases.

The paper is organized as follows. In Sec. 2 we describe the intermolecular potential and its symmetries. In Sec. 3 the expressions for the one particle function is given. Sec.4 deals with the analysis of bifurcations of the stationary phase equations of the free energy functional. An exemplary analytical and numerical computations for a simple model are carried out in Sec. 5. Some comments on the theory are given in the concluding Sec. 6. In an appendix A full description of the basic functions is given and in an appendix B we present some analytical results concerning kernel of integral equation.

2. DESCRIPTION OF POTENTIAL

In our theory we assume that only pair interactions are present. The interaction between two biaxial molecules can be described by modified Lennard-Jones potential energy

$$V_{12}=4\,\varepsilon\,[(\sigma/r)^m-(\sigma/r)^n]\,, \qquad (2.1)$$

where $\vec{r}_i$ is the position of molecule i, $\vec{r}=\vec{r}_1-\vec{r}_2$, r denotes the length of $\vec{r}$, $\vec{u}$=(sinθ cosφ, sinθ sinφ, cosθ) is the unit vector in direction of $\vec{r}$, the parameter ε measures the minimum of V_{12}, $R_i=(\varphi_i, \theta_i, \psi_i)$ are the three Euler angles that define the orientation of molecule i in a reference frame, $R_u=(\varphi, \theta, \psi)$ are the three Euler angles for $\vec{u}$ (ψ is included for the sake of future calculations; our formulae do not depend on its value), the parameter σ depends on R_1, R_2, R_u.

We require that V_{12} satisfies the following symmetry conditions:

(i) Translational invariance - already satisfied, because V_{12} depends on r.

(ii) Rotational invariance - V_{12} should not depend on a choice of the reference frame. This means that for any rotation R

$$\sigma(RR_1, RR_2, RR_u)=\sigma(R_1, R_2, R_u)\,. \qquad (2.2)$$

(iii) Permutation of molecules should leave V_{12} invariant, therefore

$$\sigma(R_2, R_1, R_{-u})=\sigma(R_1, R_2, R_u), \qquad (2.3)$$

where $R_{-u}=(\varphi+\pi, \pi-\theta, \psi)$.

(iv) V_{12} must be real, therefore σ must be real.

(v) The symmetry operations on the individual molecules should leave the potential V_{12} (and σ) invariant (biaxial molecules have D_{2h} symmetry group).

Keeping in mind conditions (2.2) and (2.3) we can use for σ the expression proposed by Blum and Torruella[3] (which is evidently invariant under rotations and translations):

$$\sigma(R_1, R_2, R_u)=\sum_{jkl}\sum_{\mu\nu} g_{\mu\nu}^{jkl} \sum_{\rho\sigma\lambda} \begin{pmatrix} j & k & l \\ \rho & \sigma & \lambda \end{pmatrix} D^{(j)}_{\rho\mu}(R_1)\, D^{(k)}_{\sigma\nu}(R_2)\, D^{(l)}_{\lambda 0}(R_u)\,, \tag{2.4}$$

where $\begin{pmatrix} j & k & l \\ \rho & \sigma & \lambda \end{pmatrix}$ are the 3-j symbols and where $D^{(j)}_{\mu\nu}$ are standard rotation matrix elements[4]. Now we apply for σ the conditions (iii), (iv) and (v). From (v) we find the following relations (see appendix A):

$$\sigma(R_1R_z(\pi), R_2, R_u)=\sigma(R_1, R_2R_z(\pi), R_u)=\sigma(R_1, R_2, R_u), \tag{2.5}$$

$$\sigma(R_1R_y(\pi), R_2, R_u)=\sigma(R_1, R_2R_y(\pi), R_u)=\sigma(R_1, R_2, R_u). \tag{2.6}$$

As a result we obtain several conditions for coefficients $g_{\mu\nu}^{jkl}$:

$$g_{\mu\nu}^{jkl} \neq 0 \text{ only if } \mu,\ \nu \text{ are even}, \tag{2.7}$$

$$g_{-\mu\nu}^{jkl}=(-1)^j\, g_{\mu\nu}^{jkl}\,, \tag{2.8}$$

$$g_{\mu-\nu}^{jkl}=(-1)^k\, g_{\mu\nu}^{jkl}\,, \tag{2.9}$$

$$(g_{\mu\nu}^{jkl})^*=(-1)^l\, g_{\mu\nu}^{jkl}\,, \tag{2.10}$$

$$g_{\nu\mu}^{kjl}=(-1)^{j+k}\, g_{\mu\nu}^{jkl}\,. \tag{2.11}$$

In Sec. 5 we will show how $g_{\mu\nu}^{jkl}$ can be determined for given kind of molecules.

