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Microscopic theory of binary mixtures of uniaxial nematic liquid crystals

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Based on the Bogoliubou-Born-Green-Kirkwood-Yvon hierarchy equations a microscopic theory of binary mixtures of nematic liquid crystals has been derived. The resulting integral equations for the equilibrium single-particle distribution functions are of the Hammerstein type. The functional form of the free energy has been constructed on the basis of the state equations. A realistic soft intermolecular potential is applied to the theory. A potential for two different molecules is proposed as a function of characteristic parameters for molecules of the type A and B. A general discussion of the stability conditions is presented for both homogeneous and heterogeneous mixtures.

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I. INTRODUCTION

Soluability of some liquid crystalline substances in other liquid crystalline substances is the cornerstone in custom design of the mixtures with tailored physical properties. One of the best examples is the design of the cholesteric serving as a working medium in liquid crystalline displays. The cholesteric pitch is easily controlled by varying the proportions of individual pure liquid crystalline substances out of which the cholesteric in question is composed [1–3]. Another good example is provided by application of nematics in the hydrokinetic devices [4]. These devices as a rule require a working fluid with highly anisotropic viscosity coefficients and high phase transition temperatures (a very wide temperature range for the nematic phase). Chemically pure substances with the desired properties are hard to find. Again the custom prepared mixtures easily meet the required technical parameters. There are many similar examples.

All that has induced a great interest in how to develop a theory of liquid crystalline mixtures suitable for understanding the physical properties of mixtures and thus helping in the design of mixtures with the prescribed technical parameters.

Some microscopic models of binary nematic mixtures are related to the Onsager [5] theory of the isotropic-nematic transition of a system of monodisperse thin hard rods. Stroobants and Lekkerkerker [6] have extended the simple Onsager model to mixtures of rodlike and disklike particles. Using this approach Odijk and Lekkerkerker [7] have successfully explained fractional effect, widening of the unmiscibility region, and reentrant nematic-isotropic transitions. The further development is the proof of the existence of the isotropic-nematic-nematic triple point in the binary system of the rigid hard rods (Vroege and Lekkerkerker [8]) and tricritical point in the polar liquid crystals (Szumilin and Milczarek [9]).

The other approaches, not related to the Onsager thin rod model, are of the mean field type. The mean field type arguments are extended to cover the case of binary mixtures and answer the question of how the biaxiality on the molecular level can influence the bulk properties of the samples (see [10] and the references therein).

In 1979 Stecki and Kloczkowski [11] generalized the Onsager theory to a system of arbitrary molecules with orientational degrees of freedom and interacting via an arbitrary pair potential. This theory was applied to many problems in liquid crystals. The examples are the following: the statistical theory of the elastic constants in nematics [12], the analysis of the isotropic phase stability against nematic and smectic A phase formation [13], and next—the unified theory of isotropic-nematic-smectic A phases [14]. Then, one can mention the theory of elastic constants in liquid crystals composed of disklike molecules [15] and finally the unified theory of static and hydrodynamic properties of nematics [16].

In papers [14–16] interaction between molecules was described by a soft pair potential of the Corner type [17]. This potential when inserted into Stecki-Kloczkowski theory leads to realistic and, what is important, analytic description of the pure substance nematic liquid crystal properties. The purpose of the present paper is to extend this description for nematic binary mixtures.

The starting point is the Liouville equation for $(N_A + N_B)$-particle distribution function F^{N_A,N_B}, which is formulated taking into account rotational degrees of freedom. By introducing reduced distribution functions F^{S_A,S_B} the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of coupled equations for F^{S_A,S_B} for the mixture is obtained. From the analysis of the first equations of the BBGKY hierarchy for the single-particle distribution functions $F_1(A)$ and $F_1(B)$ in the equilibrium case the set of two state equations is derived. Taking the limit that density of nematic B approaches zero this set transforms into the previously elaborated [18,19] Hammerstein equation of state for the unary nematic. It is shown that the two-particle correlation function must be of the simple form $e^{-\beta U_{12}}$,

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where U_{12} is the interaction potential. Since solutions $F_1(A)$ and $F_1(B)$ for the equilibrium state must satisfy the conditions for minimum of the free energy of the system it is possible to obtain the full expression for the free energy for the nematic mixture. Its structure is formally in agreement with the formula of Stecki and Kloczkowski [11] for the uniform system and becomes equal to this formula taking the limit $d_B \to 0$.

In the following sections the stability problem is discussed in detail. Since it frequently happens that the stability analysis in liquid crystals is not provided in the completely correct way, all necessary conditions are discussed and all misunderstandings are clarified. Especially we pay attention to the Gibbs-Duhem relation which for the case of nematics, to our knowledge, has not been properly presented so far. Statistical microscopic theories should be in agreement with thermodynamical premises so this relation can be treated as a check of correctness of considerations.

The Ruijgrok potential [17–19] and its generalized form for two different molecules is shown to be easily applied to this theory.

II. THE EQUATIONS OF STATE

The state of a molecule of nematic liquid crystal can be described by the center of mass motion and rotation of the long axis. Thus let $\vec{r}$ be the position of the center of mass of the molecule, $\vec{v}$ its velocity, $\vec{n}$ the orientation of the molecule, and $\vec{\Omega}$ the angular velocity. The change in the orientation $d\vec{n}$ resulting from rotation through the infinitesimally small angle $\delta\vec{\phi}$ is equal to $d\vec{n} = \delta\vec{\phi} \times \vec{n}$. Hence $\frac{d\vec{n}}{dt} = \vec{\Omega} \times \vec{n}$, with angular velocity $\vec{\Omega} = \frac{d\vec{\phi}}{dt}$. The angular momentum $\vec{M}$ can be represented in the form $\vec{M} = \mathcal{J}\vec{\Omega}$, where $\mathcal{J}$ denotes the tensor of inertia. The set $x_i : (\vec{r_i}, \vec{p_i}, \vec{n_i}, \vec{M_i})$ can be regarded as the phase of the molecule i.

Let us take into consideration a mixed system of N_A particles of the kind A and N_B particles of the kind B. The system is described by the $(N_A + N_B)$-particle distribution function: $F^{N_A,N_B}(x_{1_A}, \ldots, x_{N_A}, x_{1_B}, \ldots, x_{N_B})$ in $10(N_A + N_B)$-dimensional Γ space, the phase space of all $N_A + N_B$ molecules of the system. The probability distribution F^{N_A,N_B} is normalized as follows:

$$\int_\Gamma F^{N_A,N_B} dx_{1_A} \cdots dx_{N_A} dx_{1_B} \cdots dx_{N_B} = 1, \tag{1}$$

with

$$\int dx_i = \int_V d\vec{r_i} \int_{-\infty}^{+\infty} d\vec{p_i} \int_{\Omega_v} d\vec{n_i} \int_{-\infty}^{+\infty} d\vec{M_i}. \tag{2}$$

The time evolution of F^{N_A,N_B} is given by the Liouville equation [21–24]:

$$\frac{\partial F^{N_A,N_B}}{\partial t} = \{H_{N_A,N_B}, F^{N_A,N_B}\} = -iL_{N_A,N_B} F^{N_A,N_B}, \tag{3}$$

where $\{\ ,\ \}$ are the Poisson brackets, H_{N_A,N_B} is the Hamilton function of the system, and L_{N_A,N_B} is the Liouville operator.

