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A statistical-mechanical model for calculating equilibrium properties of a nematic liquid crystal

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Abstract. — We have proposed an optimized statistical-mechanical model of a nematic liquid crystal using the method of conditional distributions due to Rott. The calculations have been carried out for hexagonal and cubic close packings with the nearest neighbour Gay-Berne intermolecular potential. The theory takes pair intermolecular correlations into account. The hexagonal close packing proves to be favourable as compared to the cubic one. Optimized values of the cell model parameter have been calculated providing the minimum Helmholtz free energy of a liquid crystal.

1. Introduction.

The purpose of this work is to construct an optimized statistical-mechanical model of a nematic liquid crystal (NLC) at equilibrium. The model fluid under consideration consists of ellipsoidal molecules interacting via angle-dependent nonseparable pair potentials.

Many molecular fluids consisting of anisometric molecules exhibit one or several liquid crystalline phases between the usual isotropic liquid and the solid phases [1]. The simplest among those liquid crystals (LC) is the NLC which is characterized by a short-range translational and long-range orientational order. Whether or not a given molecular liquid will have a nematic phase depends in a rather subtle way on the shape of the constituent molecules. First of all, the intermolecular interactions have to be sufficiently anisotropic to favour orientational ordering [2]. Therefore, a good model for a nematogen has to be also anisotropic.

The description of systems of ellipsoidal molecules at equilibrium is an important goal of the

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theory of NLC. One of the useful approaches to this problem is the integral equation theory. This theory has been applied to the investigation of many systems interacting via angle-dependent potentials [4-7], but relatively few studies [8] have centred on nematic systems.

In this paper we make an attempt to combine the advantages of integral equation theory and of the cell model approach to construct an optimized statistical-mechanical model for calculating equilibrium properties of NLC. Recently a closed statistical scheme for calculating the structural and thermodynamical properties of NLC based on the method of conditional distribution (MCD) originally proposed by Rott [9] has been developed [10, 11].

In this work we generalize our previous results [10, 11] and introduce an improved model which corresponds more strictly to the equilibrium state of NLC. Moreover, the method goes at least one step beyond the mean-field level. We know that the simplest model (the Maer-Saupe theory) gives the accurate values of the order-parameter \( \langle P_2 \rangle \) at the isotropic-nematic transition but if one wants to understand the nature of the correlations between orientational and translational degrees of freedom in anisotropic systems one must use a theory which takes these correlations into account. To improve upon the crude molecular-field approximation, it is necessary to include effects of correlations. It can be made, for example, in the framework of the optimized statistical mechanical model.

It is the main purpose of the present article to present a new statistical mechanical theory for the description of anisotropic classical systems. The second purpose of this paper is to show how the general formalism can be used to derive useful results for other problems. In particular, the new theory enables one to examine the cell packings. These problems involve one in still more complicated studies longer-ranged correlations.

The plan of this paper is as follows. A short description of the model is given in section 2, the theory of integral equations is presented in section 3, the computational procedure is given in section 4, the intermolecular potential is described in section 5, the results are discussed in section 6, and finally the conclusions are given in section 7.

2. Cell model.

One of the most important points of any cell model is the choice of the cell shape. This choice can be made on the basis of two conditions. First, we consider the system in the equilibrium state which is related to the Helmholtz free energy minimum conditions, i.e.

\[
(\delta F)_{V,T} = 0, \quad (\delta^2 F)_{V,T} \geq 0,
\]

where \( V \) and \( T \) are the volume and the temperature of the system, respectively. This condition is efficiently used, for example, for the determination of vacancy fraction in a solid [13]. The model we use here however implies that every cell is occupied by a molecule, thus the number of cells equals that of particles, which seems reasonable for a condensed system.

The second condition is related to the choice of a cell shape. Equations (1) cannot be immediately used for the determination of the shape. A nematic liquid crystal is composed of anisotropic molecules characterized by cylindrical symmetry. The symmetry of a cell should be consistent with that of a molecule. This implies that the most suitable shape for a cell is a cylinder. However cylindrical cells do not yield a close packed structure (see Fig. 1a). This is why we consider further two types of close packings: hexagonal and cubic. These structures are sketched in figures 1b, c, respectively.

