Nematic model in the presence of a finite disorienting field: Integral equation approach

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A fluid of uniaxial particles in a disorienting field is considered as a simple model of biaxial nematics. The model stability with respect to the spontaneous formation of a biaxial phase is investigated by means of the integral equation method. The orientational instability condition is obtained explicitly and turns into known results for the limiting cases of zero and of infinite fields. It is shown that the biaxiality induced by small fields can expand considerably the region of spontaneously ordered fluid and could be useful to obtain mesomorphic phases in nonmesogens. The effect of small disorienting fields is more pronounced in systems with short-range anisotropic interactions between particles.

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Biaxial phases of nematic fluids compel more and more attention. The point is that even a pure system of uniaxial molecules can form a biaxial nematic phase under the influence of a certain external factors. This takes place near the interface with the other medium (wall) if nematic molecules prefer to be parallel to the surface plane [1]. The biaxiality can be induced also by a disorienting field [2]. It can be either the electric or the magnetic field since many nematics have a negative anisotropy, and the molecules tend to align perpendicularly to the field [3,4]. In this case a spontaneous ordering forms a structure having two principal directions: (1) the direction of a disorienting field; and (2) the direction of spontaneous ordering $\hat{n}$ lying in the plane that is perpendicular to the field direction. The biaxiality induced by strong fields appears to cause significant changes of physical properties. In particular, the orientational phase transition changes its order from the first to the second one [2]. It was found [5] that the biaxiality induced by strong fields significantly increases the temperature-pressure region of spontaneously ordered fluid. Its ordering and elastic properties increase also. Since the important technical problem in applications of anisotropic fluids is to expand the ordered fluid region and to increase the anisotropic properties, the induced biaxiality can be interesting from the practical point of view. For example, the induced biaxiality can be useful to obtain mesomorphic phases in nonmesogens (systems that do not display liquid crystalline behavior usually). Recently, nematic phases were found in para-dimethylbenzene. Molecules of para-dimethylbenzene are nonpolar and prefer to be parallel to the surface prepared in a special way. It was shown [6] that near such a surface hundreds of molecular layers demonstrate a uniform nematic ordering with a director parallel to the surface. The orientational ordering in this nonmesogen can be explained as a result of biaxiality induced by the surface.

In Ref. [5] a nonpolar nematic model was investigated in the infinite disorienting field, when the molecules are constrained to orient perpendicularly to the field direction. With increasing density (or decreasing temperature) the system demonstrates spontaneous ordering into a limiting biaxial phase. For this problem an analytical solution of the Ornstein-Zernike (OZ) equation was obtained [5]. The calculated phase diagrams and elastic constants for the infinite field case were compared with the usual case of a uniaxial nematic ordering at zero field. It was shown, for example, that the infinite disorienting field makes the pressure of spontaneous nematic ordering four to five times less. Thus, strong disorienting fields do favor a nematic ordering. But the question arises about the strength of the field needed to achieve significant changes of the physical properties. To clarify this point one has to investigate the general case of moderate biaxiality induced by finite external fields.

In this paper we study the phase transition into a biaxial nematic phase in the presence of finite fields. We shall consider this biaxial phase as the ''oriented'' one. The phase without the spontaneous ordering will be referred to as the ''nonoriented'' one, though the latter phase possesses a uniaxial anisotropy induced by the external field. We use the integral equation method here. This approach does not impose any approximation other than a closure for the OZ equation and allows to treat correlations (including the long-range ones) correctly. One can estimate the influence of the field of a given strength on the region of the spontaneously ordered phase by calculating the limit of orientational stability of the ''nonoriented'' phase with respect to the ''oriented'' one. It is this limit that is calculated and analyzed in the present paper.

