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Orientational ordering in fluids with partially constrained molecule orientations

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Molecular orientations in anisotropic fluids can be partially constrained as a result of electric or magnetic fields or interface influences. A statistical approach for the investigation of the orientational ordering in such systems is proposed. The long-range correlations are taken into account consistently. The method is illustrated for the well-known thermotropic nematic model in an infinite disorienting field $\boldsymbol{W}$, when the molecules are constrained to orient perpendicularly to the field direction. For this problem the analytical solution of the anisotropic Ornstein-Zernike equation is obtained, and the asymptotic expression for the long-range correlations on large distances is given. The phase diagram and elastic constants are calculated for $W\to\infty$ and are compared with the usual case of a uniaxial nematic ordering at $W=0$. In the case $W\to\infty$ when the temperature decreases the orientational phase transition of the second order becomes the one of the first order at a tricritical point. The disorienting field W increases much the region of an ordered fluid. It is shown that at a given pressure the orientational ordering temperature for $W\to\infty$ is higher about 1.2–1.5 times than the one at $W=0$. The orientational ordering pressure is less about 4–5 times than the pressure of the uniaxial nematic ordering ($W=0$) at the same temperature. The disorienting field increases elastic properties of the model under consideration.

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The formation of a one-component biaxial nematic phase is usually associated with fluids consisting of molecules (or aggregates of molecules) that do not have axial symmetry. Indeed, there is no example where a pure system of uniaxial molecules forms a biaxial nematic without external influences [1]. But at some conditions this system does become biaxial. This takes place near the interface with other medium (wall) if nematic molecules prefer to be parallel to the surface plane [2]. The biaxiality can be induced also by a disorienting field [3]. It can be either the electric or the magnetic field since many nematics have a negative anisotropy, and their molecules tend to align perpendicularly to the field [4]. In the limiting case of a strong disorienting field $\vec{W}$ directed along the z axis the particles are constrained to be parallel to the xy plane (Fig. 1). For this case one can use the description that will be referred in this paper as the plane rotator (PR) models. These models (in which an orientation of the particle i is completely determined by the single angle φ_i) were studied intensively for the lattice systems (see Refs. [5–7], and references therein). The similar situation of partially constrained orientations can appear in systems of nonuniaxial molecules. On the experimental side, this situation could take place for para-azoxy-anisole (PAA) in a strong electric field. PAA molecule is usually described as a rigid bar with the permanent electric dipole in its center forming a 62° angle with the long axis. In the strong enough electric field the dipoles align [8], and the orientation of the long axis of any particle can be determined by the single angle φ in the plane perpendicular to the field direction (Fig. 2).

Any oriented plane rotator (OPR) model (in a result of spontaneous ordering, for example) is a biaxial system in fact, because it has two principal directions: (1) that perpendicular to the plane of particle rotations, (2) that given by the direction of ordering $\hat{n}$ lying in this plane. In general, a biaxial system is characterized by two groups of order parameters, which describe ordering along two symmetry axes. An OPR fluid is a *limiting* biaxial system with the perfect ordering with respect to one of the symmetry axes. We can exclude from consideration the group of the order parameters describing this perfect ordering. In the coordinate system as done in Fig. 1 the axis of ''the perfect ordering'' is the z axis, and an OPR model is characterized by order parameters $S_n=\langle\cos(n\varphi)\rangle$ that depend on the temperature, density, and interparticle interaction parameters.

Let us note that models with fixed molecule orientations (fluids of parallel molecules) were studied in the context of uniaxial nematics [9]. These studies helped to estimate how thermodynamical and structural properties of uniaxial fluids differ from those of isotropic ones. Similarly, to study the

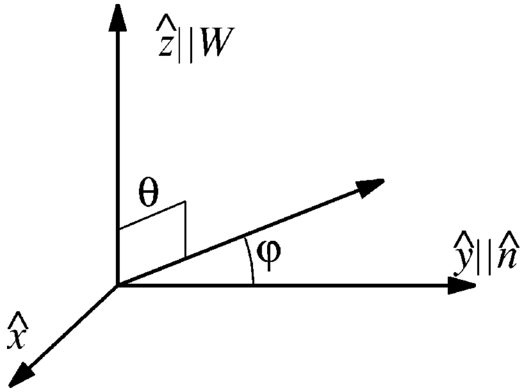

FIG. 1. The coordinate system used in this paper. $\hat{n}$ is the director, $\boldsymbol{W}$ is a disorienting field, φ determines the molecule orientation, $\theta=\pi/2$ is a constant for the PR models.

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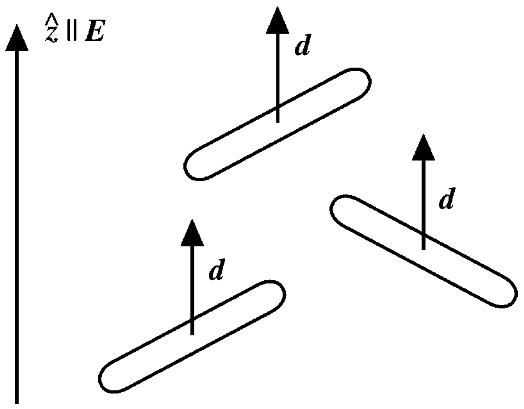

FIG. 2. The model for PAA in the strong electric field ***E***, ***d*** is a permanent electric dipole forming a 62° angle with the long axis of a molecule.

OPR fluid is to estimate the influence of biaxiality on physical properties of nematics. The behavior of nematics (including the OPR fluids) results from the interplay of orientation and density fluctuations. A consistent study of nematics has to take into account correlations of all types, including correlations between spatial and orientational variables. Moreover, in spontaneously ordered nematics there are the long-range correlations of director fluctuations. The existence of these long-range correlations is a substantial property of nematics and results from the fact that the direction of ordering is not predetermined and can be rotated without any energy cost. Their calculations are very important because the asymptotic behavior of these correlations at large distances determines the critical light scattering and elastic properties of nematics. In Refs. [10–13] the statistical approach ensuring a correct treatment of correlations was developed for uniaxial fluids. But consistent methods to calculate correlation functions in the OPR fluids have not been developed yet.