With density and number of cells being fixed, the magnitude of the cell volume is also fixed. At a given cell shape it means that a model includes one (as in the case of hexagonal close packing (hcp)) or two (as in the case of cubic close packing (ccp)) free parameters. Since
molecular volumes for hcp and ccp structures are defined as $v_{\text{hcp}} = 3 \sqrt{3} ah^2/2$ and $v_{\text{ccp}} = a \cdot b \cdot c$, respectively (see Figs. 1b, c), we can choose $h$ for hcp and $a$ and $b$ for ccp as free parameters. These are the parameters which can be determined using equation (1).

Thus, the last question we have to answer is which of the above two packings is favourable. Unfortunately, equation (1) does not answer this question. All we can do is to compare the values of the Helmholtz function for the packings under consideration at given values of $N$, $V$, $T$ and make the choice in favour of that which provides the lower value of the free energy and, as a consequence, more stable state of the system. Thus, the purpose of the theory is to relate the free parameters to the free energy of the system which will make it possible to use equation (1).

In each approximation, reduced distribution functions are introduced. They obey an infinite chain of integro-differential equations. The problem of truncation of the chain was specifically solved within the framework of the method. The initial chain of integro-differential equations was first transformed into a chain of integral equations for so-called average-force potentials. Further truncation at the lowest order equation preserved binary correlations.

It should be emphasized that the MCD is quite different from the variational self-consistent field method first applied by Kirkwood to the cell model.

In this paper we propose an optimized statistical-mechanical cell model using the above method. The model takes intermolecular correlations into account and allows us to make a choice between cubic and hexagonal close packing.

We use the statistical scheme in which the total volume \( V \) of the system of \( N \) molecules is divided into \( N \) equal cells, \( v = V/N \), every cell being occupied by a molecule. By integrating the Gibbs canonical distribution, a set of functions \( F_i(i) \), \( F_{ij}(ij) \), etc., is introduced defining the probability densities for the molecules to be found about the positions \( m = W_m \) \( (W_m = v_m \oplus \alpha_m, \alpha_m \) is the volume associated with orientations ; \( m = i, j \). The above functions satisfy the system of integral relations following from their definitions:

\[
\int_i d(i) F_i(i) = 1, \quad \int_j d(j) F_{ij}(ij) = F_i(i). \tag{2}
\]

The two-particle and the three-particle functions also obey the integral relation, etc. Below we take into account the first two functions of the infinite hierarchy; this corresponds to taking into account only pair correlations between molecules. We can present the functions as [12]

\[
F_i(i) = Q^{-1} \exp \{- \beta \varphi_i(i)\}, \tag{3}
\]

\[
F_{ij}(ij) = Q^{-2} \exp \{- \beta \left[ (\Phi_{ij}) + \varphi_{ij}(ij) \right]\}, \tag{4}
\]

where

\[
Q = \int_i d(i) \exp \{- \beta \varphi_i(i)\}, \quad \int_i = \int_{W_i}, \quad d(i) = dq_i \, de_i,
\]

here \( q_i \) is the position of the center of mass of the \( i \)-th molecule, \( e_i \) is its orientation, \( \Phi \) is the interaction potential of two molecules, \( \beta \) is the inverse temperature, \( \varphi_i(i) \) and \( \varphi_{ij}(ij) \) are the mean force potential and are of the form

\[
\varphi_i(i) = \sum_{\ell \neq i} \varphi_{i,\ell}(i), \tag{5}
\]

\[
\varphi_{ij}(ij) = \sum_{\ell \neq i, j} \varphi_{ij,\ell}(ij). \tag{6}
\]

The terms in the sum (5, 6) are given by

\[
\nabla_i \varphi_{i,\ell}(i) = \int_\ell d(\ell) \nabla_i \Phi(i,\ell) F_i(i,\ell)/F_i(i), \tag{7}
\]

\[
\nabla_i \varphi_{ij,\ell}(ij) = \int_\ell d(\ell) \nabla_i \Phi(i,\ell) F_{ij}(ij,\ell)/F_{ij}(ij). \tag{8}
\]

The quantities (7) and (8) are the mean forces on a molecule in the \( i \)-th cell due to the molecule in the \( \ell \)-th cell averaged over the state of the latter.

