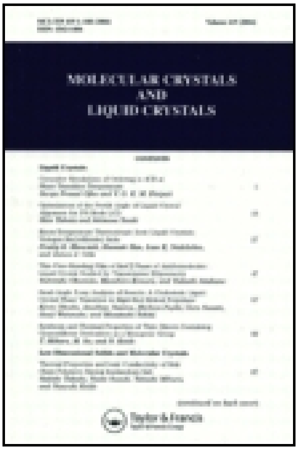

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Statistical Theory of Nematic Liquid Crystals Composed of Biaxial Ellipsoidal Particles

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Statistical theory of nematic liquid crystal whose constituent molecules are biaxial ellipsoids is proposed. The method is suggested which enables one to calculate exactly the second virial coefficient for the system of biaxial ellipsoidal particles and to obtain a simple approximation formula for the third one. By means of the so-called y-expansion, the thermodynamic potential of the system is constructed and equations of the thermodynamic and orientational state are obtained. The influence of the anisometric degree (i.e. the measure of biaxiality) of the particles on the features of orientational behavior and phase transitions among the isotropic, uniaxial and biaxial nematic phases is studied. A phase diagram for a system of biaxial ellipsoids has been calculated. It is shown that the so-called self-dual point takes place with high degree of accuracy. In the limiting cases (molecules are spheres or ellipsoids of revolution) our results are identical with earlier known ones.

Keywords: Nematic liquid; biaxial ellipsoidal particles; phase transition

1. INTRODUCTION

Together with dispersion van der Waals attraction, the reason, which is responsible for the formation of liquid-crystalline phase, is steric repulsion, connected with the mutual impenetrability of the anisometric prolate or oblate particles. Because of the difficulties in the statistical approach, the molecular flexibility is usually neglected, and the molecules are modelled as inflexible objects having some average or effective shape. A simple and most realistic model for such nonspherical molecule is hard biaxial ellipsoid. This model enables us to consider a system of hard spherical particles or disc-like/rod-like particles as limiting cases. As it is known, calculation of thermodynamic quantities in the liquid phase requires virial expansion up to high orders, which is slowly convergent one. At the same time, the so-called y-expansion (here y is density connected parameter) is widely used in the theory of ordinary liquids [1], [2] and solids [3]. This expansion is found to converge very quickly over the entire liquid phase range, and already the third order of y-expansion gives just the same results as the seventh order of the usual virial series.

In this paper a statistical theory is proposed to describe nematic liquid crystal consisting of biaxial ellipsoidal particles. We propose the extention of the earlier suggested method [4] of virial coefficients calculation, which enables us to consider the biaxial ellipsoids system. This method gives an opportunity to obtain an exact expression for the second virial coefficient and to approximate the third one. In the framework of this approach we study thermodynamic and orientational properties of the system of ellipsoidal particles (liquid crystal) in the third order of y-expansion and determine its phase diagram. It is also possible to investigate the influence of the contact steric interactions and the role of molecular biaxiality on the orientational structure and properties of real mesophases, including amphifilic systems, in which, as a result of molecular aggregation, the anisometric particles (micelles) are formed. These micelles are spontaneously ordered due to interparticular repulsions and form both uniaxial and biaxial mesophases.

2. THE SECOND VIRIAL COEFFICIENT

Consider a system of N nematogenic molecules contained in a volume V at temperature T. Let molecules have a shape of biaxial ellipsoids, whose three principal axes (a, b, c) are different $a \leqslant b \leqslant c$. The shape of the molecules can be characterized by the eccentricities of their normal sections

$$e_2 = \sqrt{1 - \frac{a^2}{b^2}}, \quad e_3 = \sqrt{1 - \frac{a^2}{c^2}}. \tag{1}$$

The limits $a = b < c$ and $a < b = c$ recover the cylindrical symmetry corresponding to prolate $(e_2 = 0, \quad e_3 \neq 0)$ and oblate $(e_2 = e_3 \neq 0)$ ellipsoids of revolution, respectively. The limit $a = b = c$, that is $e_2 = e_3 = 0$, corresponds to spherical particles.

Assume that only steric interactions caused by the mutual impenetrability of the particles occur in the system. The free energy of the system can be expanded as power series in the parameter $y = d/(1-d)$, where $d = Nv/V$ and $v = 4\pi abc/3$, to give

$$F = Nk_BT\left[\int d\hat{\Omega}\,\Psi(\hat{\Omega})\ln\Psi(\hat{\Omega}) - 1 - \Lambda + \ln y + C_2 y + \frac{1}{2}C_3 y^2 + \cdots\right]. \quad (2)$$

Here $\hat{\Omega}$ is a set of Euler angles, which indicates the orientation of the main particle axes with respect to the laboratory frame of reference, $\Psi(\hat{\Omega})$ denotes single-particle orientational distribution function, and the quantity Λ is related to the chemical potential μ_{id} of the system of noninteracting particles by the relation $\Lambda = \ln d - \mu_{id}/k_BT$. The linear combinations of the second (B_2) and the third (B_3) virial coefficients are also introduced in Eq. (2) as follows

$$C_2 = B_2 - 1, \quad C_3 = B_3 - 2B_2 + 1. \quad (3)$$

The validity of the assumption in Eq. (2) is justified by the fact that for condensed media Eq. (2) quite satisfactorily describes the macroscopic orientational effects due to the anisotropy of intermolecular interactions; in the case of ordinary liquids this assumption leads to the same results as well-known Percus-Yevick equation.

In order to obtain the expression for the free energy F, one starts with the calculation of the virial coefficients. For this reason, we consider the extension of our method [4] for the case of biaxial ellipsoids.

By definition, the second virial coefficient can be written as

$$B_2 = \frac{1}{2v}\iint d\hat{\Omega}_1 d\hat{\Omega}_2 \Psi(\hat{\Omega}_1)\Psi(\hat{\Omega}_2)E(\hat{\Omega}_1, \hat{\Omega}_2),$$

$$E(\hat{\Omega}_1, \hat{\Omega}_2) = -\frac{1}{V}\iint d\mathbf{r}_1 d\mathbf{r}_2 f(\mathbf{r}_{12}, \hat{\Omega}_1, \hat{\Omega}_2), \quad (4)$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ is the vector, connecting the centers of mass of two particles 1 and 2, located at the positions $\mathbf{r}_1$ and $\mathbf{r}_2$, and

$$f = \exp\left[-\frac{U_s(1,2)}{k_BT}\right] - 1$$

is Maier-function. In the case of hard particles, the energy $U_s(1,2)$ of steric pairwise interaction is equal to infinity, if the particles overlap, and to zero otherwise, then it holds

$$f(\mathbf{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2)=-\Theta(d_{12}-r_{12}),\quad \Theta(x)=\begin{cases}1, & x\geqslant 0,\\ 0, & x<0.\end{cases} \tag{5}$$

Here d_{12} is the distance of closest approach of two molecules with fixed orientations of their principal axes. Following Ref. [5], it can be shown that the excluded volume $E(\hat{\Omega}_1,\hat{\Omega}_2)$ of two ellipsoidal particles is given by

$$E(\hat{\Omega}_1,\hat{\Omega}_2)=\frac{1}{3}\iint \mathbf{d}_{12}\cdot\left[\frac{\partial \mathbf{d}_{12}}{\partial\theta}\times\frac{\partial \mathbf{d}_{12}}{\partial\phi}\right]d\theta\, d\phi. \tag{6}$$

Here θ and ϕ are the polar and azimuthal angles of the unit vector $\hat{N}$, which is the normal to the surface of ellipsoidal particle at the point of its contact with the other particle. To calculate the excluded volume $E(\hat{\Omega}_1,\hat{\Omega}_2)$, we assume that the center of one of the particles is located at the origin of coordinates, and of the other one – at the position $\mathbf{d}_{12}$. If these two particles are in contact, than two conditions are satisfied: one of them is the equality of the radius-vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ of the points of contact

$$\mathbf{R}_1(\hat{N}_1)=\mathbf{a}_1(\hat{N}_1),\quad \mathbf{R}_2(\hat{N}_2)=\mathbf{a}_2(\hat{N}_2)+\mathbf{d}_{12} \tag{7}$$

and the second one is the antiparallelism of the unit normals $\hat{N}_2=-\hat{N}_1$ at this point. Here

$$\mathbf{a}_i(\hat{N}_i)=\frac{\hat{N}_i+c_3^2(\hat{N}_i\hat{\nu}_{i3})\hat{\nu}_{i3}+c_2^2(\hat{N}_i\hat{\nu}_{i2})\hat{\nu}_{i2}}{\sqrt{1+c_3^2(\hat{N}_i\hat{\nu}_{i3})^2+c_2^2(\hat{N}_i\hat{\nu}_{i2})^2}},\quad i=1,2 \tag{8}$$

$$c_\alpha^2=e_\alpha^2/(1-e_\alpha^2),\quad \alpha=2,3, \tag{9}$$

and $\hat{\nu}_{i\alpha}$ is a unit vector along the α-th main axis of the i-th particle. Eq. (7) enables one to reduce two contact relations to the only one and to determine the vector $\mathbf{d}_{12}$:

$$\mathbf{d}_{12}=\mathbf{a}_1(\hat{N}_1)-\mathbf{a}_2(-\hat{N}_1). \tag{10}$$

Substitution of the Eq. (10) into Eq. (6) yields

$$E(\hat{\Omega}_1,\hat{\Omega}_2)=\frac{a^3}{3}(1+c_2^2)(1+c_3^2)\iint d\phi d\theta \sin\theta[q_1^{-3/2}+q_2^{-3/2}$$

$$+3q_1^{-2}q_2^{1/2}+3q_1^{1/2}q_2^{-2}], \tag{11}$$

$$q_i=1+c_3^2(\hat{v}_{i3}\hat{N}_1)^2+c_2^2(\hat{v}_{i2}\hat{N}_1)^2, \quad i=1,2.$$

The first and the second items under the integral sign in Eq. (11) are easily integrated and yield $2v$. The latter ones are calculated in the Appendix. Then we have

$$E(\hat{\Omega}_1,\hat{\Omega}_2)=2v\left\{1+\frac{3}{8\pi}\cdot\frac{1-e_3^2}{\sqrt{1-e_2^2}}\sum_{j=0}^{\infty}\sum_{m=-2j}^{2j}(-1)^m(4j+1)\right.$$

$$\left.\times\sum_{n=-j}^{j}\sum_{k=-j}^{j}S_{jkn}\mathscr{D}^{(2j)}_{2k,-m}(\hat{\Omega}_1)\mathscr{D}^{(2j)}_{2n,m}(\hat{\Omega}_2)\right\}, \tag{12}$$

$$S_{jkn}=f_{jk}g_{jn}+f_{jn}g_{jk},$$

where $\mathscr{D}^{(n)}_{lm}$ are elements of Wigner rotation matrices [6]. For convenience we represent the coefficients f_{jk} and g_{jn} as follows

$$f_{jm}=\sqrt{1-e_3^2}\iint q^{1/2}\frac{(-1)^j Y_{2j,-2m}(\theta,\phi)}{\sqrt{4j+1}}\sin\theta d\theta d\phi,$$

$$g_{jm}=(1-e_3^2)^{-2}\iint q^{-2}\frac{(-1)^j Y_{2j,-2m}(\theta,\phi)}{\sqrt{4j+1}}\sin\theta\, d\theta\, d\phi, \tag{13}$$

where spherical functions Y_{lm} are defined as in Ref. [6]. For instance,

$$f_{00}=\sqrt{\pi}\left\{1+\frac{2}{\pi}\int_0^{\pi/2}d\phi\frac{\mathrm{Arsh}p}{p\sqrt{1+p^2}}\right\},$$

$$f_{10}=\frac{1}{2}\left\{\frac{3\sqrt{\pi}}{4}\left[1+\frac{1}{\pi}\int_0^{\pi/2}\frac{d\phi}{p^2}\left(1-\frac{\mathrm{Arsh}p}{p\sqrt{1+p^2}}\right)\right]-f_{00}\right\},$$

$$f_{11} = -\frac{1}{4}\sqrt{\frac{3}{2\pi}}\int_0^{\pi/2} d\phi \frac{\cos 2\phi}{p^2}\left[1 - (1-4p^2)\frac{\text{Arsh}p}{p\sqrt{1+p^2}}\right],$$

$$g_{00} = \frac{2}{\pi}\int_0^{\pi/2} d\phi (1+p^2)\left[1 + \frac{1+p^2}{p}\arctan p\right],$$

$$g_{10} = -\frac{1}{2}\left\{\frac{6}{\sqrt{\pi}}\int_0^{\pi/2} d\phi \frac{1+p^2}{p^2}\left[1 - \frac{1+p^2}{p}\arctan p\right] + g_{00}\right\},$$

$$g_{11} = \sqrt{\frac{3}{2\pi}}\int_0^{\pi/2} d\phi \frac{\cos 2\phi}{p^2}(1+p^2)^2\left[1 - \frac{1-p^2}{p}\arctan p\right],$$

$$\text{here } p^2 = \frac{c_3^2 - c_2^2 \sin^2\phi}{1 + c_2^2\sin^2\phi}.$$

For the particles having shape of prolate ellipsoids of revolution ($e_2 = 0$), the Eq. (13) can be simplified:

$$f_{jm} = \delta_{m0}\frac{(-1)^{j+1}\Gamma(j+1/2)\Gamma(j-1/2)}{\Gamma(2j+3/2)} e_3^{2j}\,{}_2F_1(j-1/2, j+1, 2j+3/2; e_3^2),$$

$$g_{jm} = \sqrt{\pi}\delta_{m0}\frac{(-1)^{j+1}\Gamma(j+1/2)\Gamma(j-2)}{\Gamma(2j+3/2)} e_3^{2j}\,{}_2F_1(j+1,\ j+2, 2j+3/2; e_3^2).$$

Here $\Gamma(x)$ is gamma-function and ${}_2F_1(a, b, c; x)$ is confluent hypergeometric function [7]. In this case the excluded volume $E(\hat{\Omega}_1, \hat{\Omega}_2)$ takes immediately the well-known form for the ellipsoids of revolution particles (see, for instance, Ref. [4]).