There is an opinion in the literature[3] that when an inversion is taken into account then j must be even. This opinion is not true and we will explain it in Sec. 3

3. THE ONE PARTICLE DISTRIBUTION FUNCTION

We base our considerations on the free energy F=U-TS expressed by the one particle distribution function ρ. The similar formula was originally derived as the cluster expansion for the uniaxial systems[5]. Extension to a system of biaxial molecules formally has the same form[5]:

$$\beta F=\int d(1)\,\rho(1)\,\{\ln[\rho(1)\Lambda_6]-1\}-\frac{1}{2}\int d(1)d(2)\,f_{12}\,\rho(1)\,\rho(2), \qquad (3.1)$$

where $(1)=(\bar{r}_1, \varphi_1, \theta_1, \psi_1)$, $d(1)=d^3r_1\,dR_1=d^3r_1\,d\varphi_1\,d\theta_1\,\sin\theta_1\,d\psi_1$, $f_{12}=\exp(-\beta V_{12})-1$,

$\beta=1/(k_BT)$, $\Lambda_6=\frac{1}{h^6}\left(\frac{2\pi}{\beta}\right)^3\sqrt{m^3J_xJ_yJ_z}$, m is the mass of the molecule, J_x, J_y, J_z are the three moments of inertia, N is a number of particles in volume V and the normalization is $\int d(1)\,\rho(1)=N$.

We have derived the formula (3.1) for any particles with three rotational degrees of freedom in the thermodynamic limit ($N\to\infty$, $V\to\infty$, N/V=const) from the BBGKY hierarchy[6]. We truncated the equations of the hierarchy writing the two partictle probability density in terms of the one particle probability densities.

The uniform distribution ρ does not depend on the position of the molecule, so $\rho(1)=\rho(R_1)$. The distribution ρ for which (3.1) is at minimum should satisfy the following equation

$$\ln[\rho(1)\Lambda_6]-\int d(2)\,f_{12}\,\rho(2)=\text{const}\,. \qquad (3.2)$$

It can be proved that constant in the equation (3.2) is equal βμ, where μ(T, V, N) is the chemical potential. For convenience the new function $f(R_1)=\rho(R_1)V/N$ is introduced. It is normalized as follows:

$$\int dR\, f(R)=1, \qquad (3.3)$$

and satisfies the equation

$$\ln f(R_1)-\lambda\int dR_2\,K(R_1, R_2)\,f(R_2)=\text{const}, \qquad (3.4)$$

the kernel of this integral equation is given by

$$K(R_1, R_2)=\int dR_u\,[\sigma(R_1, R_2, R_u)/\sigma_0]^3/(2\pi), \qquad (3.5)$$

$$\lambda=\sigma_0^3\,B(T^*)\,\frac{N}{V}, \qquad (3.6)$$

$$T^*=\frac{1}{\beta\varepsilon}\,, \tag{3.7}$$

$$\sigma^3\, B(T^*)=\int d\, r\, r^2\, f_{12}\,, \tag{3.8}$$

where σ_0 is a parameter (a length).

Properties of the kernel K which follow from its definition (3.5) are:

(i) $K(RR_1, RR_2)=K(R_1, R_2)$ for any rotation R.

(ii) $K(R_2, R_1)=K(R_1, R_2)$.

(iii) $K(R^{-1}, 0)=K(R, 0)$ from (i) and (ii).

(iv) The symmetry operations on the individual molecules leave K invariant.

(v) K is real.

We require that f has the following properties:

(i) f is real

$$f(R)^*=f(R). \tag{3.9}$$

(ii) The symmetry operations (from the D_{2h} group) on the single molecule should leave f invariant

$$f(RR_y(\pi))=f(RR_z(\pi))=f(R). \tag{3.10}$$

(iii) The symmetry operations (from the D_{2h} group) on the whole phase should leave f invariant

$$f(R_y(\pi)R)=f(R_z(\pi)R)=f(R). \tag{3.11}$$

Above considerations show that K and f can be expanded into series of basic functions $F^{(j)}_{\mu\nu}$ (see appendix A):

$$K(R, 0)=\sum_j\sum_{\mu\nu} K^j_{\mu\nu}\, F^{(j)}_{\mu\nu}(R)\,, \tag{3.12}$$

$$\ln f(R)=\sum_j\sum_{\mu\nu} S^j_{\mu\nu}\, F^{(j)}_{\mu\nu}(R)\,. \tag{3.13}$$

From the property (iii) of the kernel and from the property (A.3) of the $F^{(j)}_{\mu\nu}$ functions it follows that some coefficients are equal:

$$K^j_{\nu\mu}=K^j_{\mu\nu}\,. \tag{3.14}$$

We can obtain the coefficients $K^{j}_{\mu\nu}$ and $S^{j}_{\mu\nu}$ from (3.12) and (3.13) using the orthogonality relations (A.2). From (3.4) we derive the following set of equations for $S^{j}_{\mu\nu}$ $(j\neq 0)$:

$$S^{j}_{\mu\nu}=\lambda \int dR\ f(R) \sum_{\rho} K^{j}_{\rho\nu}\, F^{(j)}_{\mu\rho}(R) \left(\frac{1}{2}\right)^{\delta_{\nu 0}} . \tag{3.15}$$

Thus we can calculate $S^{j}_{\mu\nu}$ from (3.15) and (3.3) by means of numerical methods.