I. MODEL

As a simple biaxial nematic model we propose a system of uniaxial molecules in the disorienting field **W**, where the potential of the molecule interaction with the field is

$$v(1)=v(\omega_1)=W\frac{3\cos^2\theta_1-1}{2},\quad W>0, \tag{1.1}$$

$\omega_i=(\theta_i,\varphi_i)$ being the orientation of molecule i. The above formula assumes that the field is directed along the z axis and

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states that molecule orientations along the field direction are energetically unfavorable ($W>0$). The pair potential is a sum of the hard-sphere potential for spheres of diameter σ and of the anisotropic part $v(1,2)$,

$$v(1,2)=v_2(R_{12})\frac{3\cos^2\omega_{12}-1}{2}, \tag{1.2}$$

where ω_{12} is the angle between the preferred axes of the molecules, R_{12} is the distance between the molecule mass centers, and

$$v_2(R_{12})=-K\frac{(z\sigma)^2}{z\sigma+1}\frac{\exp[-z(R_{12}-\sigma)]}{R_{12}/\sigma}. \tag{1.3}$$

In the above formula the coefficient $(z\sigma)^2/(z\sigma+1)$ is placed in order to make the integral $\int_\sigma^\infty v(1,2)R_{12}^2dR_{12}$ independent of $z\sigma$. Therefore, within the mean field approach the thermodynamics of the model is independent of $z\sigma$. Thus, K is a natural energy unit in this model. In the absence of the field ($W=0$) the model coincides with the one that was proposed in Ref. [7] for a uniaxial nematic. In the presence of an orienting field ($W<0$) the system can exhibit only uniaxial paranematic and nematic phases. When $W>0$, the same system provides the phase transition into a biaxial nematic phase. At strong disorienting fields ($W\gg 0$) the molecules align perpendicularly to the field, and the phase transition into a limiting biaxial phase takes place [5].

We should note some peculiarities about the disorienting field case. Even very weak disorienting fields ($W\to+0$) produce a negative anisotropy along the z axis, because preferred axes of molecules tend to lie in the XY plane that is perpendicular to the anisotropy axis. Thus, a negative uniaxial nematic phase (N_u^-) of ''easy plane'' type appears (see Table 4 of Ref. [3] and Sec. 10.2.3 of Ref. [4]). The order parameter of any uniaxial nematic is usually chosen as an ensemble average of the second order Legendre polynomial: $S_z=\langle P_2(\cos\theta)\rangle=\langle 3\cos^2\theta-1\rangle/2$, where θ is the angle between the preferred axis of the molecule and the system anisotropy axis. In the isotropic case $S_z\equiv 0$, in the N_u^- phase S_z is negative, since particle orientations along the field direction are energetically unfavorable. At strong disorienting fields ($W\to\infty$) all the molecules align perpendicularly to the field ($\theta=\pi/2$), and $S_z\equiv -1/2$. In the N_u^- phase, nevertheless, the orientational ordering in the XY plane *is absent*. By increasing the system density (or decreasing the temperature) a preferred direction in the XY plane appears, and the phase transition into a biaxial phase takes place. The director $\hat{n}$ of the spontaneous ordering can rotate without any energy cost in the XY plane. Next, to be very explicit, we shall choose $\hat{n}$ along the x axis. In contrast to the induced order parameter S_z, the order parameter describing spontaneous ordering in the x direction will be positive.

II. THE SINGLE-PARTICLE DISTRIBUTION FUNCTION IN THE UNIAXIAL NONORIENTED PHASE

In order to investigate the uniaxial (nonoriented) phase we can use the results of [8], where the general case of uniaxial fluids in the presence of an external field was considered. An orientational distribution is calculated in [8] from the Lovett equation for anisotropic fluids [9]

$$\boldsymbol{\nabla}_{\omega_1}\ln\rho(1)+\boldsymbol{\nabla}_{\omega_1}\frac{v(1)}{k_BT}=\int c(1,2)\boldsymbol{\nabla}_{\omega_2}\rho(2)d(2), \tag{2.1}$$

where $\boldsymbol{\nabla}_{\omega_1}$ is an angular gradient operator; $v(1)$ is a potential of interaction with a uniform external field, its spherical harmonic expansion is of the form

$$v(1)=-\sum_l v_l Y_{l0}(\omega_1), \tag{2.2}$$

$\rho(1)=\rho f(\omega_1)$, and $f(\omega_1)$ is a single-particle distribution function. Using the general expansion for the direct correlation function of linear molecules

$$c(1,2)=\sum_{\substack{mnl\\ \mu\nu\lambda}} c_{mnl}^{\mu\nu\lambda}(R)Y_{m\mu}(\omega_1)Y_{n\nu}^*(\omega_2)Y_{l\lambda}(\omega_R) \tag{2.3}$$