The Hamilton function of the system reads

$$\begin{aligned} H_{N_A,N_B} = & \sum_{i_A=1}^{N_A} \left(\frac{p_{i_A}^2}{2m_A} + \frac{\vec{M}_{i_A}^T \mathcal{J}_A^{-1} \vec{M}_{i_A}}{2} \right) \\ & + \sum_{i_B=1}^{N_B} \left(\frac{p_{i_B}^2}{2m_B} + \frac{\vec{M}_{i_B}^T \mathcal{J}_B^{-1} \vec{M}_{i_B}}{2} \right) \\ & + \frac{1}{2} \sum_{s=1,t=1}^{N_A} \Phi_{st}^{AA} + \frac{1}{2} \sum_{s=1,t=1}^{N_B} \Phi_{st}^{BB} \\ & + \frac{1}{2} \sum_{s=1,t=1}^{N_A,N_B} \Phi_{st}^{AB}. \end{aligned} \tag{4}$$

The indices i, s, t label the particles and Φ is the interaction potential energy of a pair of molecules. Using the conservation law for phase density in Γ space when moving with the phase point:

$$\frac{dF^{N_A,N_B}}{dt} = 0 \tag{5}$$

we can derive the Liouville equation for the mixture:

$$\begin{aligned} \frac{\partial F^{N_A,N_B}}{\partial t} & + \sum_{i_A=1}^{N_A} \left[\frac{\partial F^{N_A,N_B}}{\partial \vec{r}_{i_A}} \dot{\vec{r}}_{i_A} + \frac{\partial F^{N_A,N_B}}{\partial \vec{p}_{i_A}} \dot{\vec{p}}_{i_A} + \frac{\partial F^{N_A,N_B}}{\partial \vec{n}_{i_A}} \dot{\vec{n}}_{i_A} + \frac{\partial F^{N_A,N_B}}{\partial \vec{M}_{i_A}} \dot{\vec{M}}_{i_A} \right] \\ & + \sum_{i_B=1}^{N_B} \left[\frac{\partial F^{N_A,N_B}}{\partial \vec{r}_{i_B}} \dot{\vec{r}}_{i_B} + \frac{\partial F^{N_A,N_B}}{\partial \vec{p}_{i_B}} \dot{\vec{p}}_{i_B} + \frac{\partial F^{N_A,N_B}}{\partial \vec{n}_{i_B}} \dot{\vec{n}}_{i_B} + \frac{\partial F^{N_A,N_B}}{\partial \vec{M}_{i_B}} \dot{\vec{M}}_{i_B} \right] \\ & = \frac{\partial F^{N_A,N_B}}{\partial t} - \{H_{N_A,N_B}, F^{N_A,N_B}\} = 0, \end{aligned} \tag{6}$$

where the Poisson brackets are written in $x_i : (\vec{r_i}, \vec{p_i}, \vec{n_i}, \vec{M_i})$.

We can obtain the explicit form of the Liouville operator for the mixture by the use of the Hamilton equations:

$$\begin{aligned} \dot{\vec{r}} &= \vec{v}, \\ \dot{\vec{n}} &= \mathcal{J}^{-1}\vec{M} \times \vec{n}, \\ \dot{\vec{p}} &= -\frac{\partial H_{N_A,N_B}}{\partial \vec{r}}, \\ \dot{\vec{M}} &= -\frac{\partial H_{N_A,N_B}}{\partial \vec{\phi}} = -\vec{n} \times \frac{\partial H_{N_A,N_B}}{\partial \vec{n}}, \end{aligned} \tag{7}$$

where the following variational relation has been applied:

$$\delta H = \frac{\partial H}{\partial \vec{n}} \delta \vec{n} = -\delta \vec{\phi} \left(\vec{n} \times \frac{\partial H}{\partial \vec{n}} \right). \tag{8}$$

Thus the Liouville operator reads

$$-iL^{kin}_{N_A,N_B} = \sum_{i_A=1}^{N_A} \left(\frac{\vec{p}_{i_A}}{m_A} \frac{\partial}{\partial \vec{r}_{i_A}} - \vec{n}_{i_A} \times \mathcal{J}_A^{-1} \vec{M}_{i_A} \cdot \frac{\partial}{\partial \vec{n}_{i_A}} \right) + \sum_{i_B=1}^{N_B} \left(\frac{\vec{p}_{i_B}}{m_B} \frac{\partial}{\partial \vec{r}_{i_B}} - \vec{n}_{i_B} \times \mathcal{J}_B^{-1} \vec{M}_{i_B} \cdot \frac{\partial}{\partial \vec{n}_{i_B}} \right), \tag{9}$$

$$\begin{aligned} -iL^{pot}_{N_A,N_B} &= \sum_{i \neq j}^{N_A,N_A} \frac{1}{2} \Theta^{AA}_{ij} + \sum_{i \neq j}^{N_B,N_B} \frac{1}{2} \Theta^{BB}_{ij} + \sum_{i \neq j}^{N_A,N_B} \Theta^{AB}_{ij} \\ &= \sum_{i \neq j}^{N_A,N_A} \frac{1}{2} \left(\frac{\partial \Phi^{AA}_{ij}}{\partial \vec{r}_i} \frac{\partial}{\partial \vec{p}_i} + \frac{\partial \Phi^{AA}_{ij}}{\partial \vec{r}_j} \frac{\partial}{\partial \vec{p}_j} + \vec{n}_i \times \frac{\partial \Phi^{AA}_{ij}}{\partial \vec{n}_i} \frac{\partial}{\partial \vec{M}_i} + \vec{n}_j \times \frac{\partial \Phi^{AA}_{ij}}{\partial \vec{n}_j} \frac{\partial}{\partial \vec{M}_j} \right) \\ &\quad + \sum_{i \neq j}^{N_B,N_B} \frac{1}{2} \left(\frac{\partial \Phi^{BB}_{ij}}{\partial \vec{r}_i} \frac{\partial}{\partial \vec{p}_i} + \frac{\partial \Phi^{BB}_{ij}}{\partial \vec{r}_j} \frac{\partial}{\partial \vec{p}_j} + \vec{n}_i \times \frac{\partial \Phi^{BB}_{ij}}{\partial \vec{n}_i} \frac{\partial}{\partial \vec{M}_i} + \vec{n}_j \times \frac{\partial \Phi^{BB}_{ij}}{\partial \vec{n}_j} \frac{\partial}{\partial \vec{M}_j} \right) \\ &\quad + \sum_{i \neq j}^{N_A,N_B} \left(\frac{\partial \Phi^{AB}_{ij}}{\partial \vec{r}_i} \frac{\partial}{\partial \vec{p}_i} + \frac{\partial \Phi^{AB}_{ij}}{\partial \vec{r}_j} \frac{\partial}{\partial \vec{p}_j} + \vec{n}_i \times \frac{\partial \Phi^{AB}_{ij}}{\partial \vec{n}_i} \frac{\partial}{\partial \vec{M}_i} + \vec{n}_j \times \frac{\partial \Phi^{AB}_{ij}}{\partial \vec{n}_j} \frac{\partial}{\partial \vec{M}_j} \right), \end{aligned} \tag{10}$$

where, for instance, Θ^{AA}_{ij} denotes

$$\Theta^{AA}_{ij} = \frac{\partial \Phi^{AA}_{ij}}{\partial \vec{r}_i} \frac{\partial}{\partial \vec{p}_i} + \frac{\partial \Phi^{AA}_{ij}}{\partial \vec{r}_j} \frac{\partial}{\partial \vec{p}_j} + \vec{n}_i \times \frac{\partial \Phi^{AA}_{ij}}{\partial \vec{n}_i} \frac{\partial}{\partial \vec{M}_i} + \vec{n}_j \times \frac{\partial \Phi^{AA}_{ij}}{\partial \vec{n}_j} \frac{\partial}{\partial \vec{M}_j}. \tag{11}$$

Let us introduce reduced distribution functions by

$$F^{S_A,S_B}(x_{1_A}, \ldots, x_{S_A}, x_{1_B}, \ldots, x_{S_B}) = C \int_\Gamma F^{N_A,N_B} dx_{S_A+1} \cdots dx_{N_A} dx_{S_B+1} \cdots dx_{N_B}, \tag{12}$$

where $C = (4\pi V)^{S_A+S_B}$ and V denotes dimensionless volume.

The BBGKY hierarchy [21–25] of coupled equations for the F^{S_A,S_B} reads

$$\begin{aligned} \frac{\partial F^{S_A,S_B}}{\partial t} - iL_{S_A,S_B} F^{S_A,S_B} &= \frac{d_A}{4\pi} \sum_i^{S_A} \int_\Gamma \Theta^{AA}_{i,S_A+1} F^{S_A+1,S_B} dx_{S_A+1} + \frac{d_B}{4\pi} \sum_i^{S_B} \int_\Gamma \Theta^{BB}_{i,S_B+1} F^{S_A,S_B+1} dx_{S_B+1} \\ &\quad + \frac{d_B}{4\pi} \sum_i^{S_A} \int_\Gamma \Theta^{AB}_{i,S_B+1} F^{S_A,S_B+1} dx_{S_B+1} + \frac{d_A}{4\pi} \sum_i^{S_B} \int_\Gamma \Theta^{AB}_{S_A+1,j} F^{S_A+1,S_B} dx_{S_A+1}, \end{aligned} \tag{13}$$

where d_A and d_B denote number densities of particles A and B.