Now we give some comments on D_{2h} symmetry group. It is a direct product of two subgroups: D_2 and $H=\{E, C_i\}$, where E is the unit of the group D_{2h} and C_i denotes an inversion. For the D_2 symmetry group we can choose two generators: $R_y(\pi)=(0, \pi, 0)$, $R_z(\pi)=(\pi, 0, 0)$ and for the group H there is one generator C_i (see the appendix A).

Let $R=(\varphi, \theta, \psi)$ denotes the orientation of a molecule. We give description of the three generators as functions in terms of the Euler angles:

$$R\to R_A=(\pi-\varphi,\ \pi-\theta,\ \pi+\psi) \text{ for } R_y(\pi), \tag{3.16}$$

$$R\to R_B=(\pi+\varphi,\ \theta,\ \psi) \text{ for } R_z(\pi), \tag{3.17}$$

$$R\to R_C=(\pi+\varphi,\ \pi-\theta,\ \pi-\psi) \text{ for } C_i . \tag{3.18}$$

The expression (3.18) is valid only if we consider objects which favour neither of two orientations of the physical space. We can write (3.16÷18) in terms of rotation matrix elements $D^{(j)}_{\mu\nu}$:

$$D^{(j)}_{\mu\nu}(R_A)=(-1)^{j+\mu}\ D^{(j)}_{-\mu,\nu}(R)=D^{(j)}_{\mu\nu}(R_y(\pi)R), \tag{3.19}$$

$$D^{(j)}_{\mu\nu}(R_B)=(-1)^{\mu}\ D^{(j)}_{\mu\nu}(R)=D^{(j)}_{\mu\nu}(R_z(\pi)R), \tag{3.20}$$

$$D^{(j)}_{\mu\nu}(R_C)=(-1)^{j+\nu}\ D^{(j)}_{\mu,-\nu}(R)=D^{(j)}_{\mu\nu}(RR_y(\pi)). \tag{3.21}$$

The expressions (3.19÷21) prove that according to (A.4) basic functions $F^{(j)}_{\mu\nu}$ can really describe objects with D_{2h} symmetry group. Functions $F^{(j)}_{\mu\nu}$ with even j are known in the literature thus we give an example of a function $F^{(j)}_{\mu\nu}$ with odd j:

$$F^{(3)}_{22}(R)=F^{(2)}_{00}(R)\,F^{(2)}_{22}(R)-F^{(2)}_{02}(R)\,F^{(2)}_{20}(R)\,. \qquad (3.22)$$

$F^{(3)}_{22}$ in the expression above confirms all required symmetry relations.

4. ANALYSIS OF BIFURCATIONS

In order to study physical solutions of the equations (3.15) we will study bifurcations around the isotropic solution (ISO). This analysis will give us an information about interesting domains of the parameter λ. It is convenient to use λ as a temperature parameter instead of the temperature T* (note that if T*→0 than λ→∞).

We know from the experiments that for biaxial particles system we can expect the nematic phase (NLC) or biaxial nematic phase (BNLC). Therefore we consider two phase transitions: ISO→NLC and ISO→BNLC (phase transition NLC→BNLC is far more complex to study in analysis of bifurcations). A physical solution always has lower the free energy F(T, V, N) (3.1) (note that {T, V, N} are our set of state variables).

For the case of the ISO→BNLC phase transition we assume that all coefficients $S^{j}_{\mu\nu}$ are small except S^{0}_{00}. Then from (3.13), (3.3) and (3.15) we find that

$$f(R)=\exp(S^{0}_{00})\{1+\sum_{j\neq 0}\sum_{\mu\nu}S^{j}_{\mu\nu}F^{(j)}_{\mu\nu}(R)\}\,, \qquad (4.1)$$

$$S^{0}_{00}=-\ln(8\,\pi^2)\,, \qquad (4.2)$$

$$\sum_{\rho}S^{j}_{\mu\rho}\left\{\frac{\lambda}{2j+1}K^{j}_{\rho\mu}\left(\frac{1}{2}\right)^{\delta_{\nu 0}}-\delta_{\rho\nu}\right\}=0. \qquad (4.3)$$

The eigenproblem (4.3) gives bifurcation points by set of different λ. For j=2k there are at most k+1 different λ (every λ is (k+1)-fold degenerate) whereas for j=2k+1 there are at most k different λ (and every λ is k-fold degenerate).