To close the system of equations (2), we decompose the mean force potentials into irreducible parts [12]. In the case considered here we have

\[
\varphi_{ij,\ell}(ij) = \varphi_{i,\ell}(i) + \varphi_{j,\ell}(j) + \omega_{ij,\ell}(ij), \tag{9}
\]

where \( \omega_{ij,\ell}(ij) \) is the irreducible part of the mean force potential \( \varphi_{ij,\ell}(ij) \). If now the irreducible part of the potential is set equal to zero:

\[
\omega_{ij,\ell}(ij) = 0, \tag{10}
\]
which corresponds to neglecting three-particle and higher-order correlations, the expression for the binary function takes the form

$$F_{ij}(ij) = K(ij) \cdot \psi_{i,j}^{-1}(i) \cdot \psi_{j,i}^{-1}(j) \cdot F_i(i) \cdot F_j(j),$$  \hspace{1cm} (11)

where

$$K(ij) = \exp \left\{ -\beta \Phi(ij) \right\},$$  \hspace{1cm} (12)

$$\psi = \exp \left\{ -\beta \varphi \right\}.$$  \hspace{1cm} (13)

The three first factors in equation (11) reflect the correlation between molecules and distinguishes our approach from the mean field approximation. Using now relation (2) between the single and binary functions, we arrive at

$$\psi_{i,j}(i) = \int d(j) F_j(j) \psi_{j,i}(j).$$  \hspace{1cm} (14)

Since $\psi_{i,j}(i), \psi_{j,i}(j)$ and $F_j(j)$ are related to mean force potentials through equations (13) and (3) respectively, equation (14) is the system of nonlinear integral equations (NIE) for mean force potentials.

The Helmholtz free energy is [12, 13]

$$F/N = -\beta^{-1} \ln \int d(i) \psi_i(i).$$  \hspace{1cm} (15)

Thus, we have the expression for the Helmholtz free energy in terms of mean force potentials which satisfy the system of NIE. To solve the system we have to choose the form of intermolecular potential, the values of temperature and density of the system, and packing type.

4. Computational procedure.

Solution of equation (14) for the nematic phase is based upon the fact that the single function $F_i(i)$ is a function of $\cos \theta$, where $\theta_i$ is the angle between the $z_i$-axis, which coincides with the director, and the long molecular axis of the $i$-th molecule. The essential difference between a nematic phase and an isotropic fluid is that the distribution of molecular orientations has a cylindrical symmetry in the nematic phase instead of the spherical one that is found in the isotropic fluid [1]. For an axially symmetric distribution, the most general form of $F_i(i)$ is

$$F_i(i) = \psi_i(\cos \theta_i) \int d(i) \psi_i(\cos \theta_i).$$  \hspace{1cm} (16)

In order to test the practical utility of the ideas described in this article, it is necessary to have detailed computer simulation data on the structure of orientationally ordered systems. Such data are lacking at present.

The method of solution of the five-dimensional problem (14) is more complicated. We solve it numerically by an iterative method,

$$\psi_{i,j}[n+1](P_j) = \left\{ \psi_{i,j}[n](P_j) \cdot \int \frac{d(P_j) K(P_i, P_j) \psi_{j,i}[n](P_j)}{\int_{W_j} d(P_j) \psi_{j,i}[n](P_j)} \right\}^{1/2},$$  \hspace{1cm} (17)
where \( \mathbf{P}' \)'s are the vectors in five-dimensional space \( W_i = v_i \oplus \alpha_i \). The solution does not depend on the initial approximation. The basic difficulty in solving equation (14) is that algorithm (17) requires successive evaluations of five-dimensional integrals.