In this paper we propose a statistical method of the investigation of the OPR models that is based on the solution of the famous Lovett equation [14]. We consider a generally known model for thermotropic nematics in an infinitely strong disorienting field $\boldsymbol{W}$ as an illustration of our approach. The pair correlation functions and the single-particle distribution function of this system are calculated analytically by the self-consistent solution of the Ornstein-Zernike and Lovett equations. The obtained elastic constants and phase diagrams for $W\rightarrow\infty$ are compared with those for the uniaxial nematic case ($W=0$) in the same model. The suggested method can be used for a numerical solution of any other model with partially constrained orientations.

I. THE LOVETT EQUATION FOR THE FLUIDS WITH PARTIALLY CONSTRAINED MOLECULE ORIENTATIONS

The Lovett equation follows from the fundamental principle of the free energy minimization [14] and relates the pair direct correlation function $c(1,2)$ and the one-particle distribution function $f(1)$ [where $(1)=(\boldsymbol{R}_1,\omega_1)$ is a complete set of coordinates of particle 1]. For anisotropic fluids the Lovett equation takes the form

$$\nabla_{\omega_1}\ln\rho(\omega_1)=\int c(\boldsymbol{R},\omega_1,\omega_2)\nabla_{\omega_2}\rho(\omega_2)d\boldsymbol{R}d\omega_2-\nabla_{\omega_1}\frac{v(\omega_1)}{k_{\mathrm{B}}T},\tag{1.1}$$

where $\rho(\omega_1)=\rho f(\omega_1)$, ρ denotes a number density, ∇_ω is the angular gradient operator for an arbitrary particle [15], $v(\omega_1)$ is a potential of the interaction with a uniform external field. Let us consider a system of uniaxial molecules in the infinite disorienting field. We note that in general an orientation of a linear (uniaxial) molecule 1 is determined by a set of two angles $\omega_1=(\theta_1,\phi_1)$. For the disorienting field directed along the z axis we can write $v(\omega_1)=WP_2(\cos\theta_1)$, where $P_l(x)$ is the lth order Legendre polynomial. When $W\rightarrow\infty$, for the x and y components of Eq. (1.1) one obtains that $\rho(\omega_1)=0$ if $\theta_1\neq\pi/2$. Since $\omega_1\equiv(\varphi_1)$ we can use the PR description now and the Lovett equation for the anisotropic fluids with partially constrained orientations is represented by the z component of Eq. (1.1)

$$\frac{\partial}{\partial\varphi_1}\ln\rho(\varphi_1)=\int c(\varphi_1,\varphi_2)\frac{\partial}{\partial\varphi_2}\rho(\varphi_2)d\varphi_2-\frac{\partial}{\partial\varphi_1}\frac{v(\varphi_1)}{k_{\mathrm{B}}T}\tag{1.2}$$

or, after integration by parts

$$\frac{\partial}{\partial\varphi_1}\ln\rho(\varphi_1)=-\int\left[\frac{\partial}{\partial\varphi_2}c(\varphi_1,\varphi_2)\right]\rho(\varphi_2)d\varphi_2-\frac{\partial}{\partial\varphi_1}\frac{v(\varphi_1)}{k_{\mathrm{B}}T},\tag{1.3}$$

where $v(\varphi_1)$ is a potential of the interaction with the field that is directed in the xy-plane, $c(\varphi_1,\varphi_2)=\int c(\boldsymbol{R},\varphi_1,\varphi_2)d\boldsymbol{R}$. It should be noted that for a bulk phase $d\boldsymbol{R}=R^2dR\sin\theta_R d\varphi_R$, for a two-dimensional system $d\boldsymbol{R}=RdRd\varphi_R$.

It is customary to consider the Ornstein-Zernike (OZ) equation as a definition for the direct correlation function. Sometimes, one can avoid a solution of the OZ equation and express $c(1,2)$ via a pair interaction potential $\phi(1,2)$. For example, for very long-range and weak interactions (similar to those described by the Kac potential) the direct correlation function in the mean field form $c(1,2)=-\phi(1,2)/k_{\mathrm{B}}T$ equals the exact one; in the zero-density limit $c(1,2)$ may be written as the Mayer function $f(1,2)=\exp[-\phi(1,2)/k_{\mathrm{B}}T]-1$. It should be noted that in these limiting cases the symmetry of $c(1,2)$ coincides with the pair potential symmetry. But in a general case the direct correlation function of an orientationally ordered fluid loses the rotational invariance intrinsic in the pair potential and reflects the symmetry of the whole system. In this general case $c(1,2)$ should be found from the Ornstein-Zernike equation

$$h(1,2)=c(1,2)+\int\rho(3)h(1,3)c(3,2)d(3),\tag{1.4}$$

$h(1,2)$ is the total correlation function of the system, for the PR models $d(3)=d\boldsymbol{R}_3d\varphi_3$, $\rho(3)=\rho f(\varphi_3)$. In Ref. [16] this problem was solved for the partial case $f(\varphi_3)=1/2\pi$ within the hypernetted chain (HNC) and Percus-Yevick (PY) approximations. For the OPR case, when the director $\hat{n}$ is parallel to the y axis, the one-particle distribution function can be written in the form

$$f(\varphi)=Z^{-1}\exp\left(\sum_{n>0}A_n\cos(n\varphi)\right), \tag{1.5}$$

where Z is a normalization constant. For a bulk plane rotator fluid $c(1,2)$ can be represented in the form:

$$c(1,2)=\sum_{n_1,n_2}\sum_{l,m}c^{l}_{n_1n_2m}(R_{12})e^{in_1\varphi_1}e^{-in_2\varphi_2}Y_{lm}(\hat{R}_{12}), \tag{1.6}$$

and for the two-dimensional fluid in the following form:

$$c(1,2)=\sum_{n_1,n_2,m}c_{n_1n_2m}(R_{12})e^{in_1\varphi_1}e^{-in_2\varphi_2}e^{im\varphi_{R_{12}}}. \tag{1.7}$$