and the exponential form of the one-particle distribution function

$$f(\omega)=Z^{-1}\exp\left[\sum_{l>0} A_l Y_{l0}(\omega)\right], \tag{2.4}$$

one can obtain following Ref. [8] an algebraic representation of the Lovett equation for a uniaxial fluid in the external field,

$$L_l=\sum_{mn} C_{lm}Y_{mn}L_n+V_l=\sum_m C_{lm}\mathcal{P}_m+V_l, \tag{2.5}$$

where all indices take positive integer values, $V_l=v_l/k_BT$, $C_{mn}=\int c_{mn0}^{110}(R)d\boldsymbol{R}$, $Y_{mn}=\rho\langle Y_{m1}(\omega)Y_{n1}^*(\omega)\rangle_\omega$, $\langle\cdots\rangle_\omega=\int f(\omega)(\cdots)d\omega$, $L_l=\sqrt{l(l+1)}A_l$, and $\mathcal{P}_l=\rho\sqrt{l(l+1)(2l+1)}\langle P_l(\cos\theta)\rangle_\omega$, $P_l(\cos\theta)$ is the lth order Legendre polynomial. Let us note that the average values $\langle P_l(\cos\theta)\rangle_\omega$ play the role of order parameters in uniaxial anisotropic fluids. Relations (2.5) are accurate, and their use, as well as the use of the integrodifferential equation (2.1), does not introduce any approximation into the theory.

It is customary to consider the 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 (such as those described by the Kac potential) the direct correlation function in the mean field form $c(1,2)=-\phi(1,2)/k_BT$ equals the exact one; in the zero-density limit $c(1,2)$ may be written as the Mayer function $f(1,2)=\exp(-\phi(1,2)/k_BT)-1$. 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 OZ equation

$$h(1,2)=c(1,2)+\int \rho(3)h(1,3)c(3,2)d(3), \qquad (2.6)$$

$h(1,2)$ is the total correlation function of the system, and $d(3)=d\boldsymbol{R}_3 d\omega_3$.

Due to representation (2.5) it appears to be possible to obtain for our model in the nonoriented phase an analytical solution of the anisotropic OZ equation (2.6) within the mean spherical closure approximation (MSA),

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

$$h(1,2)=-1, \quad R_{12}<\sigma. \qquad (2.7)$$

We have to recall that according to Monte Carlo simulations for our model potential the MSA provides the most reliable description of the model thermodynamics [10,11]. Condition (2.7) for $h(1,2)$ follows directly from the fact that hard spheres do not overlap. The mean spherical closure (2.7) restricts correlation functions of our model to have the form

$$f(1,2)=\sum_{l_1 l_2 m} f_{l_1 l_2 m}(R_{12})Y_{l_1 m}(\omega_1)Y^*_{l_2 m}(\omega_2), \qquad (2.8)$$

($l_1, l_2=0,2$), and representation (2.5) results in equalities

$$A_2=A_2\rho\langle|Y_{21}(\omega)|^2\rangle_\omega\int c_{221}(R)d\boldsymbol{R}-\beta W,$$

$$A_2=\rho\langle Y_{20}(\omega)\rangle_\omega\int c_{221}(R)d\boldsymbol{R}-\beta W. \qquad (2.9)$$

Thus, the use of the mean spherical closure yields for our model's vanishing of coefficients A_l with $l>2$ in Eq. (2.4), and the self-consistent one-particle distribution function in the MSA takes the form

$$f(\omega)=\exp[A_2Y_{20}(\omega)]\Big/\int \exp[A_2Y_{20}(\omega)]d\omega. \qquad (2.10)$$

A uniaxial symmetry of our system leads to factorization of Eq. (2.6) on the equations with different m. At $m=\pm1, \pm2$,

$$h_{22m}(R_{12})=c_{22m}(R_{12}) + \rho\langle|Y_{2m}(\omega)|^2\rangle_\omega\int c_{22m}(R_{13})h_{22m}(R_{32})d\boldsymbol{R}_3. \qquad (2.11)$$

For $m=0$ we have a system of integral equations that after the Fourier transformation gains the matrix form

$$H_{ij}(k)=C_{ij}(k)+\sum_{i'j'} C_{ii'}(k)\rho_{i'j'}H_{j'j}(k), \qquad (2.12)$$

where $H_{ij}(k)=h_{ij0}(k)$, $C_{ij}(k)=c_{ij0}(k)$, and $\rho_{ij}=\rho\langle Y_{i0}(\omega)Y_{j0}(\omega)\rangle_\omega$, indices take the values 0 and 2.