For the case of the ISO→NLC phase transition we have to consider once again symmetries of the function f in the nematic phase. f is real and particles have D_{2h} symmetry group so conditions (3.9) and (3.10) are true. But the whole phase has higher $D_{\infty h}$ symmetry group which is a direct product of two subgroups: D_∞ and $H=\{E, C_i\}$. For the D_∞ group we can choose generators: $R_y(\pi)=(0, \pi, 0)$, $R_z(\alpha)=(\alpha, 0, 0)$ for any α. Thus we have to replace (3.11) with

$$f(R_y(\pi)R)=f(R), \tag{4.4}$$

$$f(R_z(\alpha)R)=f(R) \text{ for any } \alpha. \tag{4.5}$$

Above considerations show that f for nematic phase of biaxial particles can be expanded in set of functions $F^{(j)}_{0\nu}$:

$$\ln f(R)=\sum_j\sum_\nu S^j_{0\nu}\, F^{(j)}_{0\nu}(R)\,. \tag{4.6}$$

We should also replace the equation (3.15) with

$$S^j_{0\nu}=\lambda \int dR\ f(R) \sum_\rho K^j_{\rho\nu}\, F^{(j)}_{0\rho}(R) \left(\frac{1}{2}\right)^{\delta_{\nu 0}} \tag{4.7}$$

Now we assume that all coefficients $S^j_{0\nu}$ are small except S^0_{00}. Then from (4.6), (3.3) and (4.7) we find that

$$f(R)=\exp(S^0_{00})\{1+\sum_{j\neq 0}\sum_\nu S^j_{0\nu}\, F^{(j)}_{0\nu}(R)\}\,, \tag{4.8}$$

$$S^0_{00}=-\ln(8\,\pi^2)\,, \tag{4.9}$$

$$\sum_\rho S^j_{0\rho}\left\{\frac{\lambda}{2j+1}K^j_{\rho 0}\left(\frac{1}{2}\right)^{\delta_{\nu 0}}-\delta_{\rho\nu}\right\}=0. \tag{4.10}$$

Now for j=2k there are at most k+1 different λ whereas for j=2k+1 there are at most k different λ.

The eigenvectors from (4.3) and (4.10) can be used as starting values for numerical procedures solving (3.15), (3.3) or (4.7), (3.3) in the neighbourhood of given temperature parameter λ.

5. EXEMPLARY CALCULATIONS

In this section by means of the presented formalism we carry out analytical and numerical calculations for simple model of biaxial particles. For simplicity we limit expansion (2.4) by the following additional condition:

$$j+k+l \leq 4\,. \tag{5.1}$$

Thus using the conditions (2.7÷11) we find six independent nonzero constants $g_{\mu\nu}{}^{jkl}$ in expansion (2.4). We choose the representatives:

$$g_{00}{}^{000},\ g_{00}{}^{220},\ g_{20}{}^{220},\ g_{22}{}^{220},\ g_{00}{}^{202},\ g_{20}{}^{202}. \tag{5.2}$$

Explicit expression for σ takes the following form:

$$\sigma(R_1, R_2, R_u) = g_{00}{}^{000} + g_{00}{}^{220}\frac{1}{\sqrt{5}}F^{(2)}_{00}(R_2{}^{-1}R_1) + g_{22}{}^{220}\frac{2}{\sqrt{5}}F^{(2)}_{22}(R_2{}^{-1}R_1) +$$

$$+ g_{20}{}^{220}\frac{\sqrt{2}}{\sqrt{5}}\{F^{(2)}_{20}(R_2{}^{-1}R_1)+F^{(2)}_{02}(R_2{}^{-1}R_1)\}+g_{20}{}^{202}\frac{\sqrt{2}}{\sqrt{5}}\{F^{(2)}_{20}(R_u{}^{-1}R_1) + F^{(2)}_{02}(R_u{}^{-1}R_2)\}+$$

$$+ g_{00}{}^{202}\frac{1}{\sqrt{5}}\{F^{(2)}_{00}(R_u{}^{-1}R_1) + F^{(2)}_{00}(R_u{}^{-1}R_2)\}. \tag{5.3}$$

Now we can calculate the kernel (3.5). List of the relevant 24 nonzero coefficients is presented in the appendix B. Let us notice that the coefficients $K^{j}_{\mu\nu}$ both with even and odd j are present. It is in agreement with our thesis about necessity of using basic functions $F^{(j)}_{\mu\nu}$ with odd j.

In order to determine the coefficients (5.2) we use excluded volume method. Let assume that for fixed orientations of the molecules their minimum distance is determined by equation $V_{12}=0$ which is satisfied for $r=\sigma$.

We consider 13 different discrete molecular configurations described by R_1, R_2, $\bar{u}$. They are:

(i) $R_1=R_2=(0, 0, 0)$ - then $\bar{u}=(1, 0, 0)$, $\bar{u}=(0, 1, 0)$ or $\bar{u}=(0, 0, 1)$.

(ii) $R_1=(0, 0, 0)$, $R_2=(0, 0, \pi/2)$ - then $\bar{u}=(1, 0, 0)$ or $\bar{u}=(0, 0, 1)$.