In the present paper, we apply Sobol's method [14] using the Haar functions for calculating the multi-dimensional integrals which gives

\[
\int_0^1 \int_0^1 \ldots \int_0^1 dx_1 \ldots dx_n f(x_1, x_n) \approx \frac{1}{N} \sum_{\mathbf{P}_0} f(\mathbf{P}_0).
\]

Here \( \mathbf{P}_0 \)'s are the points uniformly (mod 1) distributed in the \( n \)-dimensional unit cube. These points belong to a \( L_{p,n} \) sequence [15], \( N \) is the number of points. The precision of our calculations is about \( R = 0 \ (N^{-1} \ln^s N) \), where \( n \) is the dimensionality of space. Our calculations were executed using \( N = 100 \). For the case with \( N = 200 \), the difference between the potentials \( \psi_{i,j}^{[00]} \) and \( \psi_{i,j}^{[200]} \) in the nematic phase

\[
\delta = \left| \psi_{i,j}^{[00]} - \psi_{i,j}^{[200]} \right| / \left| \psi_{i,j}^{[200]} \right|
\]

for \( \mathbf{P}_i \in W_i \) is about 0.1%.

Algorithm (17) was implemented as follows: the initial approximation was set to be \( \psi_{i,j}^{[0]}(\mathbf{P}_i) = \psi_{i,j}^{[0]}(\mathbf{P}_j) = 1 \). Then the integral on the right-hand side of (17) was calculated with the help of a \( L_{p,n} \) sequence. This procedure was repeated for all neighbours of the \( i \)-th particle. The coordinates \( \mathbf{P}_i \) in (17) were chosen in such a way that \( \psi_{i,j}^{[1]}(\mathbf{P}_i) \) had been calculated at the points forming the same stationary \( L_{p,n} \) sequence as that used in the evaluation of the integrals with the initial approximation \( \psi_{i,j}^{[0]}(\mathbf{P}_i) \). Then \( \psi_{i,j}^{[1]}(\mathbf{P}_j) \) was calculated by simple multiplication of \( \psi_{i,j}^{[1]}(\mathbf{P}_i) \). The procedure was then iterated until a given accuracy was achieved, where the translational invariance of the total potential was taken into account.

5. Intermolecular potential.

Calculations were carried out with the Gay-Berne potential [3] (see, also [16])

\[
\Phi(\mathbf{q}_{ij}, \mathbf{e}_i, \mathbf{e}_j) = 4 \varepsilon(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij}) \left\{ \left[ \sigma_0/\left( \mathbf{q}_{ij} - \mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij} \right) + \sigma_0 \right] \right\}^{12} - \\
\left\{ \left[ \sigma_0/\left( \mathbf{q}_{ij} - \mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij} \right) + \sigma_0 \right] \right\}^{6},
\]

(18)

\( \mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij} \) are respectively, the unit vectors along the molecular axes of symmetry, \( \mathbf{q}_{ij} \) is the distance between the molecular centers. The potential-energy parameter \( \varepsilon \) and the size parameter, \( \sigma \), depend upon molecular orientations and are given by

\[
\sigma_i(\mathbf{e}_j, \mathbf{e}_{ij}, \mathbf{e}) = \sigma_0 \left[ 1 - \chi \left( \frac{(\mathbf{e}_i \cdot \mathbf{e}_j + \mathbf{e}_j \cdot \mathbf{e}_{ij})^2}{1 + \chi \mathbf{e}_i \cdot \mathbf{e}_j} + \frac{(\mathbf{e}_i \cdot \mathbf{e}_j - \mathbf{e}_j \cdot \mathbf{e}_{ij})^2}{1 - \chi \mathbf{e}_i \cdot \mathbf{e}_j} \right) \right]^{-1/2},
\]