Using the definition (4) and integrating over the angular variables of the particles, we obtain the general expression for the second virial coefficient of the system of hard biaxial ellipsoidal particles. This expression differs from the Eq. (12) on the following points: it does not contain the factor $2v$ and the Wigner functions $\mathscr{D}_{kn}^{(l)}$ are replaced by their statistical averages

$$\langle \mathscr{D}_{kn}^{(l)}(\hat{\Omega})\rangle = \int \mathscr{D}_{kn}^{(l)}(\hat{\Omega})\Psi(\hat{\Omega})d\hat{\Omega}. \tag{14}$$

The latter one are, by definition, macroscopic order parameters of the system.

The rank of the order parameter is defined by number l. The order parameter of a given rank l has $(2l+1)^2$ components, but not everyone of them is independent. The number of independent and nonzero components of the order parameter, having rank l, is determined by the symmetry of the phase (the second inferior index in Eq. (14) connected with the symmetry of the phase) and by the molecular symmetry (the first inferior index in Eq. (14)). The method of determination of the independent order parameters taking these symmetries into account one can see in Ref. [8]. For the considered case of biaxial and nonpolar molecules (phase symmetry are not lower than D_{2h}) only four independent order parameters of the second rank may be [9], [10]

$$
\begin{aligned}
Q_{00} &= \langle q_{00}\rangle = \left\langle \frac{3}{2}\left(\cos^2\beta - \frac{1}{3}\right)\right\rangle,\\
Q_{02} &= \langle q_{02}\rangle = \left\langle \frac{\sqrt{3}}{2}\sin^2\beta\cos 2\alpha\right\rangle,\\
Q_{20} &= \langle q_{20}\rangle = \left\langle \frac{\sqrt{3}}{2}\sin^2\beta\cos 2\gamma\right\rangle, \qquad (15)\\
Q_{22} &= \langle q_{22}\rangle = \left\langle \frac{1}{2}(1+\cos^2\beta)\cos 2\alpha\cos 2\gamma - \cos\beta\sin 2\alpha\sin 2\gamma\right\rangle.
\end{aligned}
$$

It should be noted that Eq. (12) for the excluded volume of two particles, having fixed orientations of their principal axes, includes Wigner-functions of only even rank (nonpolar molecules) and even inferior indices (centrosymmetric molecules).

Restricting, as usual, to the order parameters of the second rank in the expression for the second virial coefficient, the explicit form of C_2 (Eq. (3)) becomes

$$
\begin{aligned}
C_2 = 2h\{S_{000} &+ 5[S_{100}(Q_{00}^2 + Q_{02}^2) + 2\sqrt{2}S_{110}(Q_{00}Q_{20} + Q_{02}Q_{22})\\
&+ 2S_{111}(Q_{20}^2 + Q_{22}^2)]\}, \qquad (16)
\end{aligned}
$$

$$h = \frac{3}{8\pi}(1 - e_3^2)(1 - e_2^2)^{-1/2}.$$

In the case of the axisymmetric particles ($e_2 = 0$) this expression is simplified and transformed into before known one [4].

3. THE THIRD VIRIAL COEFFICIENT

The third virial coefficient can be written as

$$B_3 = \frac{1}{3v^2}\int d\hat{\Omega}_1 d\hat{\Omega}_2 d\hat{\Omega}_3 K(\hat{\Omega}_1, \hat{\Omega}_2, \hat{\Omega}_3)\Psi(\hat{\Omega}_1)\Psi(\hat{\Omega}_2)\Psi(\hat{\Omega}_3), \qquad (17)$$

$$K(\hat{\Omega}_1, \hat{\Omega}_2, \hat{\Omega}_3) = -\int d\mathbf{r}_{12} d\mathbf{r}_{13} f(\mathbf{r}_{12}, \hat{\Omega}_1, \hat{\Omega}_2) f(\mathbf{r}_{13}, \hat{\Omega}_1, \hat{\Omega}_3) f(\mathbf{r}_{23}, \hat{\Omega}_2, \hat{\Omega}_3).$$

This coefficient can be calculated exactly only for hard spherical particles. In the case of another particles symmetry it can be determined only approximately, if any approximation for the kernel of the integral $K(\hat{\Omega}_1, \hat{\Omega}_2, \hat{\Omega}_3)$ is used. For ellipsoidal particles a good approximation is assumed [11] to have a form of symmetrized over the particle indices expression

$$K(\hat{\Omega}_1, \hat{\Omega}_2, \hat{\Omega}_3) = L[E(\hat{\Omega}_1, \hat{\Omega}_2) \cdot E(\hat{\Omega}_1, \hat{\Omega}_3) + \cdots]. \qquad (18)$$

Here the quantity L depends on the eccentricities of the particles and, in general, on their mutual orientations. It takes on the value 15/32 for spherical particles [4], [11] and in the completely ordered system [11], [12]; in the Onsager limit (the particles are long rods with aspect ratio $c/a \geqslant 100$) $L \to \infty$. In real liquid crystals the length-to-width ratio $c/a \approx 3-5$ and so we assume for simplicity $L = 15/32$ (it should be noted, that for the ellipsoid of revolution particles the approximation formula, defining L as a function of e_3, has been obtained in Ref. [4]).

Using Eqs. (17), (18), (3), (5) and (12), it follows that

$$C_3 = \sum_{j_1}\sum_{j_2}\sum_{j_3}(4j_1 + 1)(4j_2 + 1)(4j_3 + 1)\sum_{M_1}\sum_{M_2}\sum_{M_3}\begin{pmatrix} 2j_1 & 2j_2 & 2j_3 \\ M_1 & M_2 & M_3 \end{pmatrix}.$$

$$\cdot \sum_{m_1}\sum_{m_2}\sum_{m_3}\begin{pmatrix} 2j_1 & 2j_2 & 2j_3 \\ 2m_1 & 2m_2 & 2m_3 \end{pmatrix}\sum_{n_1}\sum_{n_2}\sum_{n_3} a^{j_1 j_2 j_3 M_1 M_2 M_3}_{m_1 m_2 m_3 n_1 n_2 n_3} \cdot$$

$$\cdot \langle \mathscr{D}^{(2j_1)}_{2n_1, M_1}(\hat{\Omega}_1)\rangle \langle \mathscr{D}^{(2j_2)}_{2n_2, M_2}(\hat{\Omega}_2)\rangle \langle \mathscr{D}^{(2j_3)}_{2n_3, M_3}(\hat{\Omega}_3)\rangle, \tag{19}$$

where

$$\begin{aligned} a^{j_1 j_2 j_3 M_1 M_2 M_3}_{m_1 m_2 m_3 n_1 n_2 n_3} = \frac{4}{9} L h^2 [& S_{j_2 m_2 n_2} S_{j_3 m_3 n_3} \delta_{m_1, -n_1} \\ & + S_{j_1 m_1 n_1} S_{j_3 m_3 n_3} \delta_{m_2, -n_2} + S_{j_1 m_1 n_1} S_{j_2 m_2 n_2} \delta_{m_3, -n_3}] \\ & - \frac{2}{3} v (1 - \frac{4}{3} L) [S_{j_1 n_1 n_2} \delta_{j_1, j_2} \delta_{j_3, 0} \delta_{M_1, -M_2} \delta_{M_3, 0} \delta_{n_3, 0} \\ & + S_{j_2 n_2 n_3} S_{j_2, j_3} \delta_{j_1, 0} \delta_{M_2, -M_3} \delta_{M_1, 0} \delta_{n_1, 0} \\ & + S_{j_3 n_3 n_1} \delta_{j_3, j_1} \delta_{j_2, 0} \delta_{M_3, -M_1} \delta_{M_2, 0} \delta_{n_2, 0}]. \end{aligned} \tag{20}$$

In Eq. (19) the sum is taken over all allowed values of j_1, j_2 and j_3, which obeys the triangle rule [6]; the restrictions of the summation indices in the following sums are imposed by the properties of 3j-symbols, which are defined according to Ref. [6]. We restrict ourselves to the case of second rank order parameters in Eq. (19), then it holds

$$\begin{aligned} C_3 = C_3^{is} & + 15[b_{000}(Q_{00}^2 + Q_{02}^2) + 2\sqrt{2} b_{100}(Q_{00} Q_{20} + Q_{02} Q_{22})] \\ & + 2 b_{110}(Q_{20}^2 + Q_{22}^2)] + \frac{50}{7}[c_{000} Q_{00}(Q_{00}^2 - 3 Q_{02}^2) \\ & + 3\sqrt{2} c_{100}(Q_{00}^2 Q_{20} - 2 Q_{00} Q_{02} Q_{22} - Q_{20} Q_{02}^2) \\ & + 6 c_{100}(Q_{00} Q_{20}^2 - 2 Q_{02} Q_{20} Q_{22} - Q_{00} Q_{22}^2) \\ & + 2\sqrt{2} c_{111} Q_{20}(Q_{20}^2 - 3 Q_{22}^2)]. \end{aligned} \tag{21}$$

Here the following identifications are chosen:

$$C_3^{is} = \frac{4}{3} L h^2 S_{000}^2 - 2h(1 - \frac{4}{3} L) S_{000} - \left(1 - \frac{4}{3} L\right),$$

$$b_{000}=\frac{4}{9}Lh^2(2S_{000}S_{100}+S_{100}^2+2S_{110}^2)-\frac{2}{3}hS_{100}\left(1-\frac{4}{3}L\right),$$

$$b_{100}=\frac{4}{9}Lh^2(2S_{000}S_{110}+S_{110}S_{100}+2S_{111}S_{110})-\frac{2}{3}hS_{110}\left(1-\frac{4}{3}L\right),$$

$$b_{110}=\frac{4}{9}Lh^2(2S_{000}S_{111}+S_{110}^2+2S_{111}^2)-\frac{2}{3}hS_{111}\left(1-\frac{4}{3}L\right),$$

$$c_{000}=\frac{4}{9}Lh^2(S_{100}^2-2S_{110}^2),$$

$$c_{100}=-\frac{16}{9}Lh^2S_{110}S_{111},$$

$$c_{110}=-\frac{4}{9}Lh^2(S_{110}^2+2S_{110}S_{111}+2S_{111}^2),$$

$$c_{111}=-\frac{8}{3}Lh^2S_{110}S_{111}. \tag{22}$$

In the case of ellipsoid of revolution particles, when $S_{110}=S_{111}=0$ and $b_{100}=b_{110}=c_{100}=c_{110}=c_{111}=0$ the coefficient C_3 of the y-expansion becomes indentical to the same one in Ref. [4]. In the case of spherical particles it follows from Eq. (21): $C_3=C_3^{is}=3$. Thus, the virial coefficients C_2 (Eq. (16)) and C_3 (Eq. (21)) determine the free energy of the system of ellipsoidal particles interacting via steric forces.

4. EQUATIONS OF STATE

The equation of the thermodynamic state can be derived using standard relation $P=-\partial F/\partial V$:

$$\frac{Pv}{k_BT}=y+C_2y^2+C_3y^3, \tag{23}$$

and for the chemical potential $\mu=(F+PV)/N$ we obtain

$$\frac{\mu}{k_BT}=\int d\hat{\Omega}\Psi(\hat{\Omega})\ln\Psi(\hat{\Omega})+\ln y-\Lambda$$

$$+(2C_2+1)y+\left(\frac{3}{2}C_3+C_2\right)y^2+C_3y^3. \tag{24}$$

In order to obtain the equation of the orientational state, it's worth reminding, that the orientational distribution function $\Psi(\hat{\Omega})$ can be found by minimization of the free energy (2) functional

$$\Psi(\hat{\Omega})=Z^{-1}\exp[a_{00}q_{00}+a_{02}q_{02}+a_{20}q_{20}+a_{22}q_{22}], \tag{25}$$

$$Z=\int d\hat{\Omega}\exp[a_{00}q_{00}+a_{02}q_{02}+a_{20}q_{20}+a_{22}q_{22}],$$

where the coefficients a_{lm} must be such as to minimize the free energy F at the equilibrium value of the order parameters Q_{lm}:

$$\frac{\partial F}{\partial Q_{lm}}=0. \tag{26}$$

Performing the averaging in Eq. (15) with the help of Eq. (25), one obtains the set of nonlinear integral equations for the order parameters Q_{lm}, which determines the orientational state of the system. The integration extends over three Euler angles and so numerical simulations of these equations are a quite difficult task.