(iii) $R_1=(0, 0, 0)$, $R_2=(0, \pi/2, 0)$ - then $\bar{u}=(1, 0, 0)$ or $\bar{u}=(0, 1, 0)$.
(iv) $R_1=(0, 0, 0)$, $R_2=(0, \pi/2, \pi/2)$ - then $\bar{u}=(1, 0, 0)$, $\bar{u}=(0, 1, 0)$ or $\bar{u}=(0, 0, 1)$.
(v) $R_1=(0, 0, 0)$, $R_2=(\pi/2, \pi/2, 0)$ - then $\bar{u}=(1, 0, 0)$.
(vi) $R_1=(0, 0, 0)$, $R_2=(\pi/2, \pi/2, \pi/2)$ - then $\bar{u}=(1, 0, 0)$ or $\bar{u}=(0, 1, 0)$.

We write equation for every configuration using Euler angles given above and required distances between the molecules. It is very crucial to choose those distances without contradictions (note that we have 13 equations and only 6 variables (5.2)).

As an example of this procedure we consider molecules which are ellipsoids with three different axis (2a, 2b, 2c). For the orientation described by zero Euler angles long axis of the molecule (2c) is equal to the z axis of the reference frame while short axis (2a) is equal to the x axis. As a result we find $\sigma_0=2b$ and values of coefficients (5.2):

$$g_{00}{}^{000} = \frac{2}{3}(a+b+c)\,, \tag{5.4}$$

$$g_{00}{}^{202} = \frac{\sqrt{5}}{3}(2c-a-b)\,, \tag{5.5}$$

$$g_{20}{}^{202} = \frac{\sqrt{5}}{\sqrt{6}}(a-b)\,, \tag{5.6}$$

$$g_{00}{}^{220} = g_{20}{}^{220} = g_{22}{}^{220} = 0\,. \tag{5.7}$$

Now the following coefficients $K^{j}_{\mu\nu}$ (3.12) are nonzero: K^{0}_{00}, K^{2}_{00}, K^{2}_{02}, K^{2}_{20}, K^{2}_{22} (see appendix B). So there are no odd basis functions $F^{(j)}_{\mu\nu}$ in the kernel K.

We choose the following values of the molecular parameters: a=1, b=3, c=9, $\sigma_0=6$. From the analysis of bifurcations we get equation for λ:

$$\lambda^2\left(K^2_{02}\right)^2 - \left(\lambda K^2_{00} - 10\right)\left(\lambda K^2_{22} - 5\right) = 0. \tag{5.8}$$

The solution is $\lambda_1=0.61487$ and $\lambda_2=-149.69$. Let us define the order parameters

$$\left\langle F^{(j)}_{\mu\nu}\right\rangle = \int dR\; f(R)\; F^{(j)}_{\mu\nu}(R), \tag{5.9}$$

(note that $\langle 1\rangle=\langle F^{(0)}_{00}\rangle=1$). Our order parameters (5.9) are in close relation to coefficients $\psi_{1,mn}$ from the paper of Mulder[2] and to the parameters $S=\langle F_1\rangle$, $T=\langle F_2\rangle$, $U=\langle F_3\rangle$, $V=\langle F_4\rangle$ described by Straley[1].

We calulate numericaly coefficients $S^{J}_{\mu\nu}$ (3.13) which completely determine the one particle distribution function f. Phase of the system can be identified from four main order parameters: $\langle F^{(2)}_{00}\rangle$, $\langle F^{(2)}_{02}\rangle$, $\langle F^{(2)}_{20}\rangle$ and $\langle F^{(2)}_{22}\rangle$. Figure 1 shows the dependence of those parameters on λ. We observe first-order phase transition ISO→NLC at $\lambda=0.5845$ and second-order phase transition NLC→BNLC at $\lambda=3.4603$. Above results are in an agreement with the Ginzgurg-Landau theory of phase transitions[7].

Further studies of the presented model allow us constructing the phase diagram which will show the dependence of the symmetry of the phase on the shape of molecules.

6. CONCLUSIONS

The presented theory of biaxial nematic liquid crystals is based on the theory of invariants. We state that in a general case, for description of these systems we should use basic functions constructed from rotation matrix elements both with j even and odd.

The Lennard-Jones potential we used allowed us to obtain analytic form of the kernel for equation of distribution function and to postulate analytic form for the distribution function. The integral equation was transformed into the set of algebraic equations which can be solved by numerical methods. From these equations the temperature dependent parameter can be extracted by analytical means provided we are close to critical point.

Within our formalism it is easy to recover the theory of rod-like molecules[8]. In this case basic functions are $F^{(j)}_{00}(R)=P_j(\cos\theta)$ with even j.