The first equations of the BBGKY hierarchy for the single-particle distribution functions are the following:

$$\frac{\partial F^{1,0}}{\partial t} - iL_{1,0} F^{1,0} = \frac{d_A}{4\pi} \int_\Gamma \Theta^{AA}_{1,2} F^{2,0} dx_{2_A} + \frac{d_B}{4\pi} \int_\Gamma \Theta^{AB}_{1,1} F^{1,1} dx_{1_B}, \tag{14}$$

$$\frac{\partial F^{0,1}}{\partial t} - iL_{0,1} F^{0,1} = \frac{d_B}{4\pi} \int_\Gamma \Theta^{BB}_{1,2} F^{0,2} dx_{2_B} + \frac{d_A}{4\pi} \int_\Gamma \Theta^{AB}_{1,1} F^{1,1} dx_{1_A}, \tag{15}$$

or in terms $x_i : (\vec{r_i}, \vec{p_i}, \vec{n_i}, \vec{M_i})$:

$$\begin{aligned}\frac{\partial F(1_A)}{\partial t} &= -\frac{\vec{p}_{1_A}}{m_A}\cdot\frac{\partial F(1_A)}{\partial \vec{r}_{1_A}} - \vec{n}_{1_A}\times \mathcal{J}_A^{-1}\vec{M}_{1_A}\cdot\frac{\partial F(1_A)}{\partial \vec{n}_{1_A}} + \frac{d_A}{4\pi}\int_\Gamma\left[\frac{\partial \Phi_{12}^{AA}}{\partial \vec{r}_{1_A}}\cdot\frac{\partial F(1_A,2_A)}{\partial \vec{p}_{1_A}}\right.\\ &\quad \left. +\vec{n}_{1_A}\times\frac{\partial \Phi_{12}^{AA}}{\partial \vec{n}_{1_A}}\cdot\frac{\partial F(1_A,2_A)}{\partial \vec{M}_{1_A}}\right]dx_{2_A} + \frac{d_B}{4\pi}\int_\Gamma\left[\frac{\partial \Phi_{12}^{AB}}{\partial \vec{r}_{1_A}}\cdot\frac{\partial F(1_A,1_B)}{\partial \vec{p}_{1_A}} + \vec{n}_{1_A}\times\frac{\partial \Phi_{12}^{AB}}{\partial \vec{n}_{1_A}}\cdot\frac{\partial F(1_A,1_B)}{\partial \vec{M}_{1_A}}\right]dx_{1_B},\end{aligned} \tag{16}$$

$$\begin{aligned}\frac{\partial F(1_B)}{\partial t} &= -\frac{\vec{p}_{1_B}}{m_B}\frac{\partial F(1_B)}{\partial \vec{r}_{1_B}} + \vec{n}_{1_B}\times \mathcal{J}_B^{-1}\vec{M}_{1_B}\frac{\partial F(1_B)}{\partial \vec{n}_{1B}} + \frac{d_B}{4\pi}\int_\Gamma\left[\frac{\partial \Phi_{12}^{BB}}{\partial \vec{r}_{1_B}}\cdot\frac{\partial F(1_B,2_B)}{\partial \vec{p}_{1_B}}\right.\\ &\quad \left. +\vec{n}_{1_B}\times\frac{\partial \Phi_{12}^{BB}}{\partial \vec{n}_{1_B}}\cdot\frac{\partial F(1_B,2_B)}{\partial \vec{M}_{1_B}}\right]dx_{2_B} + \frac{d_A}{4\pi}\int_\Gamma\left[\frac{\partial \Phi_{12}^{AB}}{\partial \vec{r}_{1_B}}\cdot\frac{\partial F(1_A,1_B)}{\partial \vec{p}_{1_B}} + \vec{n}_{1_B}\times\frac{\partial \Phi_{12}^{AB}}{\partial \vec{n}_{1_B}}\cdot\frac{\partial F(1_A,1_B)}{\partial \vec{M}_{1_B}}\right]dx_{1_A},\end{aligned} \tag{17}$$

where

$$\begin{aligned}F(1_A) = F^{1,0} &= F_1(\vec{r}_A,\vec{p}_A,\vec{n}_A,\vec{M}_A),\\ F(1_A,2_B) = F^{1,1} &= F_2(\vec{r}_A,\vec{p}_A,\vec{n}_A,\vec{M}_A,\vec{r}_B,\vec{p}_B,\vec{n}_B,\vec{M}_B).\end{aligned}$$

We can represent the two-particle distribution function as $F_2 = F_1F_1g_c$ and assume that the correlation function g_c has the following form:

$$g_c = e^{-\beta U_{12}}. \tag{18}$$

This form of g_c, as it is shown further, leads to the state equations consistent with the phenomenological thermodynamics.

In the equilibrium state the momentum dependent terms have the well-known form of Gaussian function (Maxwell distribution function). So we can write

$$F_1(\vec{r}_A,\vec{p}_A,\vec{n}_A,\vec{M}_A) = F_1(\vec{r}_A,\vec{n}_A)Ce^{\left(-\frac{\beta p_A^2}{2m}\right)}e^{\left(-\beta\vec{M}^T\mathcal{J}^{-1}\vec{M}\right)}, \tag{19}$$

where $C^{-1} = \int e^{-\beta\vec{M}^T\mathcal{J}^{-1}\vec{M}}e^{-\frac{\beta p_A^2}{2m}}d\vec{p}d\vec{M}$ $(\beta = 1/kT)$.

In the case of equilibrium $(\frac{\partial F}{\partial t} = 0)$ Eqs. (16) and (17) read

$$\begin{aligned}0 = &-\frac{\vec{p}_{1_A}}{m_A}F(1_A)\cdot\left[\frac{1}{F(1_A)}\frac{\partial F(1_A)}{\partial \vec{r}_{1_A}} - \frac{\partial}{\partial \vec{r}_{1_A}}\left(\frac{d_A}{4\pi}\int f_{12}^{AA}F(2_A)dx_{2_A} - \frac{d_B}{4\pi}\int f_{12}^{AB}F(1_B)dx_{1_B}\right)\right]\\ &+\vec{n}_{1_A}\times\mathcal{J}_A^{-1}\vec{M}_{1_A}F(1_A)\cdot\left[\frac{1}{F(1_A)}\frac{\partial F(1_A)}{\partial \vec{n}_{1_A}} - \frac{\partial}{\partial \vec{n}_{1_A}}\left(\frac{d_A}{4\pi}\int f_{12}^{AA}F(2_A)dx_{2_A} - \frac{d_B}{4\pi}\int f_{12}^{AB}F(1_B)dx_{1_B}\right)\right],\end{aligned} \tag{20}$$

$$\begin{aligned}0 = &-\frac{\vec{p}_{1_B}}{m_B}F(1_B)\cdot\left[\frac{1}{F(1_B)}\frac{\partial F(1_B)}{\partial \vec{r}_{1_B}} - \frac{\partial}{\partial \vec{r}_{1_B}}\left(\frac{d_B}{4\pi}\int f_{12}^{BB}F(2_B)dx_{2_B} - \frac{d_A}{4\pi}\int f_{12}^{AB}F(1_A)dx_{1_A}\right)\right]\\ &+\vec{n}_{1_B}\times\mathcal{J}_B^{-1}\vec{M}_{1_B}F(1_B)\cdot\left[\frac{1}{F(1_B)}\cdot\frac{\partial F(1_B)}{\partial \vec{n}_{1_B}} - \frac{\partial}{\partial \vec{n}_{1_B}}\left(\frac{d_B}{4\pi}\int f_{12}^{BB}F(2_B)dx_{2_B} - \frac{d_A}{4\pi}\int f_{12}^{AB}F(1_A)dx_{1_A}\right)\right],\end{aligned} \tag{21}$$

where f_{12} is the Mayer function $f_{ij} = e^{-\beta U_{ij}}-1$, $F(1_A) = F(\vec{r}_A,\vec{n}_A)$, and $F(1_B) = F(\vec{r}_B,\vec{n}_B)$.

Setting both subexpressions in Eq. (20) and both subexpressions in Eq. (21) to zero, then integrating the resulting four equations, we derive the following set of equations for the single-particle distribution functions:

$$\begin{aligned}\ln F(\vec{r}_{1_A},\vec{n}_{1_A}) &- \frac{d_A}{4\pi}\int f_{12}^{AA}F(\vec{r}_{2_A},\vec{n}_{2_A})d\vec{r}_{2_A}d\vec{n}_{2_A}\\ &-\frac{d_B}{4\pi}\int f_{12}^{AB}F(\vec{r}_{1_B},\vec{n}_{1_B})d\vec{r}_{1_B}d\vec{n}_{1_B} = \text{const}_A,\end{aligned} \tag{22}$$

$$\begin{aligned}\ln F(\vec{r}_{1_B},\vec{n}_{1_B}) &- \frac{d_B}{4\pi}\int f_{12}^{BB}F(\vec{r}_{2_B},\vec{n}_{2_B})d\vec{r}_{2_B}d\vec{n}_{2_B}\\ &-\frac{d_A}{4\pi}\int f_{12}^{AB}F(\vec{r}_{1_A},\vec{n}_{1_A})d\vec{r}_{1_A}d\vec{n}_{1_A} = \text{const}_B.\end{aligned} \tag{23}$$

In that way we have achieved the equations of state for the mixed nematic system.