In order to obtain some more clear representation of the results of studying of the orientational state and of thermodynamic behavior, let's write the free energy F as power series in order parameters Q_{lm} (Landau expansion). It enables us to find some analytical results and obtain the relation between the coefficients of Landau expansion and molecular characteristics. The idea of correct deriving of such expansion in the framework of molecular statistical theory was proposed in Ref. [13]. Following [13], we obtain

$$\begin{aligned}\frac{F}{Nk_BT}&=\ln y+C_2y+\frac{C_3}{2}y^2-1-\Lambda+\frac{5}{2}\Sigma_2-\frac{25}{21}\Sigma_3\\&+\frac{425}{196}\Sigma_2^2+\frac{125}{196}\tilde{\Sigma}_2^2-\frac{10375}{3773}\Sigma_2\Sigma_3+\frac{15625}{11319}\tilde{\Sigma}_2\tilde{\Sigma}_3+\frac{2690375}{686686}\Sigma_2^3\\&+\frac{933125}{1030029}\Sigma_3^2-\frac{3278125}{6180174}\tilde{\Sigma}_3^2-\frac{8505625}{2746744}\Sigma_2\tilde{\Sigma}_2^2,\end{aligned} \tag{27}$$

where the invariant combinations of the order parameters are introduced

$$\sum\nolimits_2 = Q_{00}^2 + Q_{20}^2 + Q_{02}^2 + Q_{22}^2,$$

$$\tilde{\sum}\nolimits_2 = Q_{00}Q_{22} - Q_{02}Q_{20},$$

$$\sum\nolimits_3 = Q_{00}^3 - 3Q_{00}Q_{20}^2 - 3Q_{00}Q_{02}^2 + 3Q_{00}Q_{22}^2 + 6Q_{02}Q_{20}Q_{22},$$

$$\tilde{\sum}\nolimits_3 = 3Q_{00}^2Q_{22} - 3Q_{02}^2Q_{22} - 3Q_{20}^2Q_{22} + Q_{22}^3 + 6Q_{00}Q_{02}Q_{20}. \tag{28}$$

The set of four orientational state equations can be obtained now by minimizing of the free energy (27) with respect to order parameters–see Eq. (26).

Let's discuss some general features of the proposed approach. For this purpose we define Saupe matrix [14]:

$$S_{ij}^{\alpha\beta} = \frac{3}{2}\langle\frac{1}{2}[(\hat{M}_i\hat{L}_\alpha)(\hat{M}_j\hat{L}_\beta) + (\hat{M}_j\hat{L}_\alpha)(\hat{M}_i\hat{L}_\beta)] - \frac{1}{3}\delta_{ij}\delta_{\alpha\beta}\rangle, \tag{29}$$

which characterizes the macroscopic orientational properties of the biaxial molecules system. Here $\hat{M}_i (i = 1,2,3)$ and $\hat{L}_\alpha (\alpha = 1,2,3)$ are orthogonal unit vectors in the molecular and laboratory frames of reference, respectively. The matrix (29) is symmetric and traceless over both pairs of indices.

Taking into account the molecular and phase symmetry (not lower than D_{2h}), we can parametrize this matrix through order parameters (15); the nonzero components of this matrix are:

$$S_{11}^{xx} = \frac{1}{4}[Q_{00} - \sqrt{3}(Q_{02} + Q_{20}) + 3Q_{22}],$$

$$S_{22}^{xx} = \frac{1}{4}[Q_{00} + \sqrt{3}(Q_{20} - Q_{02}) - 3Q_{22}],$$

$$S_{33}^{xx} = \frac{1}{2}[-Q_{00} + \sqrt{3}Q_{02}],$$

$$S_{11}^{yy} = \frac{1}{4}[Q_{00} + \sqrt{3}(Q_{02} - Q_{20}) - 3Q_{22}],$$

$$S_{22}^{yy}=\frac{1}{4}[Q_{00}+\sqrt{3}(Q_{20}+Q_{02})+3Q_{22}], \tag{30}$$

$$S_{33}^{yy}=\frac{1}{2}[-Q_{00}-\sqrt{3}Q_{02}],$$

$$S_{11}^{zz}=\frac{1}{2}[-Q_{00}+\sqrt{3}Q_{20}],$$

$$S_{22}^{zz}=\frac{1}{2}[-Q_{00}-\sqrt{3}Q_{20}],$$

$$S_{33}^{zz}=Q_{00}.$$

The ordering described by Eq. (29) may be of uniaxial symmetry $D_{\infty h}$ and so three different kinds of the uniaxial states can occur. They are isomorphic under transposition of the principal axes and possess the same free energy (27), because they correspond to alignment of the nematic director along one of the principal axes of the laboratory frame.

In the case of uniaxial symmetry with respect to Z axis (the so-called "easy axis" Z or "easy plane" Z – see Ref. [15]) we have $S_{ij}^{xx}=S_{ij}^{yy}$, and then it holds $Q_{02}=Q_{22}=0$. At the same time, the sign of the order parameter Q_{00} signifies the type of the uniaxial symmetry: if $Q_{00}>0$, then the "easy axis" symmetry takes place, and $Q_{00}<0$ corresponds to "easy plane" symmetry. The sign of the order parameter

$$Q_{20}=\frac{1}{\sqrt{3}}\langle P_2(\hat{M}_1\hat{L}_z)-P_2(\hat{M}_2\hat{L}_z)\rangle$$

indicates us, which of the short molecular axes gives the contribution to the alignment along the Z-axis (for example, $Q_{20}>0$ describes the prevailing contribution of the $\hat{M}_1$ axis).

Uniaxial symmetry with respect to X-axis corresponds to $S_{ij}^{yy}=S_{ij}^{zz}$, then it holds $Q_{02}=-\sqrt{3}Q_{00}$, $Q_{22}=-\sqrt{3}Q_{20}$. From the relation $S_{ij}^{xx}=S_{ij}^{zz}$ corresponded to uniaxial symmetry with respect to Y-axis, we find $Q_{02}=\sqrt{3}Q_{00}$, $Q_{22}=\sqrt{3}Q_{20}$. These solutions are reduced to the case of uniaxial symmetry with respect to Z-axis by rotating the laboratory frame of reference through $\pi/2$.

In the vicinity of the Curie point y_0 (above this point no isotropic phase can exist, i.e. y_0 defines the limit of stability of the isotropic phase) the order parameters Q_{lm} are small, and the equations of orientational state can be solved analytically in the framework of perturbation theory. To do this we expand $Q_{lm}=Q_{lm}^{(1)}\varepsilon+Q_{lm}^{(2)}\varepsilon^2+\cdots$ in a small parameter $\varepsilon=(y-y_0)$, and equate the terms of the same order in ε in the orientational state equations (26), (27). In the lowest order in ε then we obtain the homogeneous set of equations for the amplitudes $Q_{lm}^{(1)}$:

$$\bar{\bar{A}}^0\cdot\vec{x}^{(1)}=0, \tag{31}$$

where the matrix $\bar{\bar{A}}^0$ is defined as

$$\bar{\bar{A}}^0=\begin{pmatrix} A_{11}^0 & A_{12}^0 & 0 & 0\\ A_{12}^0 & A_{22}^0 & 0 & 0\\ 0 & 0 & A_{11}^0 & A_{12}^0\\ 0 & 0 & A_{12}^0 & A_{22}^0 \end{pmatrix}$$

and

$$\begin{aligned} A_{11}^0&=b_{-1}y_0^2+2a_{-1}y_0+5,\\ A_{12}^0&=\frac{1}{2}b_0y_0^2+a_0y_0,\\ A_{22}^0&=b_1y+2a_1y_0+5. \end{aligned} \tag{32}$$

Here the following identifications are chosen

$$\begin{aligned} a_0&=20\sqrt{2}hS_{110}, & b_0&=30\sqrt{2}b_{100},\\ a_1&=20hS_{111}, & b_1&=30b_{110},\\ a_{-1}&=10hS_{100}, & b_{-1}&=15b_{000}. \end{aligned} \tag{33}$$

and column-vector $\vec{x}^{(1)}=(Q_{00}^{(1)},Q_{20}^{(1)},Q_{02}^{(1)},\Delta Q_{22}^{(1)})$.

The compatibility condition for the system (31), i.e. $\det \bar{\bar{A}}^0 = 0$ determines the value of y_0 as a function of aspect ratio of the particles:

$$\left(b_1 b_{-1} - \frac{1}{4} b_0^2\right) y_0^4 + (2a_{-1}b_1 - a_0 b_0 + 2b_{-1}a_1) y_0^3$$

$$+ (5b_{-1} + 4a_{-1}a_1 + 5b_1 - a_0^2) y_0^2 + 10(a_1 + a_{-1}) y_0 + 25 = 0. \quad (34)$$

In the case of extremely prolate ($C_3 \approx 0$) molecules having small deviations from uniaxial symmetry, we have $b_i = 0$ and Eq. (34) becomes quadratic, so

$$y_0 = -5 \cdot \frac{(a_1 + a_{-1}) \pm \sqrt{(a_1 - a_{-1})^2 + a_0^2}}{4a_1 a_{-1} - a_0^2}.$$

It should be pointed out that matrix $\bar{\bar{A}}^0$ has two eigenvalues

$$\lambda_0 = 0, \qquad \lambda_1 = A_{11}^0 + A_{22}^0, \quad (35)$$

each of which is two-fold degenerated. Since $\bar{\bar{A}}^0$ is real and symmetric matrix it is simple one. Therefore its geometrical multiple (i.e. the number of eigenvectors corresponded to eigenvalue λ_i) must coincide with the algebraic multiple (i.e. how much the factor $(\lambda - \lambda_i)$ appears in the characteristic equation $(\lambda \bar{\bar{I}} - \bar{\bar{A}}^0) = 0$, where $\bar{\bar{I}}$ is unit matrix) for all the matrix $\bar{\bar{A}}^0$ eigenvalues. Thus the linear space, where the matrix $\bar{\bar{A}}^0$ is defined, divides into two orthogonal subspaces. The subspace corresponded to the eigenvalue $\lambda_0 = 0$ is annihilate-space for matrix $\bar{\bar{A}}^0$, and solutions of the homogeneous set of equations (31) can be found as a linear combination of that subspace basis vectors. As basis vectors of annihilate-subspace for matrix $\bar{\bar{A}}^0$ it is convenient to choose the eigenvectors of matrix $\bar{\bar{A}}^0$, corresponded to the eigenvalue λ_0. They can be written as column-vectors:

$$\chi_0^{(1)} = (0,0,\alpha,1), \quad \chi_0^{(2)} = (\alpha,1,0,0), \quad \alpha = -\sqrt{A_{22}^0/A_{11}^0}. \quad (36)$$

Then column-vector $\vec{x}^{(1)}$ is a linear combination of these basis vectors:

$$\vec{x}^{(1)} = d_1 \chi_0^{(1)} + d_2 \chi_0^{(2)}. \quad (37)$$

The coefficients d_1 and d_2 can be found in the next order of expansion. In the second order in ε we have

$$\bar{\bar{A}}^0 \cdot \vec{x}^{(2)} = \vec{D}, \tag{38}$$

where matrix is the same one that in the first order expansion (31) and the column-vector $\vec{x}^{(2)} = (Q_{00}^{(2)}, Q_{20}^{(2)}, Q_{02}^{(2)}, Q_{22}^{(2)})$. The components of column-vector $\vec{D}$ are quadratic combinations of the first-order amplitudes:

$$\vec{D} = (D_1, D_2, D_3, D_4), \tag{39}$$

$$D_1 = -B_{11}^0 (Q_{00}^{(1)})^2 - A_{11}^1 Q_{00}^1 - B_{12}^0 Q_{00}^{(1)} Q_{20}^{(1)} - B_{13}^0 (Q_{20}^{(1)})^2 - A_{12}^1 Q_{20}^1 + B_{11}^0 (Q_{02}^{(1)})^2$$
$$+ B_{12}^0 Q_{02}^{(1)} Q_{22}^{(1)} + B_{13}^0 (Q_{22}^{(1)})^2,$$

$$D_2 = -\frac{1}{2} B_{12}^0 (Q_{00}^{(1)})^2 - A_{12}^1 Q_{00}^{(1)} - 2B_{13}^0 Q_{00}^{(1)} Q_{20}^{(1)} - B_{23}^0 (Q_{20}^{(1)})^2 - A_{22}^1 Q_{20}^{(1)}$$
$$+ \frac{1}{2} B_{12}^0 (Q_{02}^{(1)})^2 + 2B_{13}^0 Q_{02}^{(1)} Q_{22}^{(1)} + B_{23}^0 (Q_{22}^{(1)})^2,$$

$$D_3 = -2B_{23}^0 Q_{00}^{(1)} Q_{02}^{(1)} + B_{12}^0 Q_{20}^{(1)} Q_{02}^{(1)} - A_{11}^1 Q_{02}^1 - A_{12}^1 Q_{22}^1 + B_{12}^0 Q_{00}^1 Q_{22}^1$$
$$+ 2B_{13}^0 Q_{20}^{(1)} Q_{22}^{(1)},$$

$$D_4 = 2B_{13}^0 Q_{00}^{(1)} Q_{22}^{(1)} + 2B_{23}^0 Q_{20}^{(1)} Q_{22}^{(1)} - A_{12}^1 Q_{02}^{(1)} - A_{22}^1 Q_{22}^{(1)} + B_{12}^0 Q_{00}^{(1)} Q_{02}^{(1)}$$
$$+ 2B_{13}^0 Q_{20}^{(1)} Q_{02}^{(1)},$$

where we use notations

$$A_{11}^1 = 2(a_{-1} + b_{-1} y_0), \quad A_{12}^1 = a_0 + b_0 y_0, \tag{40}$$

$$A_{22}^1 = 2(a_1 + b_1 y_0), \quad B_{11}^0 = \frac{3}{2} c_{-2} y_0^2 - \frac{25}{7},$$

$$B_{12}^0 = c_{-1} y_0^2, \quad B_{13}^0 = \frac{c_1 y_0^2}{2} + \frac{25}{7}, \quad B_{23}^0 = \frac{3 c_2 y_0^2}{2},$$

$$c_1 = 300 c_{110}/7, \quad c_{-1} = 150\sqrt{2} c_{100}/7, \quad c_2 = 100\sqrt{2} c_{111}/7, \quad c_{-2} = 50 c_{000}/7.$$