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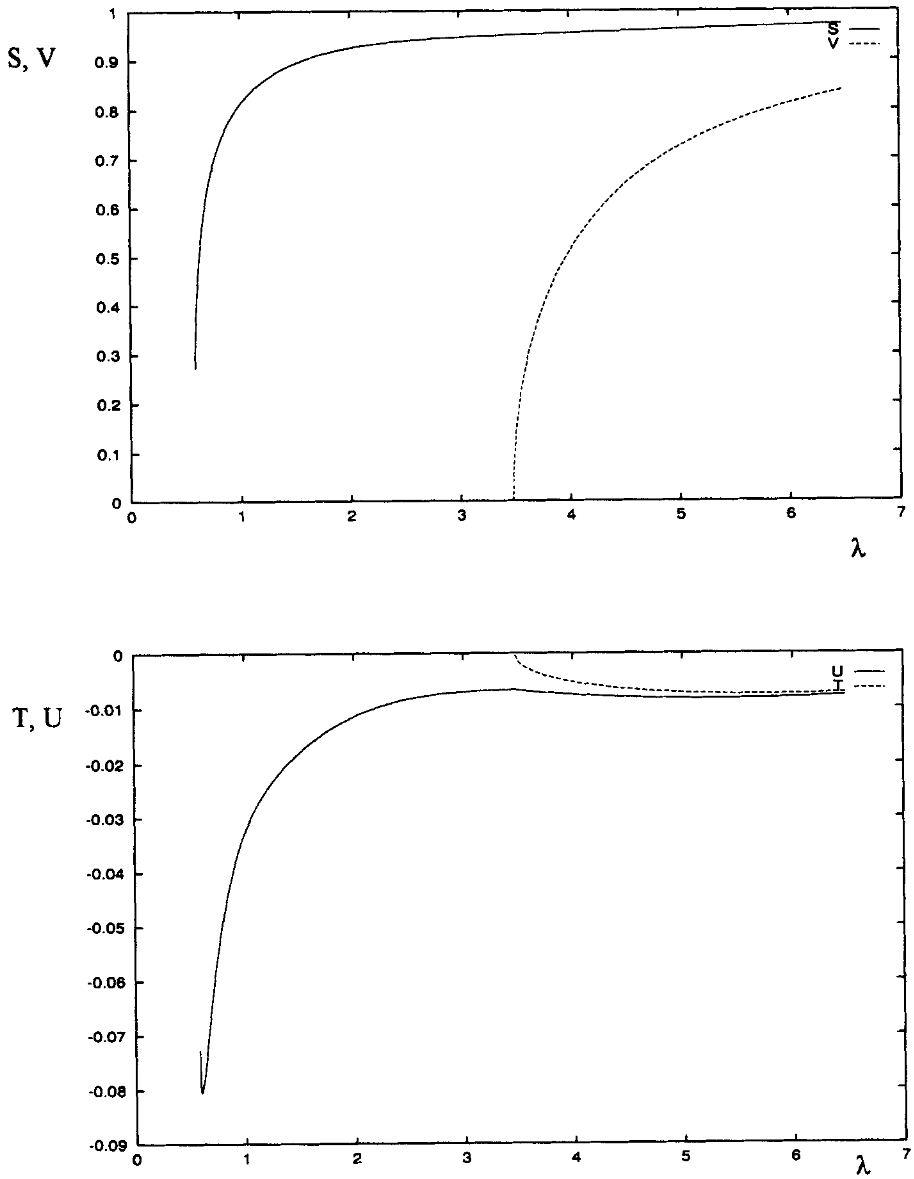

FIGURE 1 λ dependence of the four order parameters $S = < F_{00}^{(2)} >$, $V = < F_{22}^{(2)} >$, $U = \frac{2}{\sqrt{3}} < F_{02}^{(2)} >$, $T = \frac{2}{\sqrt{3}} < F_{20}^{(2)} >$ in model of ellipsoidal molecules (we use the Straley notation[1]).

APPENDIX A: PROPERTIES OF BASIC FUNCTIONS

Below we list main properties of basic functions which are relevant to the systems with the D_{2h} symmetry:

(i) We define:

$$F^{(j)}_{\mu\nu}(R)=\left(\frac{1}{\sqrt{2}}\right)^{2+\delta_{\mu 0}+\delta_{\nu 0}} \sum_{\rho\sigma\in\{1,-1\}}(-1)^{j(\sigma-\rho)/2}\, D^{(j)}_{\rho\mu,\sigma\nu}(R), \tag{A.1}$$

where j is integer, μ, ν are even, if j is even then $0 \le \mu, \nu \le j$, if j is odd then $2 \le \mu, \nu \le j$, R is a rotation parametrized by the standard Euler angles (φ, θ, ψ) and $D^{(j)}_{\mu\nu}$ are standard rotation matrix elements[4].

(ii) Functions $F^{(j)}_{\mu\nu}$ satisfy the following orthogonality relations

$$\int dR\; F^{(j)}_{\mu\nu}(R)\; F^{(k)}_{\rho\sigma}(R)=\delta_{jk}\,\delta_{\mu\rho}\,\delta_{\nu\sigma}\,8\pi^2/(2j+1)\,. \tag{A.2}$$

(iii) For given j=2k there are $(k+1)^2$ functions $F^{(j)}_{\mu\nu}$ whereas for j=2k+1 there are only k^2 functions.