Taking into account that the direct correlation function is real and invariant with respect to a particle permutation, we obtain the following expansion for $c(\varphi_1,\varphi_2)$

$$\begin{aligned}c(\varphi_1,\varphi_2)=\sum_{n_1,n_2\geqslant 0}[&c_{n_1n_2}\cos(n_1\varphi_1)\cos(n_2\varphi_2)\\&+\bar{c}_{n_1n_2}\sin(n_1\varphi_1)\sin(n_2\varphi_2)].\end{aligned} \tag{1.8}$$

When deriving Eq. (1.8) we took into account that the OPR is symmetric with respect to the yz plane, where the both principal directions lay. Substituting Eqs. (1.5) and (1.8) in Eqs. (1.3) and (1.2) we obtain relations that hold exactly for the OPR:

$$n_1A_{n_1}=\sum_{n_2,n_3}\rho\bar{c}_{n_1n_2}\langle\sin(n_2\varphi)\sin(n_3\varphi)\rangle n_3A_{n_3}, \tag{1.9}$$

$$n_1A_{n_1}=\sum_{n_2}\rho\bar{c}_{n_1n_2}n_2\langle\cos(n_2\varphi)\rangle, \tag{1.10}$$

where $\langle\cdots\rangle=\int\cdots f(\varphi)d\varphi$, $\langle\cos(n_2\varphi)\rangle=S_{n_2}$ are the order parameters of the OPR, $2\langle\sin(n_2\varphi)\sin(n_3\varphi)\rangle=S_{n_2-n_3}-S_{n_2+n_3}$ can be expressed in terms of the order parameters. Matrix equations (1.9) and (1.10) constitute an exact algebraic representation of the Lovett equation for the OPR and can be used for different fluids with partially constrained orientations. For example, they are suitable for the case presented in Fig. 2.

Equations (1.9) and (1.10) relate the coefficients A_n of the single-particle distribution function with the density, temperature, and parameters of the model potential. This dependence is determined by the direct correlation function harmonics $\bar{c}_{n_1n_2}$ that are orthogonal to the both principal directions. From the anisotropic OZ equation (1.4) and relation (1.9) it can be shown that the corresponding harmonics of the whole correlation function $\bar{h}_{n_1n_2}$ are infinite in the absence of the field $v(\varphi)$. This feature is connected with the critical nature of anisotropic fluids (the presence of the long-range correlations) and was discussed for uniaxial cases in Refs. [10] and [11]. It should be stressed that these special harmonics for the OPR phase are connected with the correlations of director fluctuations (as well as in the uniaxial case) and give infinite contributions into the transverse susceptibility (along the x direction). Therefore, the director can be rotated in the xy plane without any energy cost. At the same time these infinite harmonics do not contribute to the structure factor, which is finite (in other words, the OPR phase is mechanically stable).

We note that Eqs. (1.9),(1.10) hold not only in the whole region of the OPR, but in the point, where the isotropic PR system loses the orientational stability. In order to determine this point one has to get $c(1,2)$ from the isotropic OZ equation (1.4) $[\rho(\varphi_3)=\rho/2\pi]$ in any approximation and to equal average values in Eq. (1.9) to the isotropic ones

$$\langle\cos(n_2\varphi)\rangle=0;\ \ \langle\sin(n_2\varphi)\sin(n_3\varphi)\rangle=\frac{1}{2}\delta_{n_2n_3}. \tag{1.11}$$

From Eqs. (1.9) and (1.10), useful relations follow:

$$\sum_{m\geqslant 1}(S_{n-m}-S_{n+m})mA_m=2nS_n. \tag{1.12}$$

This rule connects the coefficients of the distribution function in the exponential form with the system order parameters. Using the assumption that in exponential form (1.5) only $A_1\neq 0$, one obtains from Eq. (1.12) the well-known recurrent relations from the theory of the cylindrical Bessel functions:

$$(S_{n-1}-S_{n+1})A_1=2nS_n. \tag{1.13}$$

This relation allows one to express all higher order parameters via A_1 and S_1 using just simple arithmetic.

II. ANALYTICAL SOLUTION OF THE MEAN SPHERICAL NEMATIC MODEL IN AN INFINITE DISORIENTING FIELD

We shall illustrate the proposed approach dealing with the known model of thermotropic nematics [17]: the pair potential is a sum of the hard-sphere potential for spheres of diameter σ and of anisotropic part $v(1,2)$:

$$v(1,2)=v_2(R_{12})\frac{3\cos^2\omega_{12}-1}{2}, \tag{2.1}$$

where ω_{12} is the angle between the preferred axes of the molecules, $\omega_i=(\theta_i,\varphi_i)$ being the orientation of molecule i, R_{12} is the distance between the molecule mass centers, and

$$v_2(R_{12})=-A(z\sigma)^2\frac{\exp(-zR_{12})}{R_{12}/\sigma}. \tag{2.2}$$

The correlation functions $h(1,2)$ and $c(1,2)$ are obtained from the OZ equation (1.4). Within the mean spherical closure (MSA)

$$c(1,2)=-v(1,2)/(k_{\mathrm{B}}T),\ \ R_{12}>\sigma \tag{2.3}$$

the model is soluble analytically in an isotropic phase $[\rho(3)=\rho/(4\pi)]$ [17] and in a uniaxial nematic case $[\rho(3)=\rho f(\theta_3)]$ [12,10]. The method developed in Ref. [10] was expanded for a numerical investigation of this model within the reference HNC, HNC, and PY approximations in Ref. [18]. The comparison with the Monte Carlo simulation carried out in a broad interval of temperatures [18] shows that the MSA gives the most reliable description of the model thermodynamics. Due to Eqs. (1.9),(1.10) it is possible to find the analytical solution in the MSA for this model in an infinite disorienting field (in other words for the OPR fluid). For this case Eq. (2.1) transforms into the pair potential

$$\begin{aligned} v_{W\to\infty}(1{,}2) &= v_2(R_{12})(3\cos^2\varphi_{12}-1)/2 \\ &= v_2(R_{12})(3\cos(2\varphi_{12})+1)/4. \end{aligned} \tag{2.4}$$

The interaction potential (2.1) we will refer to as the case of zero disorienting field $(W=0)$. In the MSA (2.3) there is a simple expansion for $c(1{,}2)$ of the OPR:

$$\begin{aligned} c_{W\to\infty}(1{,}2) = &\sum_{n_1,n_2=0,2} [c_{n_1n_2}(R)\cos(n_1\varphi_1)\cos(n_2\varphi_2)] \\ &+ \overline{c}_{22}(R)\sin(2\varphi_1)\sin(2\varphi_2). \end{aligned} \tag{2.5}$$