Since the system (38) is inhomogeneous one, its solution may be represented as a linear combination of the basis vectors of the subspace corresponded to the eigenvalue $\lambda_1 \neq 0$. The eigenvectors of the matrix $\bar{\bar{A}}^0$ corresponded to that eigenvalue may be written as

$$\chi_1^{(1)} = (0,0,-\alpha^{-1},1), \quad \chi_1^{(2)} = (-\alpha^{-1},1,0,0).$$

It is verified easily that they are orthogonal to the basis vectors of the subspace which is annihilate one for the matrix $\bar{\bar{A}}^0$, as it is must be. The column-vector $\vec{D}$ must be located in the subspace $\lambda_1 \neq 0$, i.e. it may be represented as a linear combination of the vectors $\chi_0^{(1)}$ and $\chi_0^{(2)}$. Therefore the following relationships take place

$$\bar{D} \cdot \chi_0^{(1)} = 0,$$

$$\bar{D} \cdot \chi_0^{(2)} = 0, \tag{41}$$

which enables to write the equations determined d_1 and d_2

$$e(d_1^2 - d_2^2) - \beta d_2 = 0,$$

$$d_1(2ed_2 - \beta) = 0, \tag{42}$$

where

$$e = -A_{12}^0 A_{22}^0 B_{11}^0 + \frac{3}{2} A_{22}^0 A_{11}^0 B_{12}^0 - 3A_{11}^0 A_{12}^0 B_{13}^0 + (A_{11}^0)^2 B_{23}^0, \tag{43}$$

$$\beta = [2A_{12}^1 A_{12}^0 - A_{11}^1 A_{22}^0 - A_{22}^1 A_{11}^0] A_{11}^0.$$

Solving Eqs. (42) we find the first order amplitudes $\vec{x}^{(1)} = (Q_{00}^{(1)}, Q_{20}^{(1)}, Q_{02}^{(1)}, Q_{22}^{(1)})$ – see also Eq. (37):

$$Q_{00}^{(1)} = Q_{02}^{(1)} = Q_{20}^{(1)} = Q_{22}^{(1)} = 0, \tag{44}$$

$$Q_{02}^{(1)} = Q_{22}^{(1)} = 0, \quad Q_{00}^{(1)} = \alpha Q_{20}^{(1)} = -\frac{\alpha\beta}{e}, \tag{45}$$

$$Q_{02}^{(1)} = \sqrt{3} Q_{00}^{(1)} = \sqrt{3}\frac{\alpha\beta}{2e}, \quad Q_{00}^{(1)} = \alpha Q_{20}^{(1)}, \quad Q_{02}^{(1)} = \alpha Q_{22}^{(1)}, \tag{46}$$

$$Q_{02}^{(1)} = -\sqrt{3} Q_{00}^{(1)} = -\sqrt{3}\frac{\alpha\beta}{2e}, \quad Q_{00}^{(1)} = \alpha Q_{20}^{(1)}, \quad Q_{02}^{(1)} = \alpha Q_{22}^{(1)}. \tag{47}$$

Solutions (44)–(47), which have being obtained, correpond at $e \neq 0$ to isotropic (44) or uniaxial nematic (45)–(47) phase with the director along X-axis (47), Y-axis (46) or Z-axis (45). If $e = 0$, the crossover behavior can occur: the second order phase transition from isotropic into biaxial nematic phase can take place, but, however, this case implies an additional consideration.

5. RESULTS

Figure 1 shows the phase diagram for the system of hard biaxial ellipsoidal particles with the aspect ratio $c/a = 4$. The curves $y(e_2)$ in this Figure divide the plane (y, e_2) into regions, which correspond to different phase states of the system. As it is seen from Figure 1, in the dependence on the particles eccentricity e_2 four different phases can occur: isotropic (I), uniaxial rod-like nematic (N_r), uniaxial disc-like nematic (N_p) and biaxial nematic (N_b) phases. It should be mentioned that real systems of hard particles are characterized by certain value of e_2, and possible phase states of them are determined by vertical sections of the phase plane. At low values of e_2, that

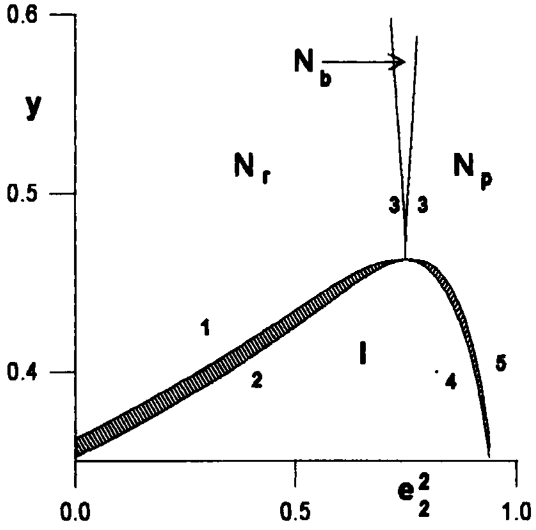

FIGURE 1 Phase diagram for the system of ellipsoidal particles with semiaxes $a \leq b \leq c$ for $c/a = 4$ (I - isotropic phase, N_r - uniaxial rod-like nematic phase, N_p - uniaxial disc-like nematic phase, N_b - biaxial nematic phase). Curves 1, 2, 4 and 5 are lines of the first order phase transition, curve 3 - the line of the second order phase transition. The shaded areas correspond to the regions of two phase coexistence.

is $b \approx a$ (rod-like particles), and at low densities, the equations of state have solutions, corresponding to isotropic phase. If density increases, the system undergoes the first order phase transition into uniaxial nematic phase N_r. The shaded area in Figure 1 corresponds to two-phase region of the system. The boundaries of this area (curves 1 and 2) determine the values of the coexisting phase densities at the point of the first order transition. At the densities exceeded the y-values on the curve 1, the equations of state have solutions, having the symmetry of the phase N_r up to the values of y, corresponding to the transition into smectic or solid crystal states; the latter ones have not being described in the framework of our approach.

As it is seen from Figure 1, the lines of the phase transitions (curves 1–5) are contacted at the isolated point on the line of the first order transition at $y_c = 0.463$, i.e. at $e_{2c}^2 = 0.749$. The second order transition from isotropic to biaxial nematic phase directly takes place at this point. This value of e_{2c} is in very good agreement with the predictions of Refs. [16], [17], [18] that at this point $b^2 \approx ac$ (the so-called self-dual point). At $e_2 < e_{2c}$, as density increases, besides the first order transition (curves 2 and 1) between the isotropic and nematic N_r phases, the second order phase transition (curve 3) to the biaxial nematic N_b phase takes place. The width of the phase separation region decreases at $e_2 \rightarrow e_{2c}$ and vanishes (the second order phase transition) at the crossover point. At $e_2 > e_{2c}$, the density increasing leads to the first order phase transition between the isotropic and uniaxial nematic N_p phases (curves 4 and 5), and then to the second order transition (curve 3) to the biaxial N_b phase. Our simulations show that the increasing of the degree of particle prolateness c/a does not change the topology of phase diagram: the densities of the coexiting phases diminish and the crossover point is displaced to the right (see Fig. 2, where the phase diagram for $c/a = 10$ ellipsoids is depicted). The self-duality condition ($b^2 = ac$) is fulfilled in this case with high degree of accuracy: the calculated value of e_{2c}^2 is equal to 0.899. The density corresponded to this crossover point is $y_c = 0.153$.

In Figure 3a the jump of the order parameter Q_{00} (and also Q_{20} – see Eq. (45) and Fig. 3b) at the first order transition point (curves 1) into isotropic phase is plotted versus eccentricity e_2 of the particles at $c/a = 4$. These dependences correspond to the values of the densities of the nematic phase, shown in Figure 1 (curves 1 and 5). At $e_2 = 0$ (uniaxial prolate particles: $b = a$) Q_{00}^c has its maximum value, and a jump of the order parameter Q_{20}^c described the ordering of the long particle axes in the (X, Y)-plane, is equal to zero, as it is must be. If the degree of the particle biaxiality increases (i.e. if the length of semiaxis b increases from $b = a$ to $b = b_c = 2a$, which is determined by the crossover condition $e = 0$ – see. Eq. (43)), the

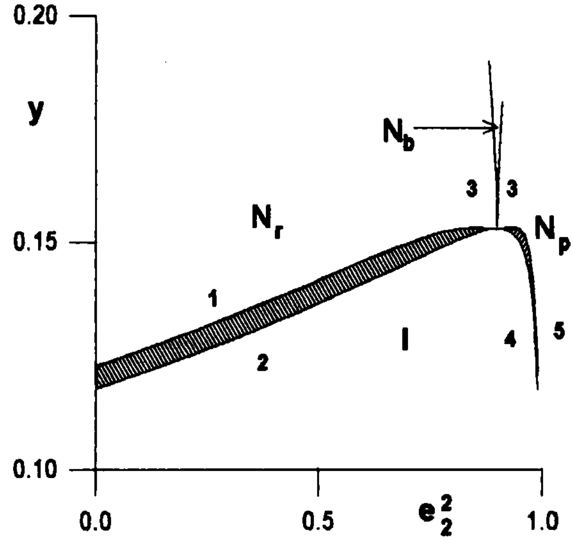

FIGURE 2 Phase diagram for the system of ellipsoidal particles with semiaxes $a \leqslant b \leqslant c$ for $c/a = 10$. The identifications are the same as in Fig. 1.

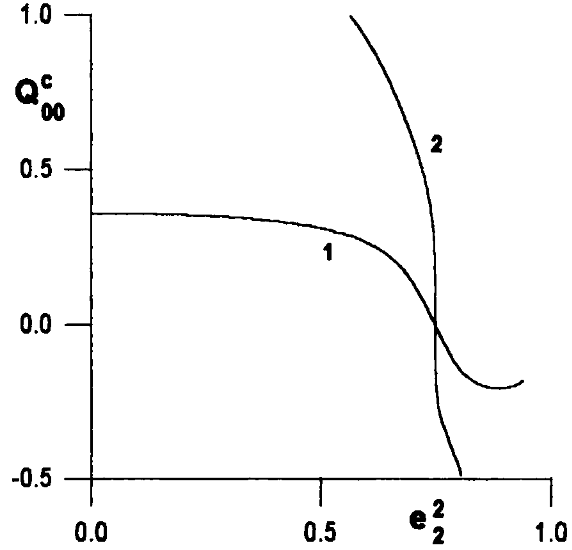

FIGURE 3 Order parameter Q_{00} (Fig. 3a) and Q_{20} (Fig. 3b) as functions of the particle eccentricity e_2 for $c/a = 4$ at the points of the first order (curve 1) and second order (curve 2) phase transitions.

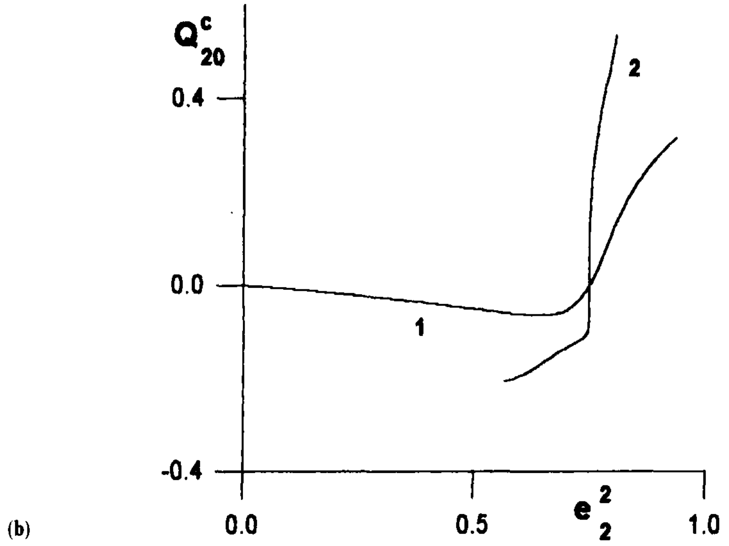

FIGURE 3 (Continued).

jump of the order parameter Q^c_{00} diminishes and vanishes (the second order transition) at the crossover point $e_2^2 = e_{2c}^2 = 0.749$. At the same time, the order parameter Q^c_{20} becomes nonzero, but, however, the nematic phase remains uniaxial as before $(Q_{02} = Q_{22} = 0)$. In the vicinity of the crossover point the jump of the order parameter Q^c_{20} has an extremum, vanishing, as Q^c_{00}, at the very crossover point. The width of the metastable region $(y_c - y_0)/y_c$, corresponded to shaded area in Figure 1 and characterized for the first order transition, vanishes (the second order transition) at $e_2 = e_{2c}$. At further increasing of e_2 (i.e. at $b \to c$), the jumps of the order parameters change their signs, that corresponds to the replacement of the types of the ordering of the c-semiaxes from "easy axis" $Z\,(Q^c_{00} > 0,\ Q^c_{20} < 0)$ to "easy plane" $Z\,(Q^c_{00} < 0)$. According to Eqs. (44)–(47), this means the arising of the ordering of the short molecular axes a in the "easy axis" Z way (see Eq. (46)). It should be mentioned that a plot of the curve 1 in Figure 3, where $Q^c_{00} > 0$, corresponds to the curve 1 in Figure 1, and therefore the transition from the isotropic to the nematic N_r phase takes place. Curve 5 in Figure 1 corresponds to the plot of the curve 1 in Figure 3 with $Q^c_{00} < 0$ and the phase transition is realized to the nematic N_p phase.