(iv) Let R^{-1} means a rotation inverse to R (when R=(φ, θ, ψ) then R^{-1}=($-\psi$, $-\theta$, $-\varphi$)). Then the following relation is fulfilled

$$F^{(j)}_{\mu\nu}(R^{-1})=F^{(j)}_{\nu\mu}(R)\,. \tag{A.3}$$

(v) Functions $F^{(j)}_{\mu\nu}$ are real.

(vi) For the symmetry group D_{2h} we can choose the following three generators: $R_z(\pi)$= (π, 0, 0) (a rotation of π around the z axis), $R_y(\pi)$=(0, π, 0) (a rotation of π around the y axis), C_i (an inversion). For any rotation R we have

$$F^{(j)}_{\mu\nu}(RR_z(\pi)) = F^{(j)}_{\mu\nu}(R_z(\pi)R) = F^{(j)}_{\mu\nu}(RR_y(\pi)) = F^{(j)}_{\mu\nu}(R_y(\pi)R) = F^{(j)}_{\mu\nu}(R) \tag{A.4}$$

(vii) For j even our functions $F^{(j)}_{\mu\nu}$ are exactly the same as functions $\Delta^{(j)}_{\mu\nu}$ introduced by Mulder[2]. For j=2 we have four $F^{(2)}_{\mu\nu}$ which are equal (up to the normalizing factor) to the functions F_s from the paper of Straley[1].

APPENDIX B: COEFFICIENTS OF KERNEL K(R, 0)

We list the results of analytical computations of coefficients $K^{j}_{\mu\nu}$ with the condition (5.1).

In order to shorten our expressions we use the following substitutions: $P=g_{00}{}^{000}/\sigma_0$, $Q=g_{00}{}^{220}/\sigma_0$, $R=g_{20}{}^{220}/\sigma_0$, $S=g_{22}{}^{220}/\sigma_0$, $T=g_{00}{}^{202}/\sigma_0$, $U=g_{20}{}^{202}/\sigma_0$.

$$K^0_{00} = \tfrac{4}{4375}\pi\,(525\,Q^2\,P+10\,Q^3\,\sqrt{5}+4375\,P^3+2100\,S^2\,P+120\,S^2\,Q\,\sqrt{5}+ 240\,R^2\,S\,\sqrt{5}-120\,R^2\,Q\,\sqrt{5}+2100\,R^2\,P+2100\,U^2\,P+168\,U\,R\sqrt{5}\,T-120\,U^2\,\sqrt{5}\,T+ 168\,S\,\sqrt{5}\,U^2+42\,T^2\,Q\,\sqrt{5}+1050\,T^2\,P+20\,\sqrt{5}\,T^3)$$

$$K^2_{00} = \tfrac{12}{875}\pi\,(50\,Q^2\,P+175\,Q\,\sqrt{5}\,P^2+5\,Q^3\,\sqrt{5}+200\,S^2\,P+40\,S^2\,Q\,\sqrt{5}- 20\,R^2\,S\,\sqrt{5}+20\,R^2\,Q\,\sqrt{5}-200\,R^2\,P+28\,Q\,\sqrt{5}\,U^2-16\,U\,R\sqrt{5}\,T-8\,U^2\,\sqrt{5}\,T+ 16\,S\,\sqrt{5}\,U^2+18\,T^2\,Q\,\sqrt{5}+70\,T^2\,P+4\,\sqrt{5}\,T^3)$$

$$K^2_{02} = -\tfrac{12}{875}\pi\sqrt{2}\,(-30\,R^3\,\sqrt{5}-20\,R\,S^2\,\sqrt{5}+10\,R\,S\,Q\,\sqrt{5}-200\,R\,S\,P- 5\,R\,Q^2\,\sqrt{5}-175\,R\,\sqrt{5}\,P^2+100\,R\,Q\,P-36\,R\,U^2\,\sqrt{5}-70\,U\,T\,P+4\,T\,Q\,U\,\sqrt{5}+ 2\,T^2\,U\,\sqrt{5}-8\,T\,S\,U\,\sqrt{5}-10\,T^2\,R\,\sqrt{5}+4\,U^3\,\sqrt{5})$$

$$K^2_{22} = \tfrac{24}{875}\pi\,(20\,S^3\,\sqrt{5}+20\,R^2\,S\,\sqrt{5}+175\,S\,\sqrt{5}\,P^2+10\,S\,\sqrt{5}\,Q^2+100\,S\,Q\,P+ 100\,R^2\,P-5\,R^2\,Q\,\sqrt{5}+28\,S\,\sqrt{5}\,U^2+8\,U\,R\sqrt{5}\,T+4\,Q\,\sqrt{5}\,U^2+70\,U^2\,P+ 18\,S\,\sqrt{5}\,T^2-8\,U^2\,\sqrt{5}\,T)$$