For the isotropic PR fluid one has $c_{22}(R)=\overline{c}_{22}(R)$ and $c_{20}(R)=c_{02}(R)=0$, so that

$$c^{\mathrm{iso}}_{W\to\infty}(1{,}2) = c_{00}(R) + c_{22}(R)\cos(2\varphi_{12}). \tag{2.6}$$

We have to note that the expansion (2.5) is invariant with respect to the transformation $\varphi_1\to\pi-\varphi_1$ and $\varphi_2\to\pi-\varphi_2$, since the orientational ordering is nonpolar in the model system for the case $W\to\infty$ as well as for the case $W=0$. For expansion (2.5) the relations (1.9) and (1.10) gain the simple form

$$1=\rho\langle\sin^2(2\varphi)\rangle\int \overline{c}_{22}(R)\,d\boldsymbol{R}, \tag{2.7}$$

$$A_2=\rho\langle\cos(2\varphi)\rangle\int \overline{c}_{22}(R)\,d\boldsymbol{R}. \tag{2.8}$$

Now, knowing the self-consistency equation for the OPR order parameters

$$\begin{aligned} \langle\cdots\rangle = &\int (\cdots)\exp\left[\frac{\langle\cos(2\varphi)\rangle\cos(2\varphi)}{\langle\sin^2(2\varphi)\rangle}\right]d\varphi \\ &\times\left\{\int \exp\left[\frac{\langle\cos(2\varphi)\rangle\cos(2\varphi)}{\langle\sin^2(2\varphi)\rangle}\right]d\varphi\right\}^{-1}, \end{aligned} \tag{2.9}$$

one can solve the OZ equation (1.4) under additional condition (2.7) analytically by the Wertheim-Baxter factorization method [10,11].

Due to the OPR symmetry the OZ equation separates partially:

$$\overline{h}_{22}(R_{12}) = \overline{c}_{22}(R_{12}) + \rho\langle\sin^2(2\varphi)\rangle\int d\boldsymbol{R}_3\,\overline{c}_{22}(R_{13})\overline{h}_{22}(R_{32}), \tag{2.10}$$

$$\begin{aligned} h_{ij}(R_{12}) = c_{ij}(R_{12}) + \rho\int d\boldsymbol{R}_3 &\sum_{k,l} c_{ik}(R_{13}) \\ &\times\langle\cos(k\varphi)\cos(l\varphi)\rangle h_{lj}(R_{32}), \end{aligned} \tag{2.11}$$

where all indices equal 0 or 2. The closure of the correlation functions in the R space are as follows:

$$R<\sigma:\ h_{00}(R)=-1,$$

the other harmonics are equal 0 under the core,

$$R>\sigma:\ c_{ii}(R)=\overline{c}_{ii}(R)=(i+1)\beta A(z\sigma)^2\sigma\frac{\exp(-zR)}{4R},$$

the other harmonics of the direct correlation function equal 0 above the core.

A detailed solution of the anisotropic OZ equation under an additional condition such as Eq. (2.7) was done in literature [10–12]. Therefore, we present only several important analytical results, which follow from Eq. (2.10).

A basis for the solution is a factor correlation function, which has the following form:

$$Q(R)=\frac{z}{\rho\langle\sin^2(2\varphi)\rangle}[Q_0(R)+\tilde{D}\exp(-zR)], \tag{2.12}$$

where Q_0 is a short-range part defined as

$$\begin{aligned} Q_0(R) &= \tilde{C}[\exp(-zR)-\exp(-z\sigma)], \quad R<\sigma, \\ Q_0(R) &= 0, \quad R>\sigma. \end{aligned} \tag{2.13}$$

We note that knowing the parameter $\langle\sin^2(2\varphi)\rangle$ one can calculate from Eq. (2.9) all order parameters. This parameter (as well as dimensionless coefficients $\tilde{D}$ and $\tilde{C}$) can be found from the purely algebraical relations following from Eqs. (2.10) and (2.7). One gets

$$\frac{3}{4}\beta A\eta\langle\sin^2(2\varphi)\rangle = R(z\sigma), \tag{2.14}$$

where $\eta=\pi\rho\sigma^3/6$,

$$\begin{aligned} R(z\sigma) &= \frac{1}{24}\tilde{D}\left[1+(1-\tilde{D})\left(1-\frac{\Delta_0^2(-z\sigma)}{k}\right)\right], \\ \tilde{D} &= \frac{-b-\sqrt{b^2-4ac}}{2a},\quad \tilde{C}=(1-\tilde{D})/k, \\ a &= -k\exp(-2z\sigma)-(k-1)[k-\Delta_0^2(-z\sigma)], \\ b &= (k-1)c-k+\Delta_0^2(-z\sigma)+k\exp(-2z\sigma), \\ c &= 2k-\Delta_0^2(-z\sigma),\quad \Delta_n(x)=\exp(x)-\sum_{l=0}^{n}\frac{x^l}{l!}, \\ k &= e^{-z\sigma}\Delta_1(z\sigma). \end{aligned} \tag{2.15}$$

A special integral transform of $Q(R)$

$$Q(k)=1-\rho\langle\sin^2(2\varphi)\rangle\int_0^\infty \exp(ikR)Q(R)dR \quad (2.16)$$

plays a particular role. It is connected with harmonics of the correlation functions

$$1-\rho\langle\sin^2(2\varphi)\rangle\int_0^\infty \exp(i\boldsymbol{k}\cdot\boldsymbol{R})\overline{c}_{22}(R)d\boldsymbol{R}=Q(k)Q(-k), \quad (2.17)$$

$$1+\rho\langle\sin^2(2\varphi)\rangle\int_0^\infty \exp(i\boldsymbol{k}\cdot\boldsymbol{R})\overline{h}_{22}(R)d\boldsymbol{R} =[Q(k)Q(-k)]^{-1}. \quad (2.18)$$