In the limiting case $e_2 = e_3$ (the particles are oblate ellipsoids of revolution with the semiaxes $a < b = c$) corresponded to the right end points of the curves in Figures 1 and 3, the nematic N_p phase is uniaxial, although the order parameter $Q^c_{20} \neq 0$. It is connected with the fact, that the order parameters Q_{00} and Q_{20} are defined with respect to the molecular axis c, but in the N_p phase, unlike to N_r phase, the short molecular axes a are ordered.

Curves 2 in Figure 3 show the order parameters at the point of the second order phase transition between the uniaxial and biaxial nematic phases as a functions of the anisometric degree of the particles – see also the corresponding curves 3 in Figure 1. The values of the order parameters on the curves 2 in Figure 3 correspond at fixed e_2 and e_3 to the points of "soft" branching of the uniaxial solutions of $Q_{lm}(y)$, shown in Figures 6. As it is seen from Figure 3, at fixed value of $c/a = 4$ the transition to the biaxial phase would be possible beginning from $e_2^2 = 0.566$, that corresponds to $b/a = 1.52$. As the ratio b/a increases, the degree of order of the molecular axes c with respect to Z-axis at the point of the biaxial phase rise from N_r phase decreases and vanishes at the crossover point ($b/a = 2$). As e_2 moves away from the crossover value ($e_2 > e_{2c}$), the degree of the molecular axes order at the branch point of biaxial solution is increased and tends to the limiting value at $b/a = 2.26$. The values $b/a \geqslant 1.52$ correspond to the transition to the biaxial phase at nonrealistic densities.

In Figure 4 the line of the second order phase transition between the isotropic and biaxial nematic N_b phases (i.e. the line of the crossover points) is shown in the (e_2, e_3) plane. Figure 5 illustrates the density of the nematic

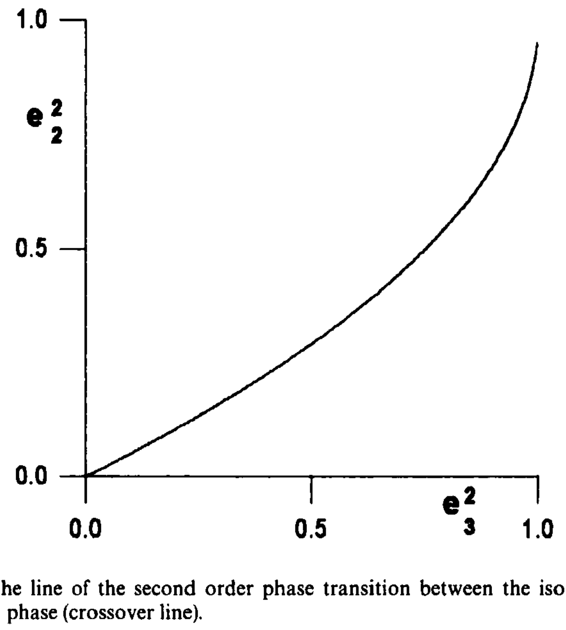

FIGURE 4 The line of the second order phase transition between the isotropic phase and biaxial nematic phase (crossover line).

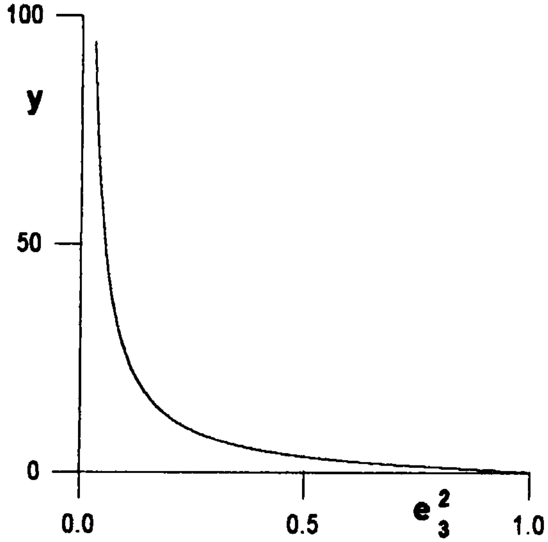

FIGURE 5 The density of the nematic phase in the crossover points as a function of the particle eccentricity e_3.

phase at the crossover points as a function of the eccentricity e_3. As it is seen from these Figures, the crossover behavior is unattainable in the systems, composed of uniaxial rod-like ($e_2 = 0$) or disc-like ($e_2 = e_3$) particles. For the nearly spherical particles ($a \approx b \approx c$) the crossover behavior can occur at the non-physical values of the density ($y \to \infty$). Thus, the possibility of the crossover is realized only in the system, composed of the sufficiently biaxial particles.

It should be noted that if only the pairwise interactions ($C_3 = 0$) are taken into account, the crossover condition $e = 0$ (Eq. (43)) is simplified and becomes

$$a_0 = \sqrt{3}(a_1 - a_{-1}),$$

where a_i are defined in Eq. (33). Then it is not difficult to show that in this case the self-dual point $b^2 = ac$, or $e_3^2 = e_2^2(2 - e_2^2)$ takes place. If $C_3 \neq 0$, and therefore the virial coefficients of higher order are resummed in y-expansion method, the self-duality condition most probably occurs too, but it is hard to prove analytically. That condition is fulfilled with high degree of accuracy: in our simulations we have $e_{2c}^2 = 0.749$ instead of 0.75 for $c/a = 4$, and $e_{2c}^2 = 0.899$ instead of 0.9 for $c/a = 10$. So the crossover line depicted in Figure 4 coincide practically with the self-dual curve $e_3^2 = e_2^2(2 - e_2^2)$.

The order parameters Q_{lm} as functions of the nematic phase density are shown in Figure 6(a, b, c, d) at $c/a = 4$ and $b/a = \sqrt{10/3}$. The above mentioned value of the ratio b/a corresponds to $e_2^2 = 0.7$ and, as it is seen from Figure 1, for this value of the eccentricity the phase transitions from the isotropic to the uniaxial nematic N_r phase and then to the biaxial nematic N_b phase are possible for the certain density range. Solutions of the orientational state equations which described N_b phase are shown by solid lines in Figure 6, and solutions corresponded to uniaxial nematic phases – by dashed lines. The physically realized values which correspond to the global minimum of the chemical potential are indicated by a bold lines.

As it is seen from Figures 1 and 6, the equations of state have only isotropic ($Q_{lm} = 0$) solutions at low densities y. As the density increases, the system undergoes the first order phase transition, which is characterized by a rather small discontinuity in density, and the order parameters have a jump up to the values, corresponding to the points A and D in Figure 6. A plot AB on the curves $Q_{00}(y)$ and $Q_{20}(y)$ describes the uniaxial ordering of the long molecular axes c with respect to Z-axis; in this case $Q_{02} = Q_{22} = 0$. The plots DE in Figure 6 correspond to uniaxial ordering of the long particle axes along the X-direction ($Q_{02} > 0$, $Q_{22} < 0$) or Y-direction ($Q_{02} < 0$, $Q_{22} > 0$).

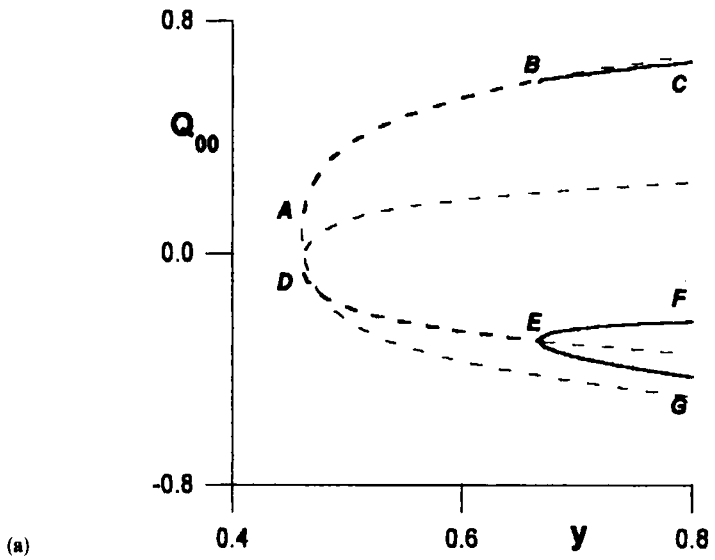

FIGURE 6 Order parameters as functions of the nematic phase density for $c/a = 4$ and $b/a = \sqrt{10/3}$.

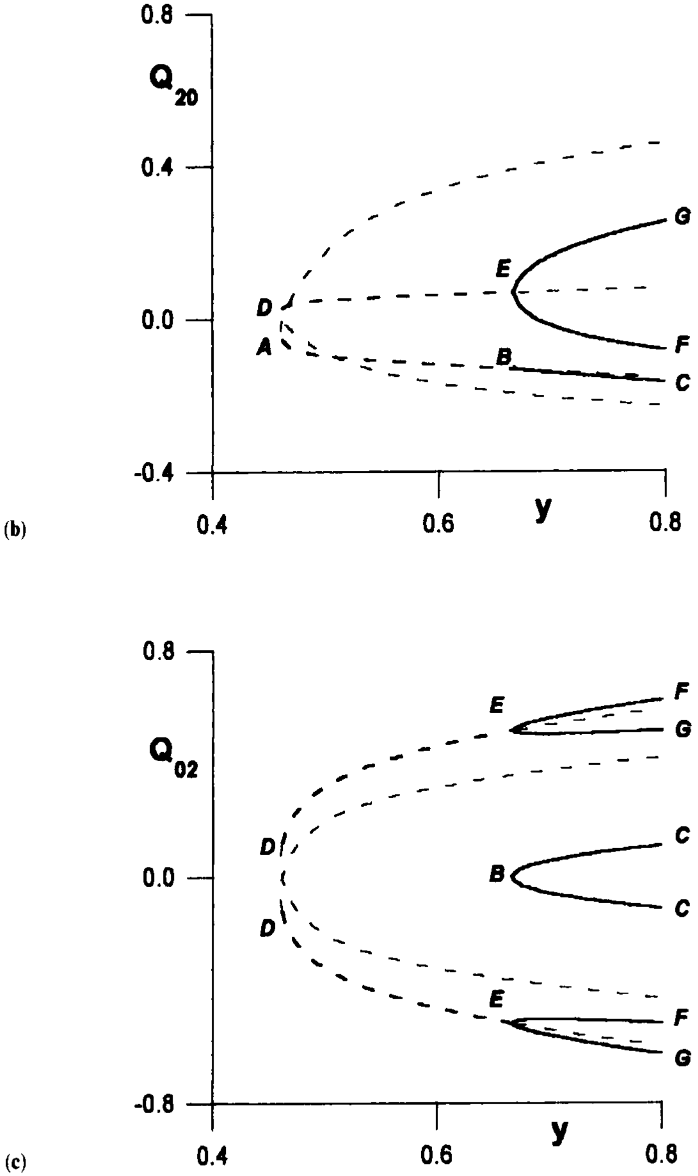

FIGURE 6 (Continued).