(19)

where \( \sigma_0 \) is the constant which will be identified below. The shape anisotropy parameter, \( \chi \), is

\[
\chi = \left\{ (\sigma_1/\sigma_s)^2 - 1 \right\} / \left\{ (\sigma_1/\sigma_s)^2 + 1 \right\},
\]

(20)

where \( \sigma_1 \) and \( \sigma_s \) are end-to-end and side-by-side separation, respectively. In other words, \( \sigma_1 \) and \( \sigma_s \) are essentially the length and breadth of particle ; \( \chi \) vanishes for spherical particles,
is one for infinitely long rods and minus one for infinitely thin disks. We shall write the depth of the well as

\[ \varepsilon(e_i, e_j, e_{ij}) = \varepsilon_0 \varepsilon^\nu(e_i, e_j) \varepsilon^\mu(e_i, e_j, e_{ij}), \]

where

\[ \varepsilon_0 \varepsilon(e_i, e_j) = \varepsilon_0 \left( 1 - \chi (e_i \cdot e_j)^2 \right)^{-1/2}, \]

\[ \varepsilon'(e_i, e_j, e_{ij}) = 1 - \frac{\chi'}{2} \left\{ \frac{(e_i \cdot e_{ij} + e_j \cdot e_{ij})^2}{1 + \chi' e_i \cdot e_j} + \frac{(e_i \cdot e_j - e_i \cdot e_j)^2}{1 - \chi' e_i \cdot e_j} \right\}, \]

where the parameter \( \chi' \) is related to the anisotropy in the well depth via

\[ \chi' = \left\{ 1 - (\varepsilon_i/\varepsilon_s) \right\}/\left\{ 1 + (\varepsilon_i/\varepsilon_s) \right\}. \]

The well depth \( \varepsilon \) and the intermolecular separation \( \sigma \) clearly change with the orientations of the molecules and the intermolecular vector. The parameters \( \chi, \chi', \nu, \mu, \varepsilon_0 \) and \( \sigma_0 \) characterize the Gay-Berne potential. The exponents \( \nu \) and \( \mu \) in equation (21) are treated as adjustable parameters. The length-to-breadth ratio, \( \sigma_0/\sigma_s \), was set equal to 3, which is typical of a mesogenic molecule and \( \varepsilon_i/\varepsilon_s \) was given the value of 1/5. In the simulation, the scaled temperature was set equal to \( \theta = kT/\varepsilon_0 = 0.43 \); 0.5 and scaled density \( \rho^* = N \sigma_0^3/V \) less than 1.0, the system exhibits a nematic phase with long range orientational order and just short range translational order. In this study, we have not attempted to locate other liquid crystal phases such as smectic A which has a layer structure with short range translational order within the layers [11]. The parametrization of the well depth function \( \varepsilon(e_i, e_j, e_{ij}) \) used in our study did not differ from that employed previously [16]. The exponents \( \nu = 2 \) and \( \mu = 1 \) were used with \( \nu = 1 \) and \( \mu = 2 \); this does not influence the relative well depths for the side-by-side or end-to-end configurations. However, with the parametrization \( (\nu = 2, \mu = 1) \) the side-by-side configuration is relatively more stable with respect to the cross and the configurations.

6. Results.

We turn now the molecular organization in a nematic phase. We shall consider two kinds of packing: simple cubic and hexagonal packing. In the first case, a cell has six nearest neighbour cells, while in the second it has eight. We restrict ourselves to the nearest neighbour approximation which is dictated by computational considerations.

We consider first the cubic packing. In this case, the scaled Helmholtz free energy \( f/\varepsilon_0 \) is a function of any two independent parameters which define the cell volume \( v = a \cdot b \cdot c \) (these parameters are shown in Fig. 1c). For example \( a \) and \( b \) are independent parameters while \( c = vl(a \cdot b) \). Solving the system of NIE (14) and then calculating the Helmholtz free energy (15) yields optimal values of the above parameters, thus providing the minimum scaled free energy. These values together with the corresponding values of the free energy are given in table I. From these calculations, one can obviously see that the shape of the optimal cell continuously changes from an oblate to a prolate box with decreasing density. We have also found that for a higher scaled temperature \( \theta = 0.5 \) the behaviour of the optimal cell shape is similar to that in the previous case.