The factor correlation function at $k=0$ is inversely proportional to the range of correlations. It follows from Eq. (2.7) that $Q(k=0)\equiv 0$ in the OPR and is connected with the long-range correlations (that were mentioned in Sec. I). Knowing the explicit form (2.12) of the factor correlation function we can obtain asymptotic expression for the single long-range harmonic $\overline{h}_{22}(R)$ of the total correlation function

$$\overline{h}_{22}(R\to\infty)\propto\frac{(z\sigma)^2}{6[(z\sigma)^2\tilde{C}\exp(-z\sigma)-2]^2\eta\langle\sin^2(2\varphi)\rangle}\,\frac{\sigma}{R}. \quad (2.19)$$

The harmonic $\overline{c}_{22}(R)$ can also be expressed explicitly in terms of the factor correlation function $Q(R)$ and its derivative $Q'(R)$:

$$2\pi R\overline{c}_{22}(R)=-Q'(R)+\rho\langle\sin^2(2\varphi)\rangle\int_0^\infty Q'(R+t)Q(t)dt. \quad (2.20)$$

After simple integration we get

$$2\pi R\overline{c}_{22}(R)=\frac{z^2}{\rho\langle\sin^2(2\varphi)\rangle}[\epsilon_-e^{-zR}+\epsilon_0+\epsilon_+e^{zR}],\quad R<\sigma, \quad (2.21)$$

where

$$\epsilon_-=\frac{1}{2}(\tilde{C}+\tilde{D})(2\tilde{C}e^{-z\sigma}-\tilde{D}-\tilde{C}+2)-\frac{1}{2}\tilde{C}\tilde{D}e^{-2z\sigma},$$

$$\epsilon_0=-\tilde{C}^2e^{-2z\sigma},$$

$$\epsilon_+=\frac{1}{2}\tilde{C}(\tilde{C}+\tilde{D})e^{-2z\sigma}.$$

Let us remind that for $R>\sigma$ the direct correlation function is defined by the MSA closure. As is to be expected, for $z\sigma\to 0$ (the Kac potential limit) our results are equivalent to the mean field solution:

$$c(1,2)=c_{\mathrm{h.s.}}(R_{12})-v(1,2)/k_{\mathrm{B}}T \text{for any } R_{12}, \quad (2.22)$$

where $c_{\mathrm{h.s.}}(R_{12})$ is the direct correlation function of hard spheres in the PY approximation, and $R(z\sigma)=1/24$.

When $\langle\sin^2\varphi\rangle=\frac{1}{2}$ from Eq. (2.14) follows the explicit equation for the line in the temperature-density space where the isotropic PR system loses orientational stability with respect to the OPR:

$$\left(\frac{\eta A}{k_{\mathrm{B}}T}\right)^*_{W\to\infty}=\frac{8}{3}R(z\sigma), \quad (2.23)$$

where the function of the interaction range parameter only $R(z\sigma)$ is connected with the instability condition of the isotropic phase with respect to the uniaxial nematic by the relation

$$\left(\frac{\eta A}{k_{\mathrm{B}}T}\right)^*_{W\to 0}=5R(z\sigma). \quad (2.24)$$

One can see from Eqs. (2.23) and (2.24) that in the presence of a strong ($W\to\infty$) ‘‘disorienting’’ field the orientational instability of an unoriented phase with respect to an oriented one appears at much higher temperatures than in usual case of zero field.

Let us emphasize some differences of the OPR ($W\to\infty$) from the uniaxial nematic ($W=0$). It was found [3] that in a strong disorienting field the orientational phase transition in nematics can change its order from the first to the second one. This takes place for systems of nonpolar molecules when the system symmetry changes from a uniaxial to a strongly biaxial one. We shall consider this point from the point of view of the integral equation approach. As it was noted above, the exact relations (1.9) and (1.10) [or Eqs. (2.7) and (2.8), for our model] hold not only in the whole region of the OPR, but also in the point where the isotropic PR system looses the orientational stability. We have to remind that in these points the long-range orientational correlations are presented, and the susceptibility tends to infinity. Therefore, at greater densities (or lower temperatures) the isotropic state is impossible. This isotropic stability condition follows from Eq. (2.7), where we have to set $\langle\sin^2(2\varphi)\rangle$ equal to its isotropic value (1/2) and to take $\overline{c}_{22}(R)$ from a solution of the isotropic OZ equation $[\rho(\varphi)=\rho/2\pi]$:

$$\frac{2}{\rho}=\int\overline{c}^{\mathrm{iso}}_{22}(R)d\boldsymbol{R}. \quad (2.25)$$

On the other hand, we can determine the limit of the OPR existence, that is the lowest density (at a given temperature) or the highest temperature (at a given density) where the OPR phase is possible. The OPR phase is characterized by a nonzero order parameter and long-range correlations of director fluctuations. From the anisotropic OZ and Lovett equations we have obtained two conditions that describe these features and must hold in the whole OPR phase: (i) the self-consistency equation for the order parameter $S_2=\langle\cos(2\varphi)\rangle$

$$S_2=\frac{\int d\varphi\cos(2\varphi)\exp[A_2\cos(2\varphi)]}{\int d\varphi\exp[A_2\cos(2\varphi)]};\quad A_2=\frac{S_2}{\langle\sin^2(2\varphi)\rangle}; \quad (2.26)$$

has to have a nonzero solution; (ii) Eq. (2.7). The latter condition ensures the existence of the long-range correlations of director fluctuations. In order to obtain the limit of the OPR existence we have to put into Eq. (2.7) the value of $\langle \sin^2(2\varphi)\rangle$ at which a nontrivial solution of self-consistency equation (2.26) appears. An equation of the form (2.26) is known to have a nontrivial solution starting with $\langle \sin^2(2\varphi)\rangle = 1/2$, S_2 smoothly raising from 0 to 1 when $\langle \sin^2(2\varphi)\rangle$ decreases from 1/2 to 0. Taking this into account, we obtain the limiting condition of the OPR

$$\frac{2}{\rho} = \int \overline{c_{22}^{\text{aniso}}}(R)\, d\boldsymbol{R}, \tag{2.27}$$

where $c_{22}^{\text{aniso}}(R)$ is a solution of the anisotropic OZ equation at $\langle \sin^2(2\varphi)\rangle = 1/2$ (which corresponds to $S_2 = 0$). Thus, Eqs. (2.25) and (2.27) coincide for our PR model. The equivalence of Eqs. (2.25) and (2.27) supports the possibility of the second order phase transition that does take place at high temperatures.