Further density increasing leads to the second order transition into biaxial nematic N_b phase (see points *B* and *E* in Figure 6); as it is seen from this Figure, the branching of solutions of the orientational state equations

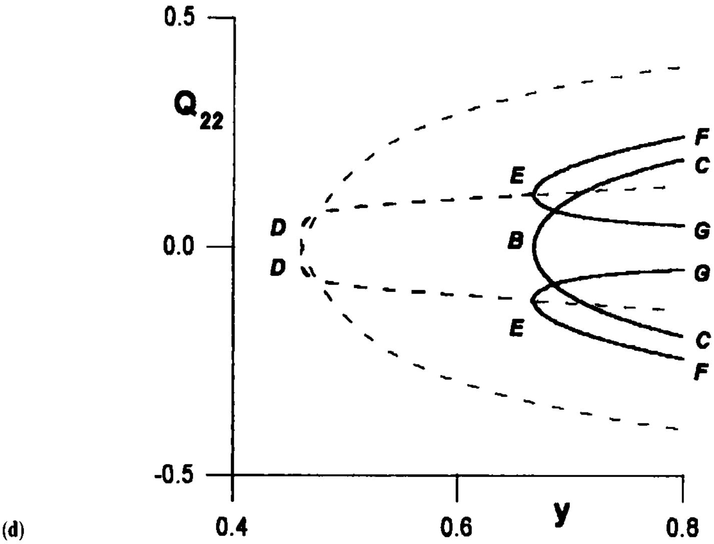

FIGURE 6 (Continued).

have taken place by a "soft" way. The plots *BC* characterize the biaxial ordering, since besides the ordering of the long particle axes along *Z*-direction there is one more preferential direction for the short molecular axes. The values of the order parameter $Q_{22}(y)$ in this density range (Fig. 6d) differ only in sign and correspond to the alignment of the short particle axes along the *X*-direction if $Q_{22} > 0$, or *Y*-direction at $Q_{22} < 0$. The order parameter Q_{02} (Fig. 6b) characterizes the difference in tendencies for the projections of the long particle axes in the (*X*, *Y*)-plane to be oriented in the *X* or *Y* directions, so the values of $Q_{02}(y)$ in plots *BC*, which differ only by the sign, are the same due to the fact, that these tendencies are equal. In the external field absence the *X* and *Y* axes are equivalent and so the above mentioned branches of the Q_{02} curves correspond to the same value of the chemical potential.

If the direction of the uniaxial ordering of the long particle axes concides with *X* or *Y* axis (the plots *DE* on $Q_{lm}(y)$ curves), then below the point *E* of the second order phase transition the biaxial orientational ordering is characterized by the plots *EF* or *EG*. If the long particle axes are oriented along *X*-direction ($Q_{02} > 0$ and $Q_{22} < 0$ on the plots *DE*), then it corresponds to the ordering of the short axes along *Y*-axis–a plot *EF* ($Q_{20} < 0$ at high densities) or along *Z*-axis–a plot *EG* ($Q_{20} > 0$). If long axes are ordered along *Y*-axis ($Q_{02} < 0$, $Q_{22} > 0$), then the plot *EF* corresponds to the ordering of the short axes along *X*-axis ($Q_{20} < 0$ at high densities), and a plot *EG*–along *Z*-direction ($Q_{20} > 0$).

Let us compare the obtained results with the Monte Carlo numerical simulations of Allen [17]. In Figure 7 we show the quantity $W = PV/(Nk_B T) - 1$ as a function of the aspect ratio b/a of the ellipsoidal particles for $c/a = 10$. The ratio b/a varies from 1 (prolate ellipsoids of revolution) to 10 (oblate ellipsoids of revolution) and is plotted in Figure 7 in the logarithmic scale. The solid lines in Figure 7 correspond to our numerical results, the circles and the dashed lines - to Monte Carlo simulations of Allen [17]. Curves $r-b$ and $p-b$ describe the values of Wat the transition points from the uniaxial nematic N_r (or N_p) phase to the biaxial nematic N_b phase, respectively. Curve $n-i$ corresponds to the line of phase transition nematic-isotropic liquid. Curves 1, and 2 show Was a function of b/a for $d/d_{cp} = 0.2$ and $d/d_{cp} = 0.3$, respectively, where $d_{cp} = \pi/(3\sqrt{2})$ is the closed packing density. The lines 1 and 2 are calculated by setting $abc = 1$, as in Ref. [17]. The circles and connecting them the dashed curves 3 and 4 correspond to $d/d_{cp} = 0.3$ and $d/d_{cp} = 0.4$, respectively. It should be pointed out that the curves 1 and 2 as distinct from the curves 3 and 4 belong fully to the ordered phases.

As it is seen from Figure 7, the position of the crossover point which is determined mainly by the geometry of the particles ($b^2 \approx ac$) is practically

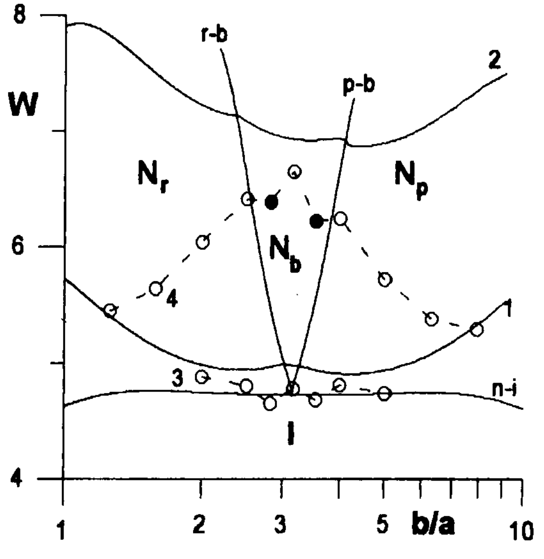

FIGURE 7 The quantity $W = PV/(Nk_B T) - 1$ as a funciton of aspect ratio b/a for $c/a = 10$. The solid lines correspond to our numerical results, the circles and the dashed lines - to Monte Carlo data of Allen [17]. $n-i$, $r-b$ and $p-b$ are the lines of phase transitions. Curve 1 – $d/d_{cp} = 0.2$, curve 2 – $d/d_{cp} = 0.3$, curve 3 – $d/d_{cp} = 0.3$, curve 4 – $d/d_{cp} = 0.4$. d_{cp}-the density of the close packing. The identifications of the phases are the same as in Fig. 1.

coincide with the result of Ref. [17] and with the predictions of Ref. [16]. This is conditioned by the fact that the contribution of C_2 predominates over C_3 in the vicinity of a crossover point and the obtained formula for C_2 (16) is exact. The contribution of higher order parameters which had not been taken into account in our calculations is negligible too near crossover point.

In Ref. [17] the lines of phase transitions had not been calculated and were plotted only approximately, nevertheless the lines $r-b$ and $p-b$ corresponded to the second order transitions $N_r - N_b$ and $N_p - N_b$ are close to these Monte Carlo data (see the black circles in curve 4 lying in the vicinity of the supposed [17] phase transition lines). Thus the proposed theory quite satisfactorily desribes the difference characteristics of the system, which are determined from the equality of the pressures or chemical potentials of the coexisting phases. More significant discrepancy between the proposed theory and the Monte Carlo simulations [17] one can see in Figure 7 in values of W for each of the phases (compare curves 2 and 3). These quantitative distinctions come principally from some significations used in the calculations, namely, Landau expansion and the restriction to the order parameters of the only second rank. Thus the quantitative agreement can be improved if higher order parameters will be taken into account and the general integral problem based on Eqs. (23–26) instead of Landau expansion (27) will be realized.

6. CONCLUSION

Unusual properties of liquid crystals, having the features of behavior both ordinary liquids and crystal solids, are conditioned by the anisotropy of the interparticular interactions. In the present paper we have proposed a statistical-thermodynamic theory of nematic liquid crystal which constituent molecules are hard biaxial ellipsoids in shape. Such approximation of a molecular shape seems to be more realistic than others discussed in literature (molecules-cylinders, spherocylinders, platelets, spheroplatelets and so on). The interparticular interactions have been assumed to be steric and so their anisotropy is connected with the shape of the particles. In order to determine the thermodynamic potential of the system the third order y-expansion method have been used. For the purpose of calculation of the second and third virial coefficients which are necessary for the theory, we have developed a suitable method. The equations of thermodynamic and orientational state have been obtained from the thermodynamic potential.

By numerical simulations of these equations of state we have constructed a phase diagram for the system of biaxial ellipsoids. This diagram shows that in the certain range of the ellipsoidal particle aspect ratio such a system can exhibit isotropic and nematic (uniaxial N_r or N_p and biaxial N_b) phases; the crossover conditions have been determined. As it is known, the simple theory of liquid-crystalline ordering (such as Onsager theory, or Maier and Saupe theory) leads to some essential width of the metastable region in the vicinity of the first order phase transition, whereas experimental data show that isotropic-nematic transition is close to the second order transition. The phase diagram determined in the present paper shows that the reason of this closeness may be due to the biaxiality of the particles (the shaded areas in Fig. 1, which correspond to the two-phase coexistence region, disappear in the crossover point).

The thermodynamic potential constructed in the framework of the molecular-statistical approach have been represented in the Landau expansion form. As a result, we may connect the coefficients of this expansion with the microscopic parameters, which characterize the shape and the dimensions of the particles. The obtained order parameters $Q_{lm}(y)$ dependences enable us to estimate the contribution of each of the molecular axes into physical quantities measured in experiment.

In conclusion, we note that in the present paper only steric interactions have been taken into account, whereas in real liquid crystal dispersion interactions give also a contribution into orientational properties of the mesophase together with the steric ones. They are described traditionally by the mean-field method and can be easily taken into account in the framework of the proposed approach (see, for example, Ref. [4]). There are no reasons whatsoever to suppose, that the phase diagram of the biaxial ellipsoid system will undergo a quantitative changes if dispersion interactions will be also taken into consideration.

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APPENDIX

Let us consider ellipsoids with the semiaxes $a \leqslant b \leqslant c$ and with the eccentricities of their normal sections (1). Defining the quantities c_2 and c_3 (Eq. (9)), we can represent the quantity q (Eq. (11)):

$$q = 1 + c_3^2(\hat{\Omega}_3\hat{N})^2 + c_2^2(\hat{\Omega}_2\hat{N})^2$$

in the following form

$$q=\frac{1}{1-e_3^2}\left[1-e_3^2\sin^2\theta\left(1-\frac{\xi^2}{e_3^2}\sin^2\varphi\right)\right],$$

where

$$(\hat{\Omega}_3\hat{N})=\cos\theta,\quad (\hat{\Omega}_2\hat{N})=\sin\theta\sin\varphi.$$

Using the relationship

$$(1-x^2)^{1/2}=-\frac{1}{2\sqrt{\pi}}\sum_{k=0}^{\infty}\frac{\Gamma(k-1/2)}{\Gamma(k+1)}x^{2k},$$

and binomial formula and changing the order of summation, one can obtain

$$q^{1/2}=-\frac{1}{\sqrt{1-e_3^2}}\frac{1}{2\sqrt{\pi}}\sum_{n=0}^{\infty}(-1)^n\frac{\sin^{2n}\theta\sin^{2n}\varphi}{n!}\xi^{2n}$$

$$\sum_{k=0}^{\infty}\frac{\Gamma(n+k-1/2)}{k!}e_3^{2k}\sin^{2k}\theta. \tag{A.1}$$

By expanding the function $\sin^{2k}\theta$ on the basis set of Legendre polynomials

$$\sin^{2k}\theta=\frac{k!^2}{2}\sum_{j=0}^{\infty}(4j+1)\frac{(-1)^j\Gamma(j+1/2)}{j!\Gamma(k-j+1)\Gamma(k+j+3/2)}P_{2j}(\hat{\Omega}_3\hat{N}),$$

one can find for the inner sum

$$\sum_{k=0}^{\infty}\frac{\Gamma(n+k-1/2)}{k!}e_3^{2k}\sin^{2k}\theta=\sum_{j=0}^{\infty}(4j+1)A_{jn}P_{2j}(\hat{\Omega}_3\hat{N}),$$

where

$$A_{jn}=\frac{(-1)^j\Gamma(j+1/2)}{2\Gamma(j+1)}\sum_{k=j}^{\infty}\frac{\Gamma(k+1)\Gamma(n+k-1/2)}{\Gamma(k-j+1)\Gamma(k+j+3/2)}e_3^{2k}.$$

Here we have changed the order of summation. Inserting this result into (A.1) and changing the order of summation once again, one obtains

$$\sum_{n=0}^{\infty}(-1)^n\frac{\sin^{2n}\theta\sin^{2n}\varphi}{n!}\xi^{2n}\sum_{k=0}^{\infty}\frac{\Gamma(n+k-1/2)}{k!}e_3^{2k}\sin^{2k}\theta$$

$$=\sum_{j=0}^{\infty}(4j+1)\left\{\sum_{n=0}^{\infty}(-1)^n\frac{(\hat{\Omega}_2\hat{N})^{2n}\xi^{2n}}{n!}A_{jn}\right\}P_{2j}(\hat{\Omega}_3\hat{N}).$$

Using the relationship

$$(\hat{\Omega}_2\hat{N})^{2n}=\frac{\sqrt{\pi}}{2^{2n+1}}\Gamma(2n+1)\sum_{l=0}^{\infty}\frac{(4l+1)}{\Gamma(n-l+1)\Gamma(n+l+3/2)}P_{2l}(\hat{\Omega}_2\hat{N}),$$

one finds finally

$$q^{1/2}=\frac{1}{2\sqrt{1-e_3^2}}\sum_{j,l=0}^{\infty}(4j+1)(4l+1)B_{jl}(e_3,\xi)P_{2j}(\hat{\Omega}_3\hat{N})P_{2l}(\hat{\Omega}_2\hat{N}), \quad \text{(A.2)}$$

where

$$B_{jl}=\frac{(-1)^{j+l+1}}{4\sqrt{\pi}}\frac{\Gamma(j+1/2)}{\Gamma(j+1)}\xi^{2l}e_3^{2j}\sum_{n=0}^{\infty}\frac{(-1)^n\Gamma(n+l+1)\xi^{2n}}{\Gamma(n+1)\Gamma(n+2l+3/2)}\cdot$$

$$\cdot\sum_{k=0}^{\infty}\frac{\Gamma(k+j+1)\Gamma(n+l+k+j-1/2)}{\Gamma(k+1)\Gamma(k+2j+3/2)}e_3^{2k}.$$