Equations (2.9) and (2.11) for $m=\pm1$ within the MSA for the corresponding harmonics

$$h_{22m}(R_{12})=0, \quad R_{12}<\sigma,$$

$$c_{22m}(R_{12})=\beta K\frac{(z\sigma)^2}{z\sigma+1}\frac{\exp[-z(R_{12}-\sigma)]}{5R_{12}/\sigma}, \quad R_{12}>\sigma \qquad (2.13)$$

constitute a complete system now. It allows us to obtain $\langle|Y_{21}|^2\rangle_\omega$ as a function of the model parameters βK, $z\sigma$, W and $\eta=\pi\rho\sigma^3/6$. The solution of Eq. (2.11) under conditions (2.9) determines the single-particle distribution function in the MSA. By the factorization method of Baxter and Wertheim (see [10,12]) the integral equation (2.11) for $m=1$ can be reduced to a system of algebraic equations,

$$\frac{12}{5}\tilde{\eta}\beta K\frac{\exp(z\sigma)}{z\sigma+1}=\tilde{D}[1-\tilde{Q}(z)], \qquad (2.14)$$

$$2\pi\tilde{g}_{221}(z)[1-\tilde{Q}(z)]=\frac{1}{2}\exp(-2z\sigma)[1-2\pi\tilde{g}_{221}(z)]\tilde{D}, \qquad (2.15)$$

$$-\tilde{C}=[1-2\pi\tilde{g}_{221}(z)]\tilde{D}, \qquad (2.16)$$

where $\tilde{\eta}=\eta\langle|Y_{21}(\omega)|^2\rangle_\omega$, $\tilde{D}$ and $\tilde{C}$ are dimensionless coefficients of the factor correlation function

$$Q(R)=\frac{z}{\rho\langle|Y_{21}(\omega)|^2\rangle_\omega}[Q_0(R)+\tilde{D}\exp(-zR)] \qquad (2.17)$$

with the short-range part

$$Q_0(R)=\tilde{C}[\exp(-zR)-\exp(-z\sigma)], \quad R<\sigma, \qquad (2.18)$$

$$Q_0(R)=0, \quad R>\sigma. \qquad (2.19)$$

$\tilde{Q}(z)$ and $\tilde{g}_{221}(z)$ are the dimensionless Laplace transforms of $Q(R)$ and $h_{221}(R)$, respectively,

$$\tilde{Q}(z)=\rho\langle|Y_{21}(\omega)|^2\rangle_\omega\int_0^\infty e^{-zt}Q(t)dt,$$

$$\tilde{g}_{221}(z)=\frac{\rho\langle|Y_{21}(\omega)|^2\rangle_\omega}{z}\int_\sigma^\infty e^{-zt}h_{221}(t)tdt. \qquad (2.20)$$

From the definition of the factor correlation function it follows that

$$1-\rho\langle|Y_{21}(\omega)|^2\rangle_\omega\int c_{221}(R)d\boldsymbol{R}=[Q(k=0)]^2, \qquad (2.21)$$

where $Q(k)$ is defined by the expression

$$Q(k)=1-\rho\langle|Y_{21}(\omega)|^2\rangle_\omega\int_0^\infty dRe^{ikR}Q(R). \qquad (2.22)$$