The similar analysis of the model for $W=0$ [12,11] shows that in a uniaxial nematic the situation is different. In this case the self-consistency equation is the well-known Mayer-Saupe one [8] which has no solution for small values of the order parameter. The bifurcation value of the order parameter ($S_2 = 0.3236$) differs from the isotropic one ($S_2 = 0$). Therefore, the conditions analogous to Eqs. (2.25) and (2.27) are not equal: the bifurcation takes place before (at smaller densities and higher temperatures) the isotropic liquid looses its orientational stability. Thus, the orientational phase transition of the second order is impossible, but the one of the first order does exist.

III. RESULTS. PHASE DIAGRAMS AND ELASTIC CONSTANTS

Using the analytical solution in the MSA for the OPR we have calculated a virial pressure

$$P_v^{W\to\infty} = \rho k_B T - \frac{\rho^2}{6}\int d\vec{R}_{12}\, d\varphi_1\, d\varphi_2\, R_{12}\frac{\partial}{\partial R_{12}} v(1,2) f(\varphi_1) \times [1 + h_{W\to\infty}(1,2)] f(\varphi_2). \tag{3.1}$$

We have found (Fig. 3) that the pressure of the OPR (at given density and temperature) is always less than in the uniaxial nematic. Let us also note that the OPR order parameter $S_2^{\text{OPR}} = \langle \cos(2\varphi)\rangle$ is always greater than the nematic order parameter $S_2^{\text{N}} = (3\langle \cos^2\theta\rangle - 1)/2$ at the same density and temperature (or at the same pressure and temperature). We have performed the Maxwell construction on the virial pressure isotherm and obtained the phase diagrams for the mean spherical model of the OPR. The phase diagram in coordinates density temperature for the $z\sigma = 0.5$ are shown in Fig. 4 and compared with the one for $W=0$ [13]. The orientational phase transition in the OPR is of the second order at high temperatures. In Fig. 4 it is shown by a thin line. At low temperatures this phase transition becomes of the first order at the tricritical point. The region with great η that marked as OPR (or N) is an oriented fluid for $W\to\infty$ (and $W=0$). One can see that the region of the OPR is much greater. This additional density-temperature region, where the OPR exists, but there is no a uniaxial nematic phase, is shadowed. The phase diagrams in the pressure-temperature coordinates are shown in Fig. 5 for different $z\sigma$. For the sake of comparison we also show the ones [13] for the MSA model of the uniaxial nematic ($W=0$). Depending on a given pressure the fraction of the phase transition temperatures $T_{W\to\infty}/T_{W=0}$ ranges from 1.2 to 1.5. The pressure of the OPR ordering is nearly 4–5 times less than that of the isotropic-nematic transition at the same temperature.

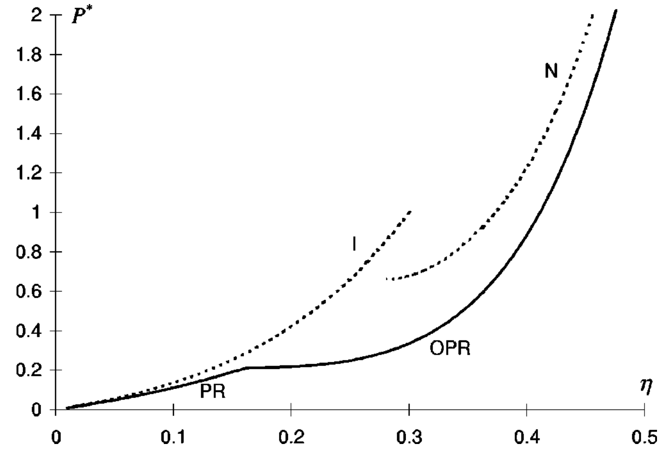

FIG. 3. The pressure $[P^* = (P/A)(\pi\sigma^3/6)]$ of the fluid at $W\to\infty$ (solid lines) and at $W=0$ (dashed lines) for $k_B T/A = 0.91$ and $z\sigma = 1.1$.

Let us consider the elastic constants of our model. As it was noted before, the ordered PR fluid is a biaxial system. Formal expressions for elastic constants in biaxial nematics are complex enough (see, for example, Ref. [19], and references therein).But in the OPR case the things are more simple. First, our OPR system has symmetry planes; then, it is nonpolar, and last, the OPR system is characterized by the director field described by a unit vector $\hat{\boldsymbol{n}}(\boldsymbol{r})$. Therefore, for the macroscopic free energy of distortion we can use the well

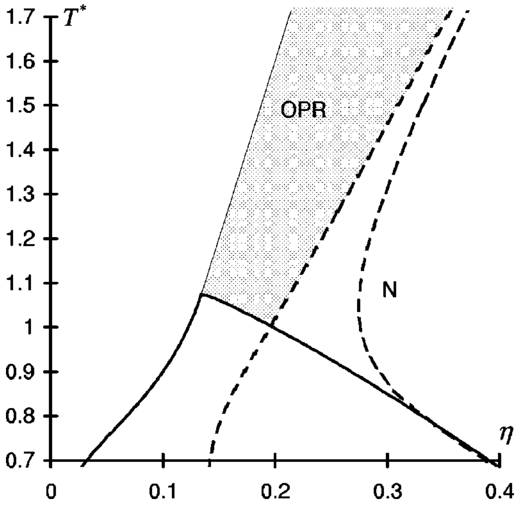

FIG. 4. The phase diagram for $z\sigma = 0.5$ in temperature-density coordinates ($T^* = k_B T/A$, $\eta = \pi\rho\sigma^3/6$). The results for $W=0$ [13] are given as dashed lines. The results for $W\to\infty$ are plotted with solid lines. OPR (N) means an oriented fluid phase. The shadowed region is a region where the OPR phase exists, but a uniaxial nematic phase is absent.