By analogy one can obtain for q^{-2}:

$$q^{-2}=\frac{(1-e_3^2)^2}{2}\sum_{j,l=0}^{\infty}(4j+1)(4l+1)D_{jl}(e_3,\xi)P_{2j}(\hat{\Omega}_3\hat{N})P_{2l}(\hat{\Omega}_2\hat{N}), \quad \text{(A.3)}$$

where

$$D_{jl}=\frac{(-1)^{j+l}}{2}\frac{\Gamma(j+1/2)}{\Gamma(j+1)}\xi^{2l}e_3^{2j}\sum_{n=0}^{\infty}\frac{(-1)^n\Gamma(n+l+1/2)\xi^{2n}}{\Gamma(n+1)\Gamma(n+2l+3/2)}\cdot$$

$$\cdot\sum_{k=0}^{\infty}\frac{\Gamma(k+j+1)\Gamma(n+l+k+j+2)}{\Gamma(k+1)\Gamma(k+2j+3/2)}e_3^{2k}.$$

Thus for the third item under the integral sign in Eq. (11) one has

$$\frac{q^{1/2}}{q'^2} = C \sum_{j_1 j_2}^{\infty} B_{j_1 j_2} \sum_{l_1 l_2}^{\infty} D_{l_1 l_2} P_{2j_1}(\hat{\Omega}_3 \hat{N}) P_{2j_2}(\hat{\Omega}_2 \hat{N}) P_{2l_1}(\hat{\Omega}'_3 \hat{N}) P_{2l_2}(\hat{\Omega}'_2 \hat{N}), \quad (A.4)$$

$$C = \frac{1}{4}(1 - e_3^2)^{3/2}.$$

It should be mentioned that the arguments of Legendre polynomials are the scalar products which are invariant with respect to the choice of frame of reference for determination of the components of vectors $\hat{\Omega}_i$, $\hat{\Omega}'_i$ and $\hat{N}$. Using the relationship

$$P_l(\hat{n}\hat{n}') = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y^*_{l,m}(\hat{n}')\, Y_{l,m}(\hat{n}), \quad (A.5)$$

it is possible to keep on the transformations. However, the right-hand side of this identity contains the spherical functions depending on the angles between the unit vectors $\hat{n}$ and $\hat{n}'$ and orthogonal unit vectors of some fixed frame of reference. One can introduce at least two frames of reference: the molecular frame connected with the principal molecular axes, that is with the unit vectors $\hat{\Omega}_i$ and $\hat{\Omega}'_i$, and laboratory one relatively which the order parameters are defined. Let us use at first the laboratory frame of reference. Inserting (A.5) into (A.4) we obtain:

$$\int \frac{\sqrt{1 + c_3^2(\hat{\Omega}_3 \hat{N})^2 + c_2^2(\hat{\Omega}_2 \hat{N})^2}}{[1 + c_3^2(\hat{\Omega}'_3 \hat{N})^2 + c_2^2(\hat{\Omega}'_2 \hat{N})^2]^2} d\hat{N} = C(4\pi)^4 \sum_{j_1 j_2} B_{j_1 j_2}(e_3, \xi) \sum_{l_1 l_2} D_{l_1 l_2}(e_3, \xi).$$

$$Y_{2j_1,m_1}(\hat{\Omega}_3)\, Y_{2j_2,m_2}(\hat{\Omega}_2)\, Y_{2l_1,n_1}(\hat{\Omega}'_3)\, Y_{2l_2,n_2}(\hat{\Omega}'_2) \int A^{m_1\, m_2\, n_1\, n_2}_{j_1\, j_2\, l_1\, l_2} d\hat{N}, \quad (A.6)$$

where

$$A^{m_1\, m_2\, n_1\, n_2}_{j_1\, j_2\, l_1\, l_2} = Y^*_{2j_1,m_1}(\hat{N})\, Y^*_{2j_2,m_2}(\hat{N})\, Y^*_{2l_1,n_1}(\hat{N})\, Y^*_{2l_2,n_2}(\hat{N}).$$

In order of calculation of the right-hand integral in (A.6) let us express the spherical functions through Wigner $\mathscr{D}$-functions:

$$Y^*_{2l,m}(\beta, \alpha) = (-1)^{l-m} \sqrt{\frac{4l+1}{4\pi}}\, \mathscr{D}^{(2l)}_{0,-m}(\alpha, \beta, \gamma)$$

and with the aid of the relationship (see [6], formula 110.2)

$$\mathscr{D}^{(j_1)}_{m_1',m_1}(\omega)\,\mathscr{D}^{(j_2)}_{m_2',m_2}(\omega)=\sum_j(2j+1)\begin{pmatrix} j_1 & j_2 & j\\ m_1' & m_2' & -m'\end{pmatrix}\begin{pmatrix} j_1 & j_2 & j\\ m_1 & m_2 & -m\end{pmatrix}\mathscr{D}^{(j)*}_{-m',-m}(\omega) \tag{A.7}$$

we find the following result for $A^{m_1 m_2 n_1 n_2}_{j_1\, j_2\, l_1\, l_2}$:

$$A^{m_1 m_2 n_1 n_2}_{j_1\, j_2\, l_1\, l_2}=\frac{(-1)^{j_1+j_2+l_1+l_2-m_1-m_2-n_1-n_2}}{(4\pi)^2}[(4j_1+1)(4j_2+1)$$

$$(4l_1+1)(4l_2+1)]^{1/2}.$$

$$\cdot\sum_{j,l}(4j+1)(4l+1)\begin{pmatrix} 2j_1 & 2j_2 & 2j\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} 2l_1 & 2l_2 & 2l\\ 0 & 0 & 0\end{pmatrix}\cdot$$

$$\cdot\begin{pmatrix} 2j_1 & 2j_2 & 2j\\ -m_1 & -m_2 & -m\end{pmatrix}\begin{pmatrix} 2l_1 & 2l_2 & 2l\\ -n_1 & -n_2 & -n\end{pmatrix}(-1)^m\,\mathscr{D}^{(2j)}_{0,m}(\hat N)\,\mathscr{D}^{(2l)*}_{0,-n}\,\hat N).$$

Using the orthogonality condition (see [6], formula 58.20)

$$\int\mathscr{D}^{(j_1)*}_{m_1',m_1}(\omega)\,\mathscr{D}^{(j_2)}_{m_2',m_2}(\omega)\frac{d\omega}{8\pi^2}=\frac{1}{2j_1+1}\delta_{j_1 j_2}\,\delta_{m_1',m_2'}\,\delta_{m_1 m_2},$$

we arrive at the following expression for the integral:

$$\int A^{m_1 m_2 n_1 n_2}_{j_1\, j_2\, l_1\, l_2}\,d\hat N=\frac{(-1)^{j_1+j_2+l_1+l_2-m_1-m_2-n_1-n_2}}{4\pi}$$

$$\cdot[(4j_1+1)(4j_2+1)(4l_1+1)(4l_2+1)]^{1/2}\sum_{j,m}(-1)^m(4j+1)\begin{pmatrix} 2j_1 & 2j_2 & 2j\\ 0 & 0 & 0\end{pmatrix}\cdot$$

$$\cdot\begin{pmatrix} 2l_1 & 2l_2 & 2j\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} 2j_1 & 2j_2 & 2j\\ -m_1 & -m_2 & -m\end{pmatrix}\begin{pmatrix} 2l_1 & 2l_2 & 2j\\ -n_1 & -n_2 & m\end{pmatrix},$$

here $d\omega=2\pi d\hat N$.

Let us return to Eq. (A.6). Substitution of the obtained result into Eq. (A.6) yields

$$\int\frac{\sqrt{1+c_3^2(\hat\Omega_3\hat N)^2+c_2^2(\hat\Omega_2\hat N)^2}}{[1+c_3^2(\hat\Omega_3'\hat N)^2+c_2^2(\hat\Omega_2'\hat N)^2]^2}d\hat N=C(4\pi)^4\sum_{j_1 m_1 j_2 m_2}B_{j_1 j_2}(e_3,\xi)\sum_{l_1 n_1 l_2 n_2}D_{l_1 l_2}(e_3,\xi)$$

$$\cdot\, Y_{2j_1,m_1}(\hat{\Omega}_3)\, Y_{2j_2,m_2}(\hat{\Omega}_2)\, Y_{2l_1,n_1}(\hat{\Omega}'_3)\, Y_{2l_2,n_2}(\hat{\Omega}'_2)\, \frac{1}{4\pi}\, (-1)^{j_1+j_2+l_1+l_2-m_1-m_2-n_1-n_2}$$

$$\cdot\, [(4j_1+1)(4j_2+1)(4l_1+1)(4l_2+1)]^{1/2} \sum_{j,m} (-1)^m (4j+1) \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ 0 & 0 & 0 \end{pmatrix}$$

$$\cdot \begin{pmatrix} 2l_1 & 2l_2 & 2j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ -m_1 & -m_2 & -m \end{pmatrix} \begin{pmatrix} 2l_1 & 2l_2 & 2j \\ -n_1 & -n_2 & m \end{pmatrix}. \tag{A.8}$$

It is convenient to introduce the functions:

$$\psi^{(1)}_{jmj_1j_2}(\omega) \tag{A.9}$$

$$= \sum_{n_1n_2} (-1)^{-n_1-n_2} \sqrt{4j+1} \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ -n_1 & -n_2 & -m \end{pmatrix} Y_{2j_1,n_1}(\hat{\Omega}_3)\, Y_{2j_2,n_2}(\hat{\Omega}_2),$$

$$\psi^{(2)}_{j-mj_1j_2}(\omega') \tag{A.10}$$

$$= \sum_{n_1n_2} (-1)^{-n_1-n_2} \sqrt{4j+1} \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ -n_1 & -n_2 & m \end{pmatrix} Y_{2j_1,n_1}(\hat{\Omega}'_3)\, Y_{2j_2,n_2}(\hat{\Omega}'_2)$$

and change the order of summation in Eq. (A.8). Then one obtains

$$\int \frac{\sqrt{1 + c_3^2(\hat{\Omega}_3\hat{N}\Omega^2 + c_2^2(\hat{\Omega}_2\hat{N})^2}}{[1 + c_3^2(\hat{\Omega}'_3\hat{N})^2 + c_2^2(\hat{\Omega}'_2\hat{N})^2]^2}\, d\hat{N} = C(4\pi)^3 \sum_{j,m} (-1)^m.$$

$$\cdot \sum_{j_1j_2} (-1)^{j_1+j_2} [(4j_1+1)(4j_2+1)] \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ 0 & 0 & 0 \end{pmatrix} B_{j_1j_2}(e_3, \xi)\, \psi^{(1)}_{jmj_1j_2}(\omega)$$

$$\cdot \sum_{l_1l_2} (-1)^{l_1+l_2} [(4l_1+1)(4l_2+1)] \begin{pmatrix} 2l_1 & 2l_2 & 2j \\ 0 & 0 & 0 \end{pmatrix} D_{l_1l_2}(e_3, \xi)\, \psi^{(2)}_{j-ml_1l_2}(\omega'),$$

where we use the notations:

$$F_{j,m} = \sum_{j_1j_2} (-1)^{j_1+j_2} [(4j_1+1)(4j_2+1)]^{1/2} \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ 0 & 0 & 0 \end{pmatrix} B_{j_1j_2}(e_3, \xi)\, \psi^{(1)}_{jmj_1j_2}(\omega),$$

$$G_{j,-m} = \sum_{l_1l_2} (-1)^{l_1+l_2} [(4l_1+1)(4l_2+1)]^{1/2} \begin{pmatrix} 2l_1 & 2l_2 & 2j \\ 0 & 0 & 0 \end{pmatrix} D_{l_1l_2}(e_3, \xi)\, \psi^{(l)}_{jml_1l_2}(\omega').$$

So we find

$$\int \frac{\sqrt{1+c_3^2(\hat{\Omega}_3\hat{N})^2+c_2^2(\hat{\Omega}_2\hat{N})^2}}{[1+c_3^2(\hat{\Omega}'_3\hat{N})^2+c_2^2(\hat{\Omega}'_2\hat{N})^2]^2}\,d\hat{N} = C(4\pi)^3 \sum_{j,m}(-1)^m F_{j,m} G_{j,-m}. \tag{A.11}$$

Let us transform the quantity $\psi^{(1)}_{jmj_1j_2}$. It depends on the angles, which the init vectors $\hat{\Omega}_3$ and $\hat{\Omega}_2$ make with the axes of laboratory frame of reference. So we do the transformation to the molecular frame of reference with the help of the identity

$$Y_{j,m}(\hat{n}_{lab}) = \sum_{m'} \mathscr{D}^{(j)}_{m',m}(\alpha,\beta,\gamma)\,Y_{j,m'}(\hat{n}_{mol}).$$