The joint use of Eqs. (2.21) and (2.9) gives us the additional equation to determine $\langle|Y_{21}(\omega)|^2\rangle_\omega$,

$$Q(k=0)=\sqrt{\frac{-\beta W}{A_2}}. \tag{2.23}$$

In a more explicit form the above equation reads

$$V=\tilde{D}+d\tilde{C}, \quad V=1-\sqrt{\frac{-\beta W}{A_2}}, \tag{2.24}$$

where $d=e^{-z\sigma}\Delta_1(z\sigma)$. Here and below we use the symbols

$$\Delta_n(x)=\exp(x)-\sum_{l=0}^{n}\frac{1}{l!}x^l. \tag{2.25}$$

Formulas (2.24), (2.15), and (2.16) allow to determine $\tilde{D}$,

$$\tilde{D}=\frac{-b-\sqrt{b^2-4ac}}{2a}, \tag{2.26}$$

where

$$a=-d\exp(-2z\sigma)-(d-1)[d-V\Delta_0^2(-z\sigma)],$$

$$c=V[2d-V\Delta_0^2(-z\sigma)],$$

$$b=(d-1)c/V+V[V\Delta_0^2(-z\sigma)-d]+dV\exp(-2z\sigma). \tag{2.27}$$

It should be noted that the signs before square roots in Eqs. (2.23) and (2.26) are chosen to provide the physical solution.

Now from Eq. (2.14) we can obtain the dependence between the ordering parameter $\langle|Y_{21}(\omega)|^2\rangle_\omega$ and the system parameters η, βK, $\beta W/A_2$, and $z\sigma$,

$$\beta K\eta\langle|Y_{21}(\omega)|^2\rangle_\omega=f(z\sigma,V),$$

$$f(z\sigma,V)=\frac{5}{24}\tilde{D}\left[2-\frac{V\Delta_0^2(-z\sigma)}{d}-\tilde{D}\left\{1-\frac{\Delta_0^2(-z\sigma)}{d}\right\}\right]\frac{z\sigma+1}{\exp(z\sigma)}. \tag{2.28}$$

A solution of Eq. (2.28) with $\langle|Y_{21}(\omega)|^2\rangle_\omega \equiv\langle\frac{15}{2}\sin^2\theta\cos^2\theta\rangle_\omega$, where averaging $\langle\cdots\rangle_\omega$ is made with the self consistent $f(\omega)$ defined by Eq. (2.10), gives us $\langle|Y_{21}(\omega)|^2\rangle_\omega$ and A_2. Further calculation of average values can be carried out in a simple arithmetic way. First, Eqs. (2.9) yield $A_2=\langle Y_{20}(\omega)\rangle_\omega/\langle|Y_{21}(\omega)|^2\rangle_\omega$. Thus, one obtains $\langle P_2(\cos\theta)\rangle_\omega\equiv\langle Y_{20}(\omega)\rangle_\omega/\sqrt{5}$ expressed in terms of $\langle|Y_{21}(\omega)|^2\rangle_\omega$ and A_2. On the other hand, one can use the well-known expressions for $|Y_{2m}(\omega)|^2$ in terms of Legendre polynomials (see, for example, [13]),

$$|Y_{21}(\omega)|^2=1+\frac{5}{7}P_2(\cos\theta)-\frac{12}{7}P_4(\cos\theta),$$

$$|Y_{22}(\omega)|^2=1-\frac{10}{7}P_2(\cos\theta)+\frac{3}{7}P_4(\cos\theta),$$

and express $\langle|Y_{22}(\omega)|^2\rangle_\omega$ via $\langle|Y_{21}(\omega)|^2\rangle_\omega$ and A_2,

$$\langle|Y_{22}(\omega)|^2\rangle_\omega\equiv\left\langle\frac{15}{8}\sin^4\theta\right\rangle_\omega =\frac{5}{4}\left(1-\frac{A_2\langle|Y_{21}|^2\rangle_\omega}{\sqrt{5}}-\frac{\langle|Y_{21}|^2\rangle_\omega}{5}\right). \tag{2.29}$$

In an analogous way, one can find the last orientational average contained in Eq. (2.12),

$$\langle|Y_{20}(\omega)|^2\rangle_\omega=1+\frac{10}{7}\langle P_2(\cos\theta)\rangle_\omega+\frac{18}{7}\langle P_4(\cos\theta)\rangle_\omega.$$

III. THE STABILITY OF THE MODEL

In the previous section we obtained the single-particle distribution function and, therefore, all order parameters. Now we can investigate the stability condition of the nonoriented uniaxial phase with respect to the spontaneous ordering into the biaxial nematic. A problem of this kind for the case $W=0$ and the pair potential (1.2) and (1.3) was solved in the well-known paper by Kloczkowski and Stecki [7]. The local stability condition of the isotropic phase with respect to uniaxial variations of the distribution function