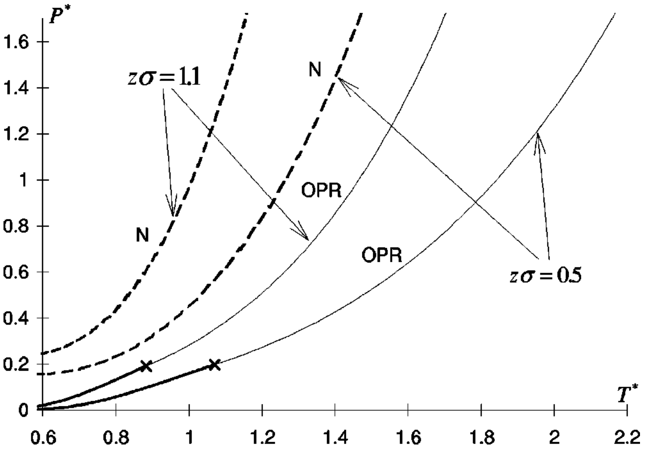

FIG. 5. The phase diagram of the MSA model in the pressure-temperature coordinates $[P^*=(P/A)(\pi\sigma^3/6),\ T^*=k_BT/A]$ for different interaction ranges (determined by $z\sigma$ parameter). The isotropic-nematic phase transition (dashed lines) is of the first order (results of Ref. [13]). The OPR phase transition (solid lines) is of the second order at high temperatures (thin lines) and of the first order at low temperatures (bold lines), crosses are the tricritical points. N denotes the uniaxial nematic region, OPR denotes the OPR one.

known expression for a uniaxial nematic containing three bulk elastic constants: K_1 (splay), K_2 (twist), K_3 (bend) [1]:

$$F_d=\frac{1}{2}K_1[\nabla_{\boldsymbol{r}}\cdot\hat{\boldsymbol{n}}(\boldsymbol{r})]^2+\frac{1}{2}K_2[\hat{\boldsymbol{n}}(\boldsymbol{r})\cdot\nabla_{\boldsymbol{r}}\times\hat{\boldsymbol{n}}(\boldsymbol{r})]^2 +\frac{1}{2}K_3[\hat{\boldsymbol{n}}(\boldsymbol{r})\times\nabla_{\boldsymbol{r}}\times\hat{\boldsymbol{n}}(\boldsymbol{r})]^2. \tag{3.2}$$

On the other hand, the orientational distribution function (1.5) depends on a single argument. One can expand the free energy functional in just the same way as it was done for the distorted system of a uniaxial nematic [20,1] and obtain Eq. (3.6) of Ref. [1]:

$$F_d/k_BT=\frac{1}{4}\rho^2\int d\boldsymbol{r}d\boldsymbol{R}d\hat{\boldsymbol{u}}d\hat{\boldsymbol{u}}'\dot{f}[\hat{\boldsymbol{n}}(\boldsymbol{r})\cdot\hat{\boldsymbol{u}}]\dot{f}[\hat{\boldsymbol{n}}(\boldsymbol{r})\cdot\hat{\boldsymbol{u}}'] \times\{(\boldsymbol{R}\cdot\nabla_{\boldsymbol{r}})\hat{\boldsymbol{n}}(\boldsymbol{r})\cdot\hat{\boldsymbol{u}}\}\{(\boldsymbol{R}\cdot\nabla_{\boldsymbol{r}})\hat{\boldsymbol{n}}(\boldsymbol{r})\cdot\hat{\boldsymbol{u}}'\}c(\boldsymbol{R},\hat{\boldsymbol{u}},\hat{\boldsymbol{u}}'), \tag{3.3}$$

where $\hat{\boldsymbol{u}}$ is a unit vector along the molecular symmetry axis, the dot over f denotes differentiation of the distribution function with respect to its single argument, that is, $\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{u}}$. After that, we have to take into account that in the OPR system there are the director fluctuations along the x axis only. Therefore, three possible distortions of the director field can take place: (1) splay in the x direction $\hat{\boldsymbol{n}}(x,y,z)=\hat{\boldsymbol{e}}_y+\epsilon x\hat{\boldsymbol{e}}_x$; (2) twist in the z direction $\hat{\boldsymbol{n}}(x,y,z)=\hat{\boldsymbol{e}}_y+\epsilon z\hat{\boldsymbol{e}}_x$; (3) bend along the y axis $\hat{\boldsymbol{n}}(x,y,z)=\hat{\boldsymbol{e}}_y+\epsilon y\hat{\boldsymbol{e}}_x$. Inserting these one by one into Eq. (3.3) one can simply read off the corresponding bulk elastic constants

$$\beta K_i^{\mathrm{OPR}}=\frac{1}{2}\int d\boldsymbol{R}d\varphi_1d\varphi_2\frac{\partial\rho(\varphi_1)}{\partial\varphi_1}\frac{\partial\rho(\varphi_2)}{\partial\varphi_2}c(1,2)(R_i)^2, \tag{3.4}$$

where $R_1=R_x$, $R_2=R_z$, $R_3=R_y$. It should be noted that K_i (3.4) are elastic constants of a strongly biaxial nematic. Other bulk elastic constants defined for a biaxial nematic are connected with the distortions that a prohibited by the infinite field $\boldsymbol{W}$ and are, therefore, undefined for the OPR model.

For our model interaction potential (in both the cases $\boldsymbol{W}\rightarrow 0$ and $\boldsymbol{W}\rightarrow\infty$) the simultaneous rotation of a pair of molecules (at fixed position of the molecule mass centers) does not change their interaction energy. It was noted in Ref. [8] that this causes directly

$$K_1=K_2=K_3=K, \tag{3.5}$$

which is not fulfilled in real nematics, of course. Our solution reproduces Eq. (3.5) automatically, because $c(1,2)$ in Eq. (3.4) does not depend on $\hat{\boldsymbol{R}}$. Carrying out the integrations with respect to φ and using the explicit expressions for $c(1,2)$ and $\rho(1)$, one can verify that only $\overline{c}_{22}(R)$ gives a contribution into K_i^{OPR}. Since we have the analytical expression for $\overline{c}_{22}(R)$ (see the previous section), the calculation of K_i^{OPR} is trivial.