Here the angles α, β, γ define the rotation of the molecular frame of reference relatively the laboratory one. Note that for a such transformation it is holds

$$Y_{j,m}(\hat{\Omega}_3) = i^j \sqrt{\frac{2j+1}{4\pi}}\,\mathscr{D}^{(j)}_{0,m}(\alpha,\beta,\gamma) = Y_{j,m}(\theta,\phi), \tag{A.12}$$

$$Y_{l,m}(\hat{\Omega}_1) = \frac{i^l}{\sqrt{\pi}}\sqrt{\frac{2l+1}{4\pi}}\sum_{m'}(-1)^{|m'|+((m'+|m'|)/2)}\,i^{m'}\,2^{|m'|}\left[\frac{(l-|m'|)!}{(l+|m'|)!}\right]^{1/2}.$$

$$\cdot\cos\left(\frac{\pi}{2}(l+|m'|)\right)\frac{\Gamma[\frac{1}{2}(l+1+|m'|)]}{\Gamma[\frac{1}{2}(l+2-|m'|)]}\,\mathscr{D}^{(l)}_{m',m}(\alpha,\beta,\gamma), \tag{A.13}$$

$$Y_{l,m}(\hat{\Omega}_2) = \frac{i^l}{\sqrt{\pi}}\sqrt{\frac{2l+1}{4\pi}}\sum_{m'}(-1)^{|m'|+((m'+|m'|)/2)}\,2^{|m'|}\left[\frac{(l-|m'|)!}{(l+|m'|)!}\right]^{1/2}.$$

$$\cdot\cos\left(\frac{\pi}{2}(l+|m'|)\right)\frac{\Gamma[\frac{1}{2}(l+1+|m'|)]}{\Gamma[\frac{1}{2}(l+2-|m'|)]}\,\mathscr{D}^{(l)}_{m',m}(\alpha,\beta,\gamma). \tag{A.14}$$

Taking into account that

$$\cos\left(\frac{\pi}{2}(2j_2+|m'|)\right) = \begin{cases} 0, & m'=2k+1; \\ (-1)^{j_2+k}, & m'=2k, \end{cases}$$

and making the transformation $m' \to 2m'$ in Eqs. (A.13)–(A.14), we arrive after the substitution into Eqs. (A.9)–(A.10) at the following expression:

$$\psi^{(1)}_{jmj_1j_2}(\omega) = \frac{(-1)^{j_1-m}}{4\pi^{3/2}} [(4j_1+1)(4j_2+1)(4j+1)]^{1/2}$$

$$\sum_{m_1,m_2m'} 2^{2|m'|} \left[\frac{(2j_2-2|m'|)!}{(2j_2+2|m'|)!}\right]^{1/2} \cdot$$

$$\cdot \frac{\Gamma(j_2+|m'|+1/2)}{\Gamma(j_2-|m'|+1)} \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ -m_1 & -m_2 & -m \end{pmatrix} \mathscr{D}^{(2j_1)}_{0,m_1}(\omega)\, \mathscr{D}^{(2j_1)}_{2m',m_2}(\omega).$$

Using the relationship for the product of two $\mathscr{D}$-functions (A.7) and the orthogonality condition for the $3j$-symbols

$$(2j+1)\sum_{m_1m_2} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & -m' \end{pmatrix} = \delta_{j,j'}\,\delta_{m,m'}$$

we obtain the final result for $\psi^{(1)}_{jmj_1j_2}(\omega)$:

$$\psi^{(1)}_{jmj_1j_2}(\omega) = \frac{(-1)^{j_1-m}}{4\pi^{3/2}} [(4j_1+1)(4j_2+1)(4j+1)]^{1/2}$$

$$\sum_{m'} 2^{2|m'|} \left[\frac{(2j_2-2|m'|)!}{(2j_2+2|m'|)!}\right]^{1/2} \cdot$$

$$\cdot \frac{\Gamma(j_2+|m'|+1/2)}{\Gamma(j_2-|m'|+1)} \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ 0 & 2m' & -2m' \end{pmatrix} \mathscr{D}^{(2j_1)*}_{-2m',m}(\omega). \tag{A.15}$$

Using this result in $F_{j,m}$ and changing the order of summation, we find

$$F_{j,m} = \frac{\sqrt{4j+1}}{4\pi^{3/2}} \sum_{m'} f_{j,m'}\, \mathscr{D}^{(2j_1)}_{2m',-m_2}(\omega), \tag{A.16}$$

$$f_{j,m'} = 2^{2|m'|} \sum_{j_1,j_2} (-1)^{j_2}(4j_1+1)(4j_2+1)\, B_{j_1,j_2}(e_3,\xi) \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ 0 & 0 & 0 \end{pmatrix} \cdot$$

$$\cdot \begin{pmatrix} 2j_1 & 2j_2 & 2j \\ 0 & 2m' & -2m' \end{pmatrix} \left[\frac{(2j_2-2|m'|)!}{(2j_2+2|m'|)!}\right]^{1/2} \frac{\Gamma(j_2+|m'|+1/2)}{\Gamma(j_2-|m'|+1)}. \tag{A.17}$$

Calculations similar to those performed above lead to the following results for $\psi^{(2)}_{j-ml_1l_2}(\omega')$ and $G_{j,-m}$:

$$\psi^{(2)}_{j-ml_1l_2}(\omega')=\frac{(-1)^{l_1+m}}{4\pi^{3/2}}\left[(4l_1+1)(4l_2+1)(4j+1)\right]^{1/2}$$

$$\sum_{n'}2^{2|n'|}\left[\frac{(2l_2-2|n'|)!}{(2l_2+2|n'|)!}\right]^{1/2}\cdot$$

$$\cdot\frac{\Gamma(l_2+|n'|+1/2)}{\Gamma(l_2-|n'|+1)}\begin{pmatrix}2l_1 & 2l_2 & 2j\\ 0 & 2n' & -2n'\end{pmatrix}\mathscr{D}^{(2j)*}_{-2n',-m}(\omega'),$$

$$G_{j,-m}=\frac{\sqrt{4j+1}}{4\pi^{3/2}}\sum_{n'}g_{j,n'}\mathscr{D}^{(2j)}_{2n',m}(\omega'),$$

$$g_{j,n'}=2^{2|n'|}\sum_{l_1,l_2}(-1)^{l_2}(4l_1+1)(4l_2+1)D_{l_1,l_2}(e_3,\xi)\begin{pmatrix}2l_1 & 2l_2 & 2j\\ 0 & 0 & 0\end{pmatrix}\cdot$$

$$\cdot\begin{pmatrix}2l_1 & 2l_2 & 2l\\ 0 & 2n' & -2n'\end{pmatrix}\left[\frac{(2l_2-2|n'|)!}{(2l_2+2|n'|)!}\right]\frac{\Gamma(l_2+|n'|+1/2)}{\Gamma(l_2-|n'|+1)}.$$

Thus the third item in Eq. (11) can be written as:

$$\int\frac{\sqrt{1+c_3^2(\hat{\Omega}_3\hat{N})+c_2^2(\hat{\Omega}_2\hat{N})^2}}{[1+c_3^2(\hat{\Omega}'_3\hat{N})^2+c_2^2(\hat{\Omega}'_2\hat{N})^2]^2}\,d\hat{N}$$

$$=4C\sum_{j=0}^{\infty}(4j+1)\sum_{m=-j}^{j}(-1)^m\sum_{m',n'=-j}^{j}f_{j,m'}g_{j,n'}\mathscr{D}^{(2j)}_{2m',-m}(\omega)\mathscr{D}^{(2j)}_{2n',m}(\omega')$$

Let us calculate now this item directly in the molecular frame of reference. Using Eq. (A.5) we find

$$q^{1/2}=\frac{(4\pi)^2}{2\sqrt{1-e_3^2}}\sum_{j,m}\sum_{l,n}B_{jl}(e_3,\xi)\,Y^*_{2j,m}(\hat{\Omega}_3)Y^*_{2l,n}(\hat{\Omega}_2)Y_{2j,m}(\hat{N})\,Y_{2l,m}(\hat{N}).\quad\text{(A18)}$$

Note that in the molecular frame of reference we have

$$Y^*_{2j,m}(\hat{\Omega}_3)=Y^*_{2j,m}(0,0)=(-1)^j\sqrt{\frac{4j+1}{4\pi}}\delta_{m,0},$$

$$Y^*_{2j,2m}(\hat{\Omega}_1) = Y^*_{2j,2m}\left(\frac{\pi}{2}, 0\right)$$

$$= (-1)^{j+m}\frac{\sqrt{4j+1}}{2\pi}2^{2|m|}\left[\frac{(2j-2|m|)!}{(2j+2|m|)!}\right]^{1/2}\frac{\Gamma(j+1/2+|m|)}{\Gamma(j+1-|m|)},$$

$$Y^*_{2j,2m}(\hat{\Omega}_2) = Y^*_{2j,2m}\left(\frac{\pi}{2}, \frac{\pi}{2}\right)$$

$$= \sqrt{\frac{4j+1}{2\pi}}2^{2|m|}\left[\frac{(2j-2|m|)!}{(2j+2|m|)!}\right]^{1/2}\frac{\Gamma(j+1/2+|m|)}{\Gamma(j+1-|m|)}.$$

Inserting these quantities in Eq. (A.18) and multiplying by

$$(-1)^j\frac{\sqrt{1-e_3^2}}{\sqrt{4j+1}}Y^*_{2j,2m'}(\hat{N}),$$

one can integrate over $\hat{N}$, using the identity:

$$\int Y_{2j_1,0}(\hat{N})Y^*_{2j,2m'}(\hat{N})Y_{2j_2,2m'}(\hat{N})\,d\hat{N} = (-1)^{j_1+j_2-j+2m'}.$$

$$\cdot\begin{pmatrix}2j_1 & 2j_2 & 2j\\ 0 & 2m & -2m'\end{pmatrix}\begin{pmatrix}2j_1 & 2j_2 & 2j\\ 0 & 0 & 0\end{pmatrix}\left[\frac{(4j_1+1)(4j_2+1)(4j+1)}{4\pi}\right]^{1/2}.$$

After some algebra we find

$$\sqrt{1-e_3^2}\int b^{1/2}\frac{(-1)^j Y^*_{2j,2m}(\hat{N})}{\sqrt{4j+1}}d\hat{N}$$

$$= 2^{2|m|}\sum_{j_1,j_2}(-1)^{j_2}(4j_1+1)(4j_2+1)B_{j_1,j_2}(e_3,\xi)$$

$$\cdot\begin{pmatrix}2j_1 & 2j_2 & 2j\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}2j_1 & 2j_2 & 2j\\ 0 & 2m & -2m\end{pmatrix}\left[\frac{(2j_2-2|m|)!}{(2j_2+2|m|)!}\right]^{1/2}\frac{\Gamma(j_2+|m|+1/2)}{\Gamma(j_2-|m|+1)}.$$

Note that the quantity in the right-hand part is $f_{j,m}$ – see Eq. (A.17). Performing the similar calculations for $g_{j,m}$ we arrive at Eqs. (13). Also note that in the above formulas the unit vectors $\hat{\Omega}_i$ must be taken in the molecular frame of reference which is connected with the principal axes of the ellipsoids. This means that $\hat{\Omega}_1 = (1,0,0)$; $\hat{\Omega}_2 = (0,1,0)$; $\hat{\Omega}_3 = (0,0,1)$.

Calculations similar to those performed above allows one to detemine the forth item in $E(\hat{\Omega}_1, \hat{\Omega}_2)$. Collecting all of these items, one can write Eq. (12).

References

[1] B. Barboy and W. M. Gelbart, *J. Chem. Phys.*, **71**, 3053 (1979).
[2] B. Tjipto-Margo and G. T. Evans, *J. Chem Phys.*, **93**, 4254 (1990).
[3] A. Daanoun, C. F. Tejero and M. Baus, *Phys. Rev. E.*, **50**, 2913 (1994).
[4] A. N. Zakhlevnykh and P. A. Sosnin, *Statistical Thermodynamics of a Hard Ellipsoid Liquid. Steric and Dispersion Interactions* (Sverdlovsk, Urals Br. Ac. Sci., USSR, 1988).
[5] A. Isihara, *J. Chem. Phys.*, **19**, 1142 (1951).
[6] L. D. Landau and E. M. Lifshitz, *Quantum mechanics – Non Relativistic Theory* (Pergamon, London, 1958).
[7] I. M. Ryzhik and I. S. Gradshtein, *Tables of integrals, sums and products* (Moscow-Leningrad, Gostehizdat, 1951).
[8] C. Zannoni, *Nuclear Magnetic Resonance of Liquid Crystals, Proc NATO Adv. Study Inst.*, edited by J. M. Emsley (Dordrecht e.a.) 1 (1985).
[9] J. P. Straley, *Phys. Rev. A.*, **10**, 1881 (1974).
[10] P. Palffy-Muhoray and G. L. Hoatson, *Phys. Rev. A*, **44**, 5052 (1991).
[11] B. M. Mulder and D. Frenkel, *Mol. Phys.*, **50**, 1193 (1985).
[12] J. L. Lebowitz and J. W. Perram, *Mol. Phys.*, **50**, 1207 (1983).
[13] V. V. Rusakov and M. I. Shliomis, *J. de Physique Lett.*, **46**, 935 (1985).
[14] P. G. De Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1974).
[15] A. N. Zakhlevnykh and M. I. Shliomis, *Sov. Phys. JETP*, **59**, 764 (1984).
[16] B. Mulder, *Phys. Rev. A.*, **39**, 360 (1989).
[17] M. P. Allen, *Liq. Cryst.*, **8**, 499 (1990).
[18] R. Holyst and A. Poniewierski, *Mol. Phys.*, **69**, 193 (1990).