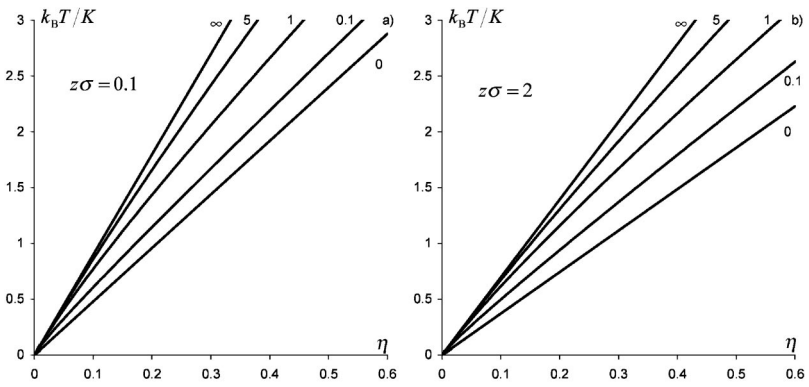

FIG. 1. Orientational instability lines for different ranges of the pair potential: (a) $z\sigma=0.1$; (b) $z\sigma=2$. The numbers attached to the lines are values of the disorienting field W/K.

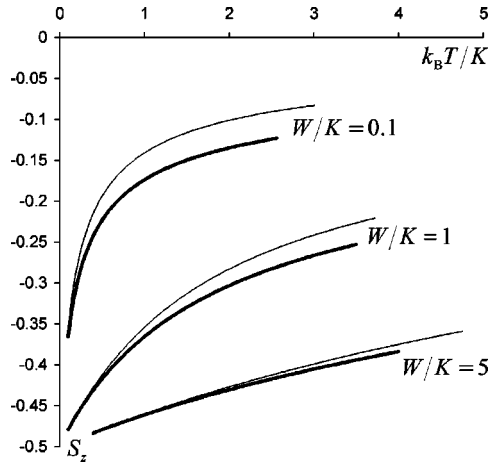

FIG. 2. The order parameter $S_z=\langle(3\cos^2\theta-1)/2\rangle_\omega$ in the instability points for finite fields W/K. Thin lines correspond to $z\sigma=0.1$; thick lines show the results for $z\sigma=2$.

$$\delta\rho(i)=\sum_{L=0}^{\infty} s_L P_L(\cos\theta_i) \tag{3.1}$$

was written in Ref. [7],

$$\int d(1)d(2)\left[\frac{\delta(1,2)}{\rho/4\pi}-c(1,2)\right]\delta\rho(1)\delta\rho(2)>0, \tag{3.2}$$

where $c(1,2)$ was the direct correlation function of the isotropic phase. More general stability conditions of nematic phases were discussed in [14,12]. It is worth noting that the stability condition of nematics at zero field has some special features. The point is that rotations of the director of spontaneous ordering do not change the nematic free energy. This results in Goldstone mode singularities that are connected with the long-range correlations of the director fluctuations. A detailed discussion of these singularities within the integral equation approach was presented in [10,12,14]. Here we quote the stability condition in the presence of the field ($W>0$),

$$\int d(1)d(2)[\delta(1,2)-c(1,2)\rho(1)]\delta\rho^*(1)\delta\rho(2)>0, \tag{3.3}$$

where $\rho(1)$ and $c(1,2)$ are the single-particle distribution function and the direct correlation function of the nonoriented uniaxial fluid, * means a complex conjugation, and

$$\delta\rho(1)=\sum_{l\mu}\Delta_{l\mu}Y_{l\mu}(\omega_1) \tag{3.4}$$

is a general orientational variation of the distribution function.