We also note that within the accuracy of our calculations the parameters \( a \) and \( b \) proved to be equal to \( a = b \), i.e., the optimal shape of the cell is like a box with a square cross-section. This implies that there is only one independent parameter. The dependence of
Table I. — Calculated optimal values of the parameters $a$, $b$ and $c$ ($v = abc$) and the Helmholtz free energy potential for the reduced temperature $\theta = 0.43$. The exponents $\nu$ and $\mu$ in equation (21) equal $\nu = 1$, $\mu = 2$ for the first column, and $\nu = 2$, $\mu = 1$ for the second column: calculations were performed for the nematic PAA with the values $\sigma_0 = 5.01 \text{ \AA}$, $\varepsilon_0/k = 520$ K.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>4.0</th>
<th>3.0</th>
<th>2.0</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>1.15</td>
<td>1.08</td>
<td>1.58</td>
<td>1.68</td>
</tr>
<tr>
<td>$b$</td>
<td>1.15</td>
<td>1.08</td>
<td>1.58</td>
<td>1.69</td>
</tr>
<tr>
<td>$c$</td>
<td>3.02</td>
<td>3.43</td>
<td>1.21</td>
<td>1.06</td>
</tr>
<tr>
<td>$f/\varepsilon_0$</td>
<td>2.58</td>
<td>6.64</td>
<td>0.176</td>
<td>2.75</td>
</tr>
</tbody>
</table>

the scaled Helmholtz free energy on this parameter at a fixed density is plotted in figure 2. One can readily see from the figure that the free energy has a distinct maximum as a function of $a$. In other words, it means that there is an optimal square cross-section for the fixed density which provides the equilibrium packing of NLC.

We have also calculated the shape of the optimal cell for the hexagonal close packing which is characterized by one independent parameter (see Fig. 1b). The results are given in table II.

![Figure 2](image)

**Fig. 2.** — Free Helmholtz energy vs. the cell shape. (The cell shape is like a hard rod of a square cross section with length $c$ and thickness $a = b$) for $\rho^* = 0.25$ and $\theta = 0.43$ (curve 1); 0.5 (curve 2).

Table II. — Calculated optimal values of the parameters $a$ and $h$ ($v = \frac{3\sqrt{3}h^2a}{3}$) and the Helmholtz free energy potential for $\theta = 0.43$. The exponents $\nu$ and $\mu$ in equation (21) were set equal to $\nu = 1$ and $\mu = 2$.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>4.0</th>
<th>3.0</th>
<th>2.0</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>0.674</td>
<td>0.646</td>
<td>0.648</td>
<td>0.648</td>
</tr>
<tr>
<td>$h$</td>
<td>3.39</td>
<td>2.77</td>
<td>1.83</td>
<td>0.92</td>
</tr>
<tr>
<td>$f/\varepsilon_0$</td>
<td>8.79</td>
<td>8.78</td>
<td>8.60</td>
<td>8.59</td>
</tr>
</tbody>
</table>
From this case we have found that the optimal shape of a cell has a tendency to shorten its height with increasing density or decreasing scaled volume.

We can now compare the two competing close packings and answer the question which is more favourable. Comparing the values of the Helmholtz free energy for the two structures studied we see that the value for hexagonal close packing is lower than that for cubic one. We come to the conclusion that the hexagonal close packing is favourable for the ranges of density and temperature used in the calculations.

The results obtained show that the parameters of the statistical-mechanical cell model are not arbitrary, the optimal structure is the hexagonal close packing and the ratio \( a/h \) is the temperature and volume dependent parameter which is defined by the equilibrium condition (1).

---

Fig. 3. — Temperature dependence of the order parameter \( \langle P_2 \rangle \) for different values of the ellipticity parameter: \( \omega = \sigma_1/\sigma\_s = 2.0 \) (curve 1); 2.5 (curve 2); 3.0 (curve 3), where the points are the experimental data of [18] (V).