Assuming that d_B passes to zero Eqs. (22) and (23) reduce to the previously elaborated [18,19] Hammerstein equation of state for the unary nematic.

III. THE FREE ENERGY

In order to find the general expression for the free energy for the mixture it will be convenient to rewrite (22) and (23) in terms of distribution functions ρ_A and ρ_B normalized to the total numbers of particles:

$$\begin{aligned} &\textstyle\int_\Gamma \rho_A d\vec{r}_A d\vec{n}_A = N_A^{\rm glob}, \\ &\textstyle\int_\Gamma \rho_B d\vec{r}_B d\vec{n}_B = N_B^{\rm glob}, \end{aligned} \tag{24}$$

where $\rho = \frac{d}{4\pi}F(1)$.

Thus the state equations read

$$\ln\rho(\vec{r}_{1_A},\vec{n}_{1_A}) - \int f_{12}^{AA}\rho(\vec{r}_{2_A},\vec{n}_{2_A})d\vec{r}_{2_A}d\vec{n}_{2_A} - \int f_{12}^{AB}\rho(\vec{r}_{1_B},\vec{n}_{1_B})d\vec{r}_{1_B}d\vec{n}_{1_B} = \text{const}_A, \tag{25}$$

$$\ln\rho(\vec{r}_{1_B},\vec{n}_{1_B}) - \int f_{12}^{BB}\rho(\vec{r}_{2_B},\vec{n}_{2_B})d\vec{r}_{2_B}d\vec{n}_{2_B} - \int f_{12}^{AB}\rho(\vec{r}_{1_A},\vec{n}_{1_A})d\vec{r}_{1_A}d\vec{n}_{1_A} = \text{const}_B. \tag{26}$$

Functions ρ_A and ρ_B for the equilibrium state should satisfy the conditions for minimum of the free energy of the system under the constraints that they are normalized to the numbers of particles and the considered process has isochoric V=const and isothermic T=const character.

$$\begin{aligned} \frac{\delta\mathcal{A}}{\delta\rho_A} &= 0, \\ \frac{\delta\mathcal{A}}{\delta\rho_B} &= 0, \end{aligned} \tag{27}$$

where the functional $\mathcal{A}$ is the free energy enriched with the Lagrange conditional terms:

$$\begin{aligned} \mathcal{A} = \mathcal{F} &- \lambda_A\left(\int_\Gamma \rho_A d\vec{r}_A d\vec{n}_A - N_A^{\rm glob}\right) \\ &-\lambda_B\left(\int_\Gamma \rho_B d\vec{r}_B d\vec{n}_B - N_B^{\rm glob}\right) \\ &-\lambda_V\left(V - V^{\rm glob}\right) - \lambda_T\left(T - T^{\rm glob}\right), \end{aligned} \tag{28}$$

where λ_A, λ_B, λ_V, and λ_T are the Lagrange undetermined multipliers.

From (25)–(28) we deduce that the expression for the free energy for the mixture is the following:

$$\begin{aligned} \beta\mathcal{F} = &\int[\ln\rho_{1_A} - 1]\rho_{1_A}d\vec{r}_{1_A}d\vec{n}_{1_A} + \int[\ln\rho_{1_B} - 1]\rho_{1_B}d\vec{r}_{1_B}d\vec{n}_{1_B} - \tfrac{1}{2}\int f^{AA}\rho_{1_A}\rho_{2_A}d\vec{r}_{1_A}d\vec{n}_{1_A}d\vec{r}_{2_A}d\vec{n}_{2_A} \\ &-\tfrac{1}{2}\int f^{BB}\rho_{1_B}\rho_{2_B}d\vec{r}_{1_B}d\vec{n}_{1_B}d\vec{r}_{2_B}d\vec{n}_{2_B} - \int f^{AB}\rho_{1_A}\rho_{1_B}d\vec{r}_{1_A}d\vec{n}_{1_A}d\vec{r}_{1_B}d\vec{n}_{1_B} \end{aligned} \tag{29}$$

and the Lagrange multipliers λ_A and λ_B must be equal to the relevant constants in (25) and (26).

$$\begin{aligned} \lambda_A &= \text{const}_A, \\ \lambda_B &= \text{const}_B. \end{aligned} \tag{30}$$

Structure of the free energy is formally in agreement with the formula of Stecki and Kloczkowski [11] for the unary system and becomes equal to this formula taking the limit $d_B \to 0$.

IV. STABILITY ANALYSIS FOR NEMATIC BINARY MIXTURE

The free energy for the system under consideration is dependent on the following variables:

$$\mathcal{F} = \mathcal{F}(\rho_A, \rho_B, V, T). \tag{31}$$

In the equilibrium state the distribution functions ρ_A and ρ_B are transcendental functions of variables T, V, N_A, N_B. As it is shown in Sec. IX, the distribution functions have the following forms:

$$\begin{aligned} \rho_A &= \frac{d_A}{4\pi}\exp\left(a_0 + a_1\cos^2\theta_A + a_2\cos^4\theta_A + a_3\cos^6\theta_A\right), \\ \rho_B &= \frac{d_B}{4\pi}\exp\left(b_0 + b_1\cos^2\theta_B + b_2\cos^4\theta_B + b_3\cos^6\theta_B\right), \end{aligned} \tag{32}$$

where θ is the angle between the director and the long axis of a molecule and the coefficients a_i and b_i play the role of order parameters which are also transcendental functions of variables T, V, N_A, N_B. In nonequilibrium we will regard them as degrees of freedom connected with anisotropy and ordering. Thus the free energy is a function [compare Eq. (29)]:

$$\mathcal{F} = \mathcal{F}(a_i, b_i, N_A, N_B, T, V). \tag{33}$$

The infinitesimal change in the free energy is

$$\begin{aligned} d\mathcal{F} = &\frac{\partial\mathcal{F}}{\partial T}dT + \frac{\partial\mathcal{F}}{\partial V}dV + \frac{\partial\mathcal{F}}{\partial N_A}dN_A + \frac{\partial\mathcal{F}}{\partial N_B}dN_B \\ &+\sum_i \frac{\partial\mathcal{F}}{\partial a_i}da_i + \sum_i \frac{\partial\mathcal{F}}{\partial b_i}db_i, \end{aligned} \tag{34}$$

where $i = 1, 2, 3$.

By the use of the thermodynamic definitions for pressure, entropy, and chemical potentials:

$$p=\left(-\frac{\partial \mathcal{F}}{\partial V}\right)_{T,N_A,N_B,eq}, \tag{35}$$

$$S=\left(-\frac{\partial \mathcal{F}}{\partial T}\right)_{V,N_A,N_B,eq}, \tag{36}$$

$$\mu_A=\left(\frac{\partial \mathcal{F}}{\partial N_A}\right)_{T,V,N_B,eq}, \tag{37}$$

$$\mu_B=\left(\frac{\partial \mathcal{F}}{\partial N_B}\right)_{T,V,N_A,eq}, \tag{38}$$

the general expression for $d\mathcal{F}$ reads

$$\begin{aligned} d\mathcal{F} &= -SdT - pdV + \mu_A dN_A + \mu_B dN_B \\ &\quad + \sum_i \frac{\partial \mathcal{F}}{\partial a_i} da_i + \sum_i \frac{\partial \mathcal{F}}{\partial b_i} db_i . \end{aligned} \tag{39}$$

In the case considered in our microscopic approach the system is described by the free energy $\mathcal{A}$ (28) which includes the influence of certain restrictions.