Any nonpolar biaxial phase is characterized by two nontrivial order parameters: $S_z=\langle P_2(\cos\theta_i)\rangle_B$ and $S_x=\langle\sin^2\theta_i\cos(2\varphi_i)\rangle_B$, and S_x is proportional to $\langle Y_{22}(\omega_1)+Y_{22}^*(\omega_1)\rangle_B$. The subscript B means the averaging with a biaxial orientational distribution $\rho_B(1)$. To obtain the stability condition with respect to the biaxial phase we can consider variations $\delta\rho(1)=\rho_B(1)-\rho(1)$ in Eq. (3.3). These variations can contain terms like Eq. (3.1) that describe fluctuations of S_z and can have terms of a new type,

$$\delta\rho(1)\sim S_x[Y_{22}(\omega_1)+Y_{22}^*(\omega_1)], \tag{3.5}$$

that describe fluctuations connected with appearance of the new biaxial symmetry. We note that in Eq. (3.5) we retained only the lowest term. Inserting these simplest variations into Eq. (3.3) and taking into account the MSA form of the direct correlation function (2.8), one obtains

$$1-\langle|Y_{22}|^2\rangle_\omega\rho\int c_{222}(R)d\boldsymbol{R}>0. \tag{3.6}$$

In other words, the system becomes orientationally unstable with respect to spontaneous biaxial nematic ordering at

$$1-\langle|Y_{22}|^2\rangle_\omega\rho\int c_{222}(R)d\boldsymbol{R}=0. \tag{3.7}$$

In order to obtain condition (3.7) in an explicit and analytical form, one can use results and the method of the previous section. The factorization method applied to Eq. (2.11) with $m=2$ yields the same system (2.14)–(2.16) that we got for $m=\pm1$ with the only difference: $\tilde{\eta}=\eta\langle|Y_{22}(\omega)|^2\rangle_\omega$. Equation (3.7) gives an additional condition like Eq. (2.24), but with $V=1$,

$$1=\tilde{D}+d\tilde{C}. \tag{3.8}$$

As a result one obtains an explicit form for Eq. (3.7)

$$\frac{K}{k_B\overline{T}}\overline{\eta}\langle|Y_{22}(\omega)|^2\rangle_\omega=f(z\sigma,V=1), \tag{3.9}$$

where equilibrium $\langle|Y_{22}(\omega)|^2\rangle_\omega$ has to be calculated from Eqs. (2.29) and (2.28) at temperature $\overline{T}$ and density $\overline{\eta}$ for a given field $\overline{W}$. If Eq. (3.9) is satisfied, it means that ($\overline{T}$, $\overline{\eta}$, $\overline{W}$) is an instability point.

TABLE I. Temperature of instability at $\eta=0.3$ for different ranges of interaction $z\sigma$ and its growth in an external disorienting field (the field strength W/K is specified in parentheses after $t=k_BT/K$).

$z\sigma$	$t(0)$	$t(0.1)/t(0)$	$t(1)/t(0)$	$t(5)/t(0)$	$t(\infty)/t(0)$
0.1	1.44	1.16	1.43	1.68	15/8
2	1.11	1.23	1.50	1.72	15/8

IV. RESULTS AND CONCLUSIONS

Let us consider Eq. (3.9) in two limiting cases, when one can do without Eqs. (2.29) and (2.28). At zero field ($W\to0$) the nonoriented phase coincides with the isotropic

phase, and $\langle|Y_{22}(\omega)|^2\rangle_\omega \equiv 1$. In this case Eq. (3.9) gives the instability condition of the isotropic phase with respect to the nematic phase formation [7,12]. At the infinite field ($W \to \infty$) $\langle|Y_{22}(\omega)|^2\rangle_\omega \equiv 15/8$, and Eq. (3.9) transforms into the instability condition with respect to the limiting biaxial phase [5]. In both the cases $(K/k_B\overline{T})\,\overline{\eta}$ depends on $z\sigma$ only. Therefore, the corresponding instability points lie on straight lines in the temperature-density coordinates (see Fig. 1). This is a consequence of a symmetry of the MSA solution we found in the previous section: Eq. (2.28) shows that at fixed $(K/k_BT)\,\eta$ and (W/k_BT) the orientational distribution is fixed, and the equilibrium value of $\langle|Y_{22}(\omega)|^2\rangle_\omega$ is constant. Then, it follows from orientational instability condition (3.9) that if we change the field strength W proportionally to the temperature (keeping W/k_BT constant), the orientational instability points will belong to a straight line in the temperature-density coordinates. At $W=0$ and at $W=\infty$ any temperature scaling does not change W/k_BT, which results in straight instability lines at the fixed field strength. The situation differs at a finite W. In this case the orientational distribution in orientational instability points (and all its moments $\langle\cdots\rangle_\omega$) depends on both the temperature and the density. Therefore, instability points in the general case lie on a curve.