Fig. 4. — Dependence of the orientational correlation function of two molecules on the ellipticity parameter for the same values of \( T \) as in figure 3.
Knowing the average force potential $\psi_{i,j}(i)$ we can also calculate the order parameter
\[ \langle P_2 \rangle = \langle P_2(\cos \theta_i) \rangle = (3 \langle \cos^2 \theta_i \rangle - 1)/2, \]
where angular bracket mean
\[ \langle \ldots \rangle = \int d(Q_i) F_i(Q_i) \langle \ldots \rangle, \]
$P_1(\cos \theta_i)$ is the Legendre polynomial of order 1, $\theta_i$ is the polar angle between the molecular axis and the director and the correlations between orientations
\[ \langle P_2(\cos \theta_i) P_2(\cos \theta_j) \rangle = [9 \langle \cos^2 \theta_i, \cos^2 \theta_j \rangle - 3 \langle \cos^2 \theta_i \rangle - 3 \langle \cos^2 \theta_j \rangle + 1]/4. \]
The calculation of the order parameter (Fig. 3) shows that it decreases with increasing temperature; this agrees with the experimental results [18]. However, the order parameter increases with increasing ellipticity parameter. The correlation of the angular positions of two nearest-neighbour molecules increases slightly with increasing temperature, and strongly increases with increasing ellipticity parameter (Fig. 4). The ellipticity parameter has an insignificant

Fig. 5. — a) Plot of the ODF on the reduced temperature $\theta = (kT/\epsilon_0) \times 10$ and angle $\theta_i$, b) Plot of the orientational distribution function (ODF) $F_1(\cos \theta_i)$ on the reduced volume $v/\sigma_0^3$ and the angle $\theta_i$. 
effect on the orientational distribution function (ODF) \( F_i(\cos \theta_i) \); with increasing temperature \( \theta = (kT/\varepsilon_0) \times 10 \) (Fig. 5a) and the reduced volume \( v/\sigma_0^3 \) (Fig. 5b) \( F_i(\cos \theta_i) \) tends to smooth out, and this reflects orientational disorder in the nematic liquid crystal. It is known that the one-particle function \( F_i(\cos \theta_i) \) of NLC has a rather sharp maximum at the point \( \theta_i = 0 \) (i.e., around the director \( n \)), rapidly decreasing as \( \theta_i \) tends to \( \theta_i = \pi/2 \). At \( \theta = \pi/2 \) the function value is small but finite. So, the value of \( F(\pi/2) \) defines the « gate » width in orientation space through which the molecule diffuses from one orientation to another. The calculation of the order parameter (OP) (Fig. 6) shows that it decreases with increasing temperature. At this point, the angular correlation is stronger and the nematic phase is less stabilized for \( v/\sigma_0^3 > 4.0 \). By means of MFPs (5), the scaled Helmholtz free energy \( f/\varepsilon_0 \) has been calculated (15) (Fig. 7). Both the orders of magnitude of the quantities and the nature of the dependence of the results are consistent with the known results obtained by using other approaches [1, 7, 16].
7. Conclusion.

We have proposed an optimized statistical-mechanical cell model of a nematic liquid crystal using the method of conditional distributions due to Rott. We have carried out the calculations for two close packings: hexagonal and cubic with the nearest-neighbour Gay-Berne interaction potential. The theory takes pair intermolecular correlations into account. We have shown that the hexagonal close packing is favourable, as compared to the cubic one for the intermolecular interaction potential and the ranges of density and temperature used in the calculations. We have also shown that the models are characterized by one size parameter and determined the optimal values of the parameter for both close packings corresponding to the equilibrium state of a liquid crystal.
Fig. 7. — Plot of the scaled Helmholtz free energy \( f/\varepsilon_0 \) on the reduced volume \( v/\sigma_0^3 \) and the reduced temperature \( \theta = (kT/\epsilon_0) \times 10 \).

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References