Let us reiterate the restrictions imposed on the system:

$$\begin{aligned} T &= T^{\text{glob}}, \\ V &= V^{\text{glob}}, \\ \int_\Gamma \rho_A d\vec{r}_A d\vec{n}_A &= N_A^{\text{glob}}, \\ \int_\Gamma \rho_B d\vec{r}_B d\vec{n}_B &= N_B^{\text{glob}}. \end{aligned} \tag{40}$$

Under these restrictions the change in the free energy $d\mathcal{A}$ reads

$$\begin{aligned} d\mathcal{A} &= \sum_i \frac{\partial \mathcal{A}}{\partial a_i} da_i + \sum_i \frac{\partial \mathcal{A}}{\partial b_i} db_i + (p-\lambda_V)dV \\ &\quad +(S-\lambda_T)dT + (\mu_A-\lambda_A)dN_A + (\mu_B-\lambda_B)dN_B, \end{aligned} \tag{41}$$

where

$$\begin{aligned} \frac{\partial \mathcal{A}}{\partial a_i} &= \frac{\partial \mathcal{F}}{\partial a_i} - \frac{\partial}{\partial a_i}\lambda_A \left(\int \rho_A d(1_A) - N_A^{\text{glob}}\right), \\ \frac{\partial \mathcal{A}}{\partial b_i} &= \frac{\partial \mathcal{F}}{\partial b_i} - \frac{\partial}{\partial b_i}\lambda_B \left(\int \rho_B d(1_B) - N_B^{\text{glob}}\right). \end{aligned} \tag{42}$$

Analysis of the terms (43) is presented in Appendix A. It shows that the condition (27) is equivalent to the following set of equations:

$$\begin{aligned} \frac{\partial \mathcal{A}}{\partial a_i} &= 0, \\ \frac{\partial \mathcal{A}}{\partial b_i} &= 0. \end{aligned} \tag{43}$$

where $i = 1,2,3$.

The necessary condition requires that $d\mathcal{A}$ must vanish. This requirement determines values of the Lagrange multipliers λ_A, λ_B, λ_V, and λ_T.

The sufficient stability condition requires the positive determined second differential form $d^2\mathcal{A}$:

$$d^2\mathcal{A} = \sum_{i,j} \frac{\partial^2 \mathcal{A}}{\partial Y_i \partial Y_j} dY_i dY_j = \sum_{i,j} M_{ij} dY_i dY_j, \tag{44}$$

where $Y_i = V, T, N_A, N_B, a_1, a_2, a_3, b_1, b_2, b_3$.

This condition is satisfied if all the eigenvalues of the matrix M are positive or, equivalently, all the leading minors of the matrix M are positive:

$$M_{11} > 0, \quad \begin{vmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{vmatrix} > 0, \ \ldots, \text{Det}M > 0. \tag{45}$$

In order to check the sufficient stability condition we have to calculate expressions for all elements of the matrix M then, taking into account a particular interaction potential and solutions for a_i and b_i, find their values and obtain desired eigenvalues or minors.

V. TYPES OF SOLUTIONS OF THE STATE EQUATIONS

The state equations (27) [or have a look for their explicit form (25) and (26)] may have different types of solutions for the distribution functions. First of all they are always fulfilled by the trivial solution of the isotropic phase (I) ($a_i = b_i = 0$). Within a certain range of variables T, V, N_A, N_B we can encounter nontrivial solutions ($a_i, b_i \neq 0$) which correspond to anisotropic phases (N).

The following solutions of the state equations are possible

(1) The sufficient condition is not satisfied for any solution. It means that the considered example is nonrealistic. One should consider the phase separation problem.

(2) The condition (45) is satisfied only for (I) solution. Thus the mixture is homogeneous and isotropic.

(3) The condition (45) is satisfied for (N) solution and not for (I). Then the mixture is homogeneous and nematic.

(4) The condition (45) is satisfied both for (N) and (I) solutions. When the solution (N) has lower minimum than (I) then the mixture would be in the nematic state. When the solution for (I) is deeper, then the system is isotropic.

(5) The state equations can have more than one nematic solution which may also fulfill the sufficient condition. Then the mixture will exist in the state with the lowest free energy.

It may happen that the homogeneous state is not of the most important preference. Then we will deal with the case of the spontaneously broken symmetry in the phase separation. It means that the free energy calculated for different separated phases has lower value than for the homogeneous state provided that the condition (45) extended for the phase separation case is also fulfilled. The problem of the phase separation must be added to the analysis of all the above mentioned possibilities. In the next section we will discuss in detail the phenomenon of the system exhibiting separated phases.

VI. PHASE SEPARATION

Let us analyze the case of the binary mixture exhibiting two different phases I and II.

The free energy has the form

$$\begin{aligned}\mathcal{F} &= \mathcal{F}\left(\rho_A^I, \rho_A^{II}, \rho_B^I, \rho_B^{II}, V^I, V^{II}, T^I, T^{II}\right) \\ &= \mathcal{F}\left(\rho_A^I, \rho_B^I, V^I, T^I\right) + \mathcal{F}\left(\rho_A^{II}, \rho_B^{II}, V^{II}, T^{II}\right) \\ &= \mathcal{F}^I + \mathcal{F}^{II}. \end{aligned} \tag{46}$$

For now and for simplicity we do not take into account the surface tension.

The restrictions imposed on our system are the following:

$$\int \rho_A^I d\vec{n} d\vec{r} + \int \rho_A^{II} d\vec{n} d\vec{r} = N_A^{\text{glob}}, \tag{47}$$

$$\int \rho_B^I d\vec{n} d\vec{r} + \int \rho_B^{II} d\vec{n} d\vec{r} = N_B^{\text{glob}}, \tag{48}$$

$$V^I + V^{II} = V^{\text{glob}}, \tag{49}$$

$$T^I = T^{\text{glob}}, \tag{50}$$

$$T^{II} = T^{\text{glob}}. \tag{51}$$

The free energy with Lagrange terms is as follows:

$$\begin{aligned}\mathcal{A} = \mathcal{F}^I + \mathcal{F}^{II} &- \lambda_V\left(V^I + V^{II} - V^{\text{glob}}\right) \\ &-\lambda_{T^I}(T^I - T^{\text{glob}}) \\ &-\lambda_A\left(\int \rho_A^I d\vec{n} d\vec{r} + \int \rho_A^{II} d\vec{n} d\vec{r} - N_A\right) \\ &-\lambda_{T^{II}}(T^{II} - T^{\text{glob}}) \\ &-\lambda_B\left(\int \rho_B^I d\vec{n} d\vec{r} + \int \rho_B^{II} d\vec{n} d\vec{r} - N_B\right), \end{aligned} \tag{52}$$

and, accordingly, the change in the free energy $d\mathcal{A}$ has the form

$$\begin{aligned} d\mathcal{A} = {} & (\mu_A^I - \lambda_A)dN_A^I + (\mu_A^{II} - \lambda_A)dN_A^{II} + (S^I - \lambda_{T^I})dT^I + (S^{II} - \lambda_{T^{II}})dT^{II} + (p^I - \lambda_V)dV^I \\ & +(p^{II} - \lambda_V)dV^{II} + \sum_i \frac{\partial\mathcal{A}}{\partial a_i^I} da_i^I + \sum_i \frac{\partial\mathcal{A}}{\partial b_i^I} db_i^I + \sum_i \frac{\partial\mathcal{A}}{\partial a_i^{II}} da_i^{II} + \sum_i \frac{\partial\mathcal{A}}{\partial b_i^{II}} db_i^{II}. \end{aligned} \tag{53}$$

The necessary conditions read

$$\begin{gathered} \tfrac{\delta\mathcal{A}}{\delta\rho_A^I} = 0, \quad \tfrac{\delta\mathcal{A}}{\delta\rho_B^I} = 0, \quad \tfrac{\delta\mathcal{A}}{\delta\rho_A^{II}} = 0, \quad \tfrac{\delta\mathcal{A}}{\delta\rho_B^{II}} = 0, \\ \mu_A^{II} - \lambda_A = 0, \quad \mu_B^{II} - \lambda_B = 0, \\ \\ \mu_A^I - \lambda_A = 0, \quad \mu_B^I - \lambda_B = 0, \\ p^I - \lambda_V = 0, \quad p^{II} - \lambda_V = 0. \end{gathered} \tag{54}$$

They establish the state equations for the considered phases and requirements that the chemical potentials for each kind of particles must be equal in each phase and both the pressure and the temperature of each phase must be the same.

The sufficient condition stands that all the leading minors (or eigenvalues) of the following matrix:

$$M_{i,j} = \frac{\partial^2\mathcal{A}}{\partial X_i \partial X_j}, \tag{55}$$

where $X_j = T^I, V^I, N_A^I, N_B^I, a_i^I, b_i^I, T^{II}, V^{II}, N_A^{II}, N_B^{II}, a_i^{II}, b_i^{II}$, must be positive.

VII. GIBBS-DUHEM RELATION

The consistence between thermodynamic and statistical descriptions is best proved by checking the Gibbs-Duhem relation. Since not very much attention has been paid to this feature so far and sometimes it happens that it is introduced in a nonaccurate way, we will here put forward its phenomenological form in detail and in the next sections we will introduce its microscopic representation.

The origin of all versions of the Gibbs-Duhem relation is the scaling of the thermodynamic potentials as far as extensive parameters are concerned. In the case where the free energy is used, as it almost always happens in a liquid crystal (LC), these extensive parameters are numbers of particles and volume. We cannot restrict ourselves to the isochoric process since the change in density may be much preferred by the system.