In order to calculate elastic constants we can use also the expression from the hydrodynamic fluctuation theory, because we have the analytical solution for $h(1,2)$. Using relation (3.5) and following [21] this expression can be rewritten for our OPR model in the form

$$\frac{1}{\beta K}=(S_2^{\mathrm{OPR}})^{-2}\lim_{k\rightarrow 0}k^2\int\sin\varphi_1\cos\varphi_1 f(\varphi_1)h(1,2)f(\varphi_2) \times\sin\varphi_2\cos\varphi_2\exp(i\boldsymbol{k}\cdot\boldsymbol{R}_{12})d\boldsymbol{R}_{12}d\varphi_1d\varphi_2. \tag{3.6}$$

Because of factor k^2, only the long-range behavior of $h(1,2)$ is important for calculation of K. Substituting in Eq. (3.6) the obtained asymptotic expression of the only long-range harmonic of the total correlation function (2.19) we get the simple expression

$$\frac{K^{\mathrm{OPR}}\sigma(z\sigma)^2}{A}=\frac{9}{2\pi}\frac{[(z\sigma)^2\tilde{C}\exp(-z\sigma)-2]^2}{R(z\sigma)}(\eta S_2^{\mathrm{OPR}})^2. \tag{3.7}$$

The explicit expression for the elastic constant derived from Eq. (3.4) is slightly more complex, but gives the same value for K^{OPR}. It should be noted that the formal expression for the elastic constants at $W=0$ coincides with Eq. (3.7) with the only change: one has to replace S_2^{OPR} by the nematic order parameter.

Dependences of elastic constants of the OPR (K^{OPR}) and of the uniaxial nematic (K^{N}) at constant pressure are presented in Fig. 6. One can see that the elastic constants are always greater for the OPR. It seems that this effect is more pronounced for the more short-range potential ($z\sigma=1.1$). The difference $K^{\mathrm{OPR}}(P,T)-K^{\mathrm{N}}(P,T)$ decreases with lowering temperature and tends to zero at perfect aligning, when both S_2^{OPR} and S_2^{N} equal 1.

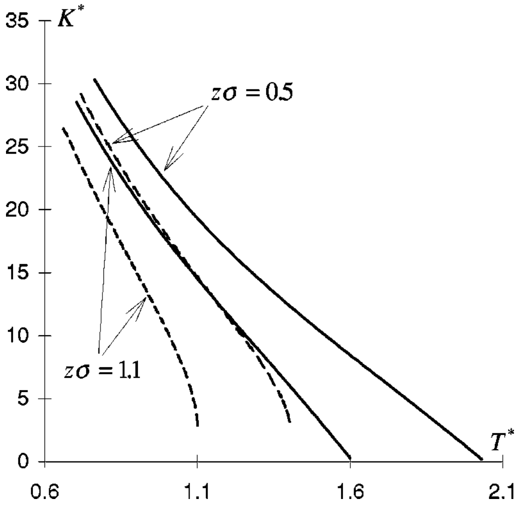

FIG. 6. The dependence of reduced elastic constants $[K^* = (K\sigma/A)(z\sigma)^2]$ on T^* at $P^* = 1.4$ for $z\sigma = 0.5$ and $z\sigma = 1.1$. The results for the MSA of the nematic are dashed lines, the solid lines are results for the MSA of the OPR.

IV. CONCLUSIONS

In this paper we consider the ordering in the fluids where the molecular orientations are partially constrained as a result of some factors: strong fields, interface influences or, in some respect, the effect of impurities. The investigation of such systems can be useful in order to estimate the influence of a strong biaxiality on physical properties of nematics. The proposed theoretical approach for the calculation of the pair correlation functions is based on the self-consistent solution of the Lovett and OZ equations. This approach does not impose any approximation other than a closure for the OZ equation. It correctly treats the long-range correlations and can be used for two- or three-dimensional anisotropic fluids with partially constrained orientations. For systems that can be described by the OPR the exact algebraic representation of the Lovett equation is obtained. In this representation one can see the presence of long-range correlations in the model, and our analysis shows that the OPR phase demonstrates a critical behavior with respect to director fluctuations. This is a substantial property of the system connected with the OPR symmetry and provides such a special physical feature as the elastic behavior.

The proposed method was applied to the well-known mean spherical model for nematics [17] under the influence of an infinite disorienting field $\boldsymbol{W}$, when the molecules are constrained to orient perpendicularly to the field direction. For this problem the analytical solution of the anisotropic OZ equation is obtained. The asymptotic expression for the long-range correlations is presented in analytical form. The phase diagrams and elastic constants are calculated for $\boldsymbol{W}\to\infty$ and are compared with those of the uniaxial nematic at $\boldsymbol{W}=\boldsymbol{0}$ [13].

The disorienting field transforms the system symmetry and makes the ordered phase biaxial. Significant changes of physical properties result from this induced biaxiality and can be summarized for our model potential as follows: (1) the temperature-pressure (or temperature-density) region of a spontaneously ordered fluid increases significantly; (2) the orientational phase transition changes its order from the first to the second one; (3) the disorienting field increases the ordering and elastic properties of the model under consideration (we say about elastic constants that are defined for the OPR).

Since the important technical problem in application of the anisotropic fluids is to expand ordered fluid region and to increase the anisotropic properties, the induced biaxiality can be interesting also from the practical point of view and be useful to obtain mesomorphic phases in nonmesogens (the systems that do not display liquid crystal behavior usually). For example, epitropic liquid crystal phases were found in para-dimethylbenzene [22]. Its molecules are nonpolar and prefer to be parallel to the surface prepared in a special way. It was shown that near such a surface hundreds of molecular layers demonstrate a uniform nematic ordering with a director parallel to the surface.

From our point of view, very promising systems are side-chain polymers. Modern technologies allow to produce polymers with various characteristics of the backbone (main chain) and of the side groups. For example, one can use mesogenic molecules as side groups. If the mesogenic groups are directly attached to the backbone, an orientational ordering is not usually exhibited [23], because the dynamics of the backbone suppresses the tendency for the mesogenic groups to orient anisotropically. But main chains can be oriented strongly by different processes (by the orienting flow, for example). In this case the rotations of mesogenic groups are partially constrained by the ordered backbones and can be analyzed within the PR description.

ACKNOWLEDGMENTS

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