$$K^3_{22} = \tfrac{8}{125}\pi\,(4\,S^3\,\sqrt{5}-12\,R^2\,S\,\sqrt{5}+3\,S\,\sqrt{5}\,Q^2+75\,S\,Q\,P-75\,R^2\,P+ 6\,R^2\,Q\,\sqrt{5}-6\,U\,R\sqrt{5}\,T+3\,Q\,\sqrt{5}\,U^2+3\,S\,\sqrt{5}\,T^2)$$

$$K^4_{00} = \tfrac{24}{48125}\pi\,(2475\,Q^2\,P+90\,Q^3\,\sqrt{5}+275\,S^2\,P+580\,S^2\,Q\,\sqrt{5}+60\,R^2\,S\,\sqrt{5}- 480\,R^2\,Q\,\sqrt{5}+1650\,R^2\,P+132\,U\,R\sqrt{5}\,T+22\,S\,\sqrt{5}\,U^2+198\,T^2\,Q\,\sqrt{5})$$

$$K^4_{02} = \tfrac{24}{9625}\pi\sqrt{6}\,(-90\,R^3+80\,S^2\,R+100\,R\,S\,Q+55\,R\,S\,\sqrt{5}\,P-15\,Q^2\,R+ 165\,Q\,R\sqrt{5}\,P+11\,U^2\,R+33\,U\,T\,Q+11\,S\,T\,U+33\,R\,T^2)$$

$$K^4_{22} = \tfrac{72}{9625}\pi\,(20\,S^3\,\sqrt{5}+20\,R^2\,S\,\sqrt{5}+31\,S\,\sqrt{5}\,Q^2+275\,S\,Q\,P+275\,R^2\,P- 26\,R^2\,Q\,\sqrt{5}+22\,U\,R\sqrt{5}\,T+11\,Q\,\sqrt{5}\,U^2+11\,S\,\sqrt{5}\,T^2)$$

$$K^4_{04} = \tfrac{24}{9625}\pi\,\sqrt{7}\,(-20\,S^2\,Q+55\,S^2\,\sqrt{5}\,P+180\,R^2\,S-60\,R^2\,Q+165\,R^2\,\sqrt{5}\,P+ 66\,U\,R\,T+22\,S\,U^2)$$

$$K^4_{24} = \tfrac{24}{9625}\pi\,\sqrt{42}\,(18\,R^3\,\sqrt{5}+20\,R\,S^2\,\sqrt{5}-8\,R\,S\,Q\,\sqrt{5}+275\,R\,S\,P+ 11\,R\,U^2\,\sqrt{5}+11\,T\,S\,U\,\sqrt{5})$$

$$K^4_{44} = \tfrac{24}{1375}\,S\,\pi\,(275\,S\,P+28\,S\,Q\,\sqrt{5}+12\,R^2\,\sqrt{5}+22\,\sqrt{5}\,U^2)$$

$$K^5_{22} = \tfrac{24}{125}\,\sqrt{5}\,\pi\,Q\,(S\,Q-R^2)$$

$$K^5_{24} = \tfrac{24}{125}\,\pi\,R\,\sqrt{10}\,(S\,Q-R^2)$$

$$K^5_{44} = \tfrac{48}{125}\,S\,\pi\,\sqrt{5}\,(S\,Q-R^2)$$

$$\begin{aligned}
K^{6}_{00} &= \tfrac{24}{1925}\sqrt{5}\,\pi\,(3\,Q^{3}+S^{2}\,Q+2\,R^{2}\,S+6\,R^{2}\,Q)\\
K^{6}_{02} &= \tfrac{24}{1925}\,\pi\,R\sqrt{7}\,(3\,R^{2}+S^{2}+4\,S\,Q+6\,Q^{2})\\
K^{6}_{04} &= \tfrac{24}{1925}\,\pi\sqrt{35}\,(S^{2}\,Q+2\,R^{2}\,S+3\,R^{2}\,Q)\\
K^{6}_{06} &= \tfrac{24}{1925}\,\pi\,R\sqrt{385}\,(R^{2}+S^{2})\\
K^{6}_{22} &= \tfrac{8}{1375}\sqrt{5}\,\pi\,(S^{3}+12\,R^{2}\,S+12\,S\,Q^{2}+24\,R^{2}\,Q)\\
K^{6}_{24} &= \tfrac{24}{275}\,R\,\pi\,(2\,R^{2}+S^{2}+4\,S\,Q)\\
K^{6}_{26} &= \tfrac{8}{275}\,S\,\pi\sqrt{11}\,(S^{2}+6\,R^{2})\\
K^{6}_{44} &= \tfrac{24}{275}\,S\,\pi\sqrt{5}\,(S\,Q+2\,R^{2})\\
K^{6}_{46} &= \tfrac{24}{275}\,\pi\sqrt{55}\,R\,S^{2}\\
K^{6}_{66} &= \tfrac{8}{25}\,S^{3}\sqrt{5}\,\pi
\end{aligned}$$

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