The scaling rule reads

$$\mathcal{F}(T, \lambda V, \lambda N_i, a_i, b_i) = \lambda\mathcal{F}(T, V, N_i, a_i, b_i), \tag{56}$$

where λ denotes scaling factor. Taking the derivative of (56) with respect to λ and then setting λ equal to unity we obtain

$$\mathcal{F} = -pV + \sum \mu_i N_i. \tag{57}$$

So the derivative of $\mathcal{F}$ should be the following:

$$d\mathcal{F} = -dpV - pdV + \sum \mu_i dN_i + \sum N_i d\mu_i. \tag{58}$$

On the other hand $d\mathcal{F}$ has the form

$$\begin{aligned} d\mathcal{F} = -pdV - SdT &+ \sum \mu_i dN_i \\ &+ \sum_i \frac{\partial\mathcal{F}}{\partial a_i} da_i + \sum_i \frac{\partial\mathcal{F}}{\partial b_i} db_i. \end{aligned} \tag{59}$$

Comparing (58) and (59) we come up with the expression for the Gibbs-Duhem relation:

$$0 = -Vdp - SdT - \sum N_i d\mu_i + \sum_i \frac{\partial \mathcal{F}}{\partial a_i} da_i + \sum_i \frac{\partial \mathcal{F}}{\partial b_i} db_i. \tag{60}$$

This form of the Gibbs-Duhem relation should be taken into account whenever considerations are based on the free energy.

The term $(-Vdp)$ is as important as the terms with chemical potentials but it often happens that it is disregarded. When this term is omitted the whole Duhem relation is no longer valid. If it is still treated as valid it cast shadows on the values of chemical potentials [8]. As it is shown in Sec. X the Gibbs-Duhem relation is automatically fulfilled if we use microscopic expressions for the desired terms.

VIII. INTERACTION POTENTIALS

The construction of the mixture theory requires determination of three two-particle potentials of interaction: U^{AA}, U^{BB}, U^{AB}. Functional dependence of the potential we use for two uniaxial identical molecules was previously suggested and elaborated in [17]. It has the form of a Lennard-Jones type interaction:

$$U = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^n \right], \tag{61}$$

where $\vec{r}$ is a vector which separates centers of two molecules and σ is a function dependent on orientations of molecules and on the unit vector $\vec{\Delta}$ pointed in the direction of $\vec{r}$:

$$\sigma = \sigma_0 (1 + S_1 (\vec{\Delta} \cdot \vec{n}_1)^2 + S_1 (\vec{\Delta} \cdot \vec{n}_2)^2 - S_2 (\vec{n}_1 \cdot \vec{n}_2)^2 + S_3 (\vec{\Delta} \cdot \vec{n}_1)^2 (\vec{\Delta} \cdot \vec{n}_2)^2), \tag{62}$$

where σ_0, S_1, S_2, S_3 are phenomenological parameters. (For explanation of $\vec{\Delta}, \vec{n}_1, \vec{n}_2$ see Fig. 1) This form has been derived for two identical molecules and is symmetrical as far as the change of molecules is concerned.

We have assumed that the interaction between two different molecules has analogous form as (61) and (62). In that case σ should read

$$\sigma = \sigma_0 (1 + S_1^{AB} (\vec{\Delta} \cdot \vec{n}_1)^2 + S_{11}^{AB} (\vec{\Delta} \cdot \vec{n}_2)^2 - S_2^{AB} (\vec{n}_1 \cdot \vec{n}_2)^2 + S_3^{AB} (\vec{\Delta} \cdot \vec{n}_1)^2 (\vec{\Delta} \cdot \vec{n}_2)^2) \tag{63}$$

where parameters S_i^{AB} are functions of relevant parameters S_i^A and S_i^B characteristic for molecules of the kind A and B (for justification see Appendix B):

$$\sigma_0^{AB} = \frac{\sigma_0^A + \sigma_0^B}{2}, \tag{64}$$

$$S_2^{AB} = \frac{1}{\sigma_0^A + \sigma_0^B} \left(\sigma_0^A S_2^A + \sigma_0^B S_2^B \right), \tag{65}$$

$$S_3^{AB} = \frac{1}{\sigma_0^A + \sigma_0^B} \left(\sigma_0^A S_3^A + \sigma_0^B S_3^B \right), \tag{66}$$

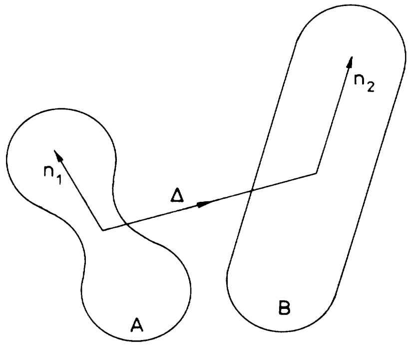

FIG. 1. Illustration for symbols in Eq. (62).

$$S_1^{AB} = \frac{1}{\sigma_0^A + \sigma_0^B} [\sigma_0^A (2S_1^A - S_2^A + S_3^A) + \sigma_0^B (S_2^B - S_3^B)], \tag{67}$$

$$S_{11}^{AB} = \frac{1}{\sigma_0^A + \sigma_0^B} [\sigma_0^B (2S_1^B - S_2^B + S_3^B) + \sigma_0^A (S_2^A - S_3^A)]. \tag{68}$$

In the theory of one-component systems the same parameter S_1 describes two terms: $S_1(\vec{\Delta} \cdot \vec{n}_1)^2$ and $S_1(\vec{\Delta} \cdot \vec{n}_2)^2$. In the case of interaction of two different molecules we have to distinguish between S_1 due to the molecule A and S_{11} due to the molecule B. If we know the characteristics of the molecule A: S_1^A, S_2^A, S_3^A and B: S_1^B, S_2^B, S_3^B we can immediately say what the change in interaction due to σ is. This is the starting point of our further considerations.

IX. THE SINGLE-PARTICLE DISTRIBUTION FUNCTIONS

Let us focus our attention on the state equations for the mixed system (22) and (23). In search for a solution of this set of equations we now restrict ourselves to the case where $f(\vec{r}_{1_A}, \vec{n}_{1_A})$ and $f(\vec{r}_{1_B}, \vec{n}_{1_B})$ are uniform in space and axially symmetric around a fixed direction. Choosing the positive z axis of our coordinate system in this direction, $f(1_A)$ and $f(1_B)$ will be functions of $\cos\theta_1, \cos\theta_2$ only, where θ_1, θ_2 are the polar angles of $\vec{n}_1, \vec{n}_2$. Moreover because the head and tail of a molecule cannot be told apart, $f(1_A)$ and $f(1_B)$ are even functions of $x_1 = \cos\theta_1$ and $x_2 = \cos\theta_2$. Then Eqs (22) and (23) can be written as

$$\ln f(x_{1_A}) - \frac{d_A}{4\pi}\int f_{12}^{AA} f(x_{2_A}) d\vec{r}_{2_A} d\vec{n}_{2_A}$$
$$-\frac{d_B}{4\pi}\int f_{12}^{AB} f(x_{1_B}) d\vec{r}_{1_B} d\vec{n}_{1_B} = \text{const}_A, \quad (69)$$

$$\ln f(x_{1_B}) - \frac{d_B}{4\pi}\int f_{12}^{BB} f(x_{2_B}) d\vec{r}_{2_B} d\vec{n}_{2_B}$$
$$-\frac{d_A}{4\pi}\int f_{12}^{AB} f(x_{1_A}) d\vec{r}_{1_A} d\vec{n}_{1_A} = \text{const}_B. \quad (70)$$

Because of the potential form $U_{12} = U(\sigma/r)$, the radial integrations in (69) and (70) can be performed analytically:

$$\int_0^\infty \left[e^{-\beta U(\sigma/r)} - 1\right] r^2 dr = \frac{1}{3}\sigma^3 B_2^*(T^*). \quad (71)$$

The reduced second virial coefficient $B_2^*(T^*)$ is a function of the reduced temperature $T^* = kT/\epsilon$.