In Fig. 2 the order parameter S_z in instability points is plotted against the temperature at different values of the field $W/K=0.1$; 1; 5. Let us note that S_z equals 0 at $W/K=0$, and S_z equals $-1/2$ at $W/K=\infty$. One can see that the effect of the field on S_z in instability points is stronger in the case of a short-range potential ($z\sigma=2$). The difference between the field effects at different $z\sigma$ is especially noticeable for weak fields and high temperatures. At low temperatures or strong fields the results for different $z\sigma$ are hardly distinguishable. It follows also from Fig. 2 that at low temperatures S_z tends to $-1/2$ for all fields. It means that at low enough temperatures even a weak field forces molecules to lie in the XY plane, as very strong fields do.

Figure 1 presents the set of instability lines, at which the system becomes orientationally unstable with respect to the spontaneously ordered phase. This phase is biaxial at $W>0$ and is uniaxial at $W=0$. One can see in Fig. 1 that the disorienting field raises the instability line (in other words, favors the orientational ordering), and the effect of finite fields is stronger in the system with shorter ranges of the anisotropic potential ($z\sigma=2$). The latter fact is also illustrated by Table I. For example, the field $W=0.1K$ raises the instability temperature by 23% for $z\sigma=2$, whereas for $z\sigma=0.1$ the increase is 16%. One can see from our results that the disorienting field influence in systems with short-range anisotropic interactions can lead to qualitative changes. For example, in Fig. 1(b) for $z\sigma=2$ at $k_BT/K=2.5$ the zero-field instability line is in the dense packing region. The disorienting field shifts the orientational instability and can place the spontaneous nematic ordering before the system crystallization: at $k_BT/K=2.5$ the densities of orientational instability are $\eta=0.57$ at $W/K=0.1$ and $\eta=0.47$ at $W/K=1$.

Small fields in the region of small densities (and low temperatures) produce orientationally ordered phases very efficiently. In Fig. 1 all curves for nonzero fields coincide at very low temperatures. But, it is expected that instability lines in this region are under the gas-liquid binodal. Therefore, this point needs an additional investigation as it was done for $W=0$ [15] and $W=\infty$ [5] cases. On the other hand, the undesirable condensation can be suppressed, for example, by inclusion of an additional isotropic repulsion between particles.

In this paper we studied a system of uniaxial particles placed in an external disorienting field. Such a system demonstrates an orientational instability with respect to a spontaneous formation of the biaxial nematic phase. Using the integral equation method we derived the orientational instability condition in an explicit form, which permitted to study the effect of the disorienting external field on the region of the spontaneously ordered nematic phase. This condition turns into known results for the limiting cases of zero or infinite fields. The instability lines we obtained coincide with the biaxial ordering lines if the phase transition is of the second order. This actually takes place for strong enough fields.

Our calculation shows that even small disorienting fields significantly raise the instability temperature and, therefore, noticeably favor the nematic phase. The effect of small fields appears to be especially visible in the systems with short-range anisotropic interactions between particles. It turns out that even weak disorienting fields (W less than $0.1k_BT$) significantly favor a nematic ordering. The point is that the disorienting field transforms the system symmetry and restricts the orientation space where particles can be present with some probability. The stronger the field, the more peaked at $\theta=\pi/2$ the orientational distribution is. Orientational fluctuations act against the field influence and weaken the induced ordering. Their role is very noticeable for weak fields, of course. There is a peculiarity about the case of disorienting fields: only one orientational fluctuation (in the field direction) counteracts the induced ordering with a negative order parameter S_z. Thus, weak disorienting fields can restrict the effective angle space efficiently enough and, eventually, further the spontaneous ordering into the biaxial phase. In practice it is small fields that are usually employed. Therefore, we believe that disorienting fields of different origins can be useful in various applications of anisotropic fluids, besides broadly used orienting fields.

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