Using abbreviations

$$\begin{aligned} \lambda^{AA} &= \tfrac{\pi}{6}(\sigma_0^A)^3 B_2^{*AA}(T^*) d_A, \\ \lambda^{BB} &= \tfrac{\pi}{6}(\sigma_0^B)^3 B_2^{*BB}(T^*) d_B, \\ \lambda^{AB} &= \tfrac{\pi}{6}(\sigma_0^{AB})^3 B_2^{*AB}(T^*) d_A, \\ \lambda^{BA} &= \tfrac{\pi}{6}(\sigma_0^{AB})^3 B_2^{*AB}(T^*) d_B, \end{aligned} \quad (72)$$

Eqs. (69) and (70) become

$$\ln f(x_{1_A}) - \lambda^{AA}\int_0^1 K^{AA}(x_{1_A}, y_{2_A}) f(y_{2_A}) dy_{2_A}$$
$$-\lambda^{BA}\int_0^1 K^{AB}(x_{1_A}, y_{1_B}) f(y_{1_B}) dy_{1_B} = \text{const}_A, \quad (73)$$

$$\ln f(x_{1_B}) - \lambda^{BB}\int_0^1 K^{BB}(x_{1_B}, y_{2_B}) f(y_{2_B}) dy_{2_B}$$
$$-\lambda^{AB}\int_0^1 K^{AB}(x_{1_B}, y_{1_A}) f(y_{1_A}) dy_{1_A} = \text{const}_B, \quad (74)$$

with symmetric kernels of the type

$$K^{ST}(x,y) = \frac{1}{\pi^2}\int [1 + S_1^{ST}(\vec{\Delta}\cdot\vec{n}_1)^2 + S_{11}^{ST}(\vec{\Delta}\cdot\vec{n}_2)^2$$
$$-S_2^{ST}(\vec{n}_1\cdot\vec{n}_2)^2$$
$$+S_3^{ST}(\vec{\Delta}\cdot\vec{n}_1)\cdot(\vec{\Delta}\cdot\vec{n}_1)]^3 d\phi_2 d\vec{\Delta}, \quad (75)$$

where $S, T = A, B$.

$K^{ST}(x,y)$ is a polynomial of sixth order in x, y of the form

$$K^{ST}(x,y) = \sum_{i,j=0}^{3} \alpha_{ij}^{ST} x^{2i} y^{2j}. \quad (76)$$

The coefficients α_{ij}^{ST} have been calculated analytically [20] by the use of the algebraic computer program MATHEMATICA. They are again polynomials now in $S_1^{ST}, S_2^{ST}, S_3^{ST}$ of order not higher than three. Equations (73) and (74) can be expressed further by introducing the functions

$$\psi(x_{1_A}) = \ln f(x_{1_A}), \quad (77)$$

$$\kappa(x_{1_B}) = \ln f(x_{1_B}). \quad (78)$$

Kernels (75) show that $\psi(x_{1_A})$ and $\kappa(x_{1_B})$ must be of the form

$$\begin{aligned} \psi(x_{1_A}) &= a_0 + a_1 x_{1_A}^2 + a_2 x_{1_A}^4 + a_3 x_{1_A}^6, \\ \kappa(x_{1_B}) &= b_0 + b_1 x_{1_B}^2 + b_2 x_{1_B}^4 + b_3 x_{1_B}^6. \end{aligned} \quad (79)$$

Introducing the functions G_i^{ST}:

$$G_i^{ST}(y) = \sum_{j=0}^{3} y^{2j}\alpha_{ij}^{ST} \quad (80)$$

into the kernel K,

$$K^{ST}(x,y) = \sum_{i=0}^{3} x^{2i} G_i^{ST}(y), \quad (81)$$

we can derive the following algebraic equations for the coefficients a_i and b_i:

$$\begin{aligned} a_i &= \lambda^{AA}\int G_i^{AA} f^A(y) dy + \lambda^{AB}\int G_i^{AB} f^B(y) dy, \\ b_i &= \lambda^{BB}\int G_i^{BB} f^B(y) dy + \lambda^{BA}\int G_i^{AB} f^A(y) dy. \end{aligned} \quad (82)$$

Equations (82) together with normalization conditions

$$\int_0^1 e^{a_0 + a_1 x_{1A}^2 + a_2 x_{1A}^4 + a_3 x_{1A}^6} dx_{1A} = 1, \quad (83)$$

$$\int_0^1 e^{b_0 + a_1 x_{1B}^2 + b_2 x_{1B}^4 + b_3 x_{1B}^6} dx_{1B} = 1 \quad (84)$$

determine completely the distribution functions. Coefficients a_i and b_i can be treated as the order parameters.

The connection of them with the traditional order parameters defined by the Legendre polynomials are the following:

$$a_i = \lambda_{AA} \sum_{j=0}^{3} \alpha_{ij}^{AA} \langle y^{2j} \rangle_A + \lambda_{AB} \sum_{j=0}^{3} \alpha_{ij}^{AB} \langle y^{2j} \rangle_B, \quad (85)$$

$$b_i = \lambda_{BB} \sum_{j=0}^{3} \alpha_{ij}^{BB} \langle y^{2j} \rangle_B + \lambda_{BA} \sum_{j=0}^{3} \alpha_{ij}^{BA} \langle y^{2j} \rangle_A, \quad (86)$$

where $y = \cos\theta$, $\langle y^{2j} \rangle = \int y^{2j} f(y) dy$, and

$$\begin{aligned} \langle y^2 \rangle &= \frac{1}{2}(1 + 2\langle P_2 \rangle), \\ \langle y^4 \rangle &= \frac{1}{35}(7 + 20\langle P_2 \rangle + 8\langle P_4 \rangle), \quad (87) \\ \langle y^6 \rangle &= \frac{1}{231}(33 + 110\langle P_2 \rangle + 72\langle P_4 \rangle + 16\langle P_6 \rangle). \end{aligned}$$

X. MICROSCOPIC EXPRESSIONS FOR THE PRESSURE AND CHEMICAL POTENTIALS

The expression for the free energy (29) can be rewritten in the form

$$\begin{aligned} \beta \mathcal{F} = {} & N_A \ln\left(\frac{N_A}{4\pi V}\right) - N_A + N_B \ln\left(\frac{N_B}{4\pi V}\right) - N_B + N_A \int_0^1 f(x_A) \ln[f(x_A] dx_A + N_B \int_0^1 f(x_B) \ln[f(x_B] dx_B \\ & - \frac{1}{2V} N_A^2 \tilde{\lambda}^{AA} \int_0^1 K(x_A, y_A) f(x_A) f(y_A) dx_A dy_A - \frac{1}{2V} N_B^2 \tilde{\lambda}^{BB} \int_0^1 K(x_B, y_B) f(x_B) f(y_B) dx_B dy_B \\ & - \frac{1}{V} N_A N_B \tilde{\lambda}^{AB} \int_0^1 K(x_A, y_B) f(x_A) f(y_B) dx_A dy_B, \end{aligned} \quad (88)$$

where $\tilde{\lambda}^{ST} = \lambda^{ST}/d_S$.

From that it is easy to find molecular expressions for the chemical potentials and pressure:

$$\begin{aligned} \beta \mu_A = \frac{\partial \beta \mathcal{F}}{\partial N_A} = {} & \ln\left(\frac{N_A}{4\pi V}\right) + \int_0^1 \ln[f(x_A)] f(x_A) dx_A - \frac{N_A}{V} \tilde{\lambda}^{AA} \int_0^1 K(x_A, y_A) f(x_A) f(y_A) dy_B dx_A \\ & - \frac{N_B}{V} \tilde{\lambda}^{AB} \int_0^1 K(x_A, y_B) f(x_A) f(y_B) dy_B dx_A, \end{aligned} \quad (89)$$

$$\begin{aligned} \beta \mu_B = \frac{\partial \beta \mathcal{F}}{\partial N_B} = {} & \ln\left(\frac{N_B}{4\pi V}\right) + \int_0^1 f(x_B) \ln[f(x_B] dx_B - \frac{N_B}{V} \tilde{\lambda}^{BB} \int_0^1 K(x_B, y_B) f(y_B) f(x_B) dy_A dx_B \\ & - \frac{N_A}{V} \tilde{\lambda}^{AB} \int_0^1 K(x_A, y_B) f(y_A) f(x_B) dy_A dx_B, \end{aligned} \quad (90)$$

$$\begin{aligned} \beta p = -\frac{\partial \beta \mathcal{F}}{\partial V} = {} & \frac{N_A}{V} + \frac{N_B}{V} - \frac{1}{2V^2} N_A^2 \lambda^{\tilde{A}A} \int_0^1 K(x_A, y_A) f(x_A) f(y_A) dx_A dy_A \\ & - \frac{1}{2V^2} N_B^2 \lambda^{\tilde{B}B} \int_0^1 K(x_B, y_B) f(x_B) f(y_B) dx_B dy_B - \frac{1}{V^2} N_A N_B \lambda^{\tilde{A}B} \int_0^1 K(x_A, y_B) f(x_A) f(y_B) dx_A dy_B. \end{aligned} \quad (91)$$

Let us write the Gibbs-Duhem rule in the form chosen as follows:

$$V \frac{dp}{dN_A} - N_A \frac{d\mu_A}{dN_A} - N_B \frac{d\mu_B}{dN_A} = 0, \quad (92)$$

where we have divided the original form by dN_A in order to obtain terms with derivatives. Inserting the microscopic expressions (89)–(91) into (92) we notice that it becomes identity.

XI. CONCLUSIONS

In the present paper we have introduced a systematic derivation of the state equations for a nematic liquid crystal binary mixture. We have started from the Liouville equation for $(N_A + N_B)$-particle distribution function $F^{N_A N_B}$ which is generalized to the case with rotational degrees of freedom. By introducing reduced distribution functions $F^{S_A S_B}$ the BBGKY hierarchy of coupled equations for $F^{S_A S_B}$ for the mixture is obtained. From the analysis of the first equations of the BBGKY hierarchy in the equilibrium the set of two state equations is derived. The assumption that the two-particle correlation function is of the form $e^{-\beta U_{12}}$, where U_{12} is the interaction potential, leads to the second virial expansion for the free energy which contains the direct correlation function having the form of the Meyer function.

The realistic intermolecular potential of a Ruijgrok type is applied to the theory. It has been shown that such a theoretical model can be easily solved. The resulting solutions for the single-particle distribution function have exponential form with the sixth order polynomial of the order parameters. The single distribution functions carry all necessary information about the system. By using of them we can obtain a number of static properties of the system such as order parameters, phase transition temperature, elastic constants, and viscosity coefficients.

Besides the knowledge of the potential for molecules of the same sort the presented way of solving the state equations also requires knowledge of the potential for two *different* molecules. Usually such a potential is assumed separately. We have proposed the special form which emerges directly from the form of the potential for the molecules of the same kind which makes our theory more realistic and consistent.

The microscopic state equations allow us to reconstruct a thermodynamic potential which is in full agreement with other theories. Given the right form of the free energy we can formulate stability analysis in general form. *General* means taking into account the role of order parameters as freedom degrees in necessary and sufficient stability conditions.

We briefly discuss all types of possible solutions for the binary mixture. We pay special attention to the case of spontaneously broken symmetry when the phase separation is a more preferred state than the homogeneous one. We test consistency between thermodynamic and statistical approaches by using the Gibbs-Duhem relation.

We would like to emphasize that, to our knowledge, so far nobody has considered the influence of order parameters on the sufficient stability conditions. It may happen that all the leading minors containing derivatives with respect to N_A and N_B are positively determined whereas at least one minor containing the derivative with respect to an order parameter is not positively determined. Such a situation would correspond to the unstable solution.

The classical theory proceeds by postulating a continuous variation of the leading minors,

$$\left|\frac{\partial^2\mathcal{A}}{\partial X_i \partial X_j}\right| \tag{93}$$

(where $X, Y = T, V, N_A, N_B$) from stable states, where they take on positive values, to unstable states, where at least one of them takes on negative values. These two regions are separated by the limits of stability, the so called "spinodal curve." The critical phase is a stable one lying on the spinodal curve.

Our general approach allows us to consider spinodals determined by the conditions including derivatives both with respect to concentrations and order parameters:

$$\left|\frac{\partial^2\mathcal{A}}{\partial X_i \partial X_j}\right| = 0, \tag{94}$$

where $X_i = T, V, N_A, N_B, a_i, b_i$.

Therefore there are possible different types of spinodals corresponding to different types of vanishing minors. Also in [20] we investigate spinodals of different ranks determined by the number of vanishing minors.

To sum up we would like to remark that this paper contains complete theory to provide statistical analysis.

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APPENDIX A

The terms containing order parameters which appear in the free energy ($d\mathcal{A}$) are the following:

$$\begin{aligned}\frac{\partial\mathcal{A}}{\partial a_i} &= \left(\frac{\partial\mathcal{F}}{\partial a_i} - \lambda_A N_A \int \frac{\partial f(x)}{\partial a_i} dx\right)\\ &= N_A \int \frac{\partial f(x)}{\partial a_i}\left[\ln\left(\frac{N_A}{4\pi V}\right) + \ln[f(x_A)] - \lambda^{AA}\int K^{AA}(x_A, y_A) f(y_A) dy_A - \lambda^{BA}\int K^{AB}(x_A, y_B) f(y_B) dy_B - \lambda_A\right]\end{aligned} \tag{A1}$$

and

$$\begin{aligned}\frac{\partial\mathcal{A}}{\partial b_i} &= \left(\frac{\partial\mathcal{F}}{\partial b_i} - \lambda_B N_B \int \frac{\partial f(x)}{\partial b_i} dx\right)\\ &= N_B \int \frac{\partial f(x)}{\partial b_i}\left[\ln\left(\frac{N_B}{4\pi V}\right) + \ln[f(x_B)] - \lambda^{BB}\int K^{BB}(x_B, y_B) f(y_B) dy_B\right.\\ &\quad \left. -\lambda^{AB}\int K^{AB}(x_A, y_B) f(y_A) dy_A - \lambda_B\right].\end{aligned} \tag{A2}$$

The necessary condition states that the above integrals must vanish, which means that the expressions in parentheses are zero, which reconstructs exactly the state equations (25) and (26). That means that the following conditions are equivalent:

$$\frac{\delta \mathcal{A}}{\delta \rho_A} = 0, \qquad \frac{\delta \mathcal{A}}{\delta \rho_B} = 0, \tag{A3}$$

and

$$\frac{\partial \mathcal{A}}{\partial a_i} = 0, \qquad \frac{\partial \mathcal{A}}{\partial b_i} = 0, \tag{A4}$$

where $i = 1, 2, 3$.

APPENDIX B

The Lennard-Jones potential $U(x)$ is strongly repulsive for $x < 1$. Setting $r = \sigma$ (that is $x = 1$) in U we obtained the $U = 0$ equipotential surface. The surface depends on relative orientation of the interacting molecules. As the potential $U(x)$ rapidly increases for x decreasing from $x = 1$ to zero, we assume that the equipotential surface $U(x) = 0$ defines the excluded volume.

If we consider the closest approach of two molecules described by S_1^{ST}, S_2^{ST}, and S_3^{ST} for which we choose the point when potential U_{12} is equal zero ($r = \sigma$) we obtain equipotential surfaces described by the following equations:

$$\frac{r}{\sigma_0^{ST}} = 1 + S_1^{ST} \cos^2 \theta + S_{11}^{ST} \cos^2 \theta - S_2^{ST} + S_3^{ST} \cos^4 \theta \tag{B1}$$

in the case when molecules are parallel to each other ($\vec{n}_1$ and $\vec{n}_2$ parallel to the z axis) and

$$\frac{r}{\sigma_0^{ST}} = 1 + S_1^{ST} \cos^2 \theta + S_{11}^{ST} \sin^2 \theta + S_3^{ST} \cos^2 \theta \sin^2 \theta \tag{B2}$$

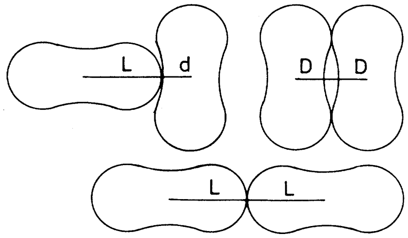

FIG. 2. Characteristic relative orientations of molecules for calculation of the potential parameters.

in the case when molecules are perpendicular ($\vec{n}_1$ parallel and $\vec{n}_2$ perpendicular to the z axis), where θ is the angle between $\vec{\Delta}$ and the positive direction of the z axis.

On the other hand we can express the closest approach in terms of geometrical parameters such as length and width. From Fig. 2 we can see that it is possible to attribute to the equipotential surface three characteristic parameters: width D, width d, and length L. Setting $\theta = \pi/2$ and $r = D$ in Eq. (B1) we obtain

$$D = \sigma_0^S \left(\frac{1 - S_2^S}{2} \right) \tag{B3}$$

whereas setting $\theta = 0$ and $r = L$ we obtain

$$L = \sigma_0^S \left(\frac{1 + 2S_1^S - S_2^S + S_3^S}{2} \right). \tag{B4}$$

Setting $\theta = \pi/2$ and $r = (L + d)/2$ in Eq. (B2) we obtain

$$d = \sigma_0^S \left(\frac{1 + S_2^S - S_3^S}{2} \right). \tag{B5}$$

Analyzing geometrical configurations (Fig. 2) for two different molecules whose equipotential surfaces are characterized by $L^A, D^A, d^A, L^B, D^B, d^B$ and by the use of conditions (B1) and (B2) we can derive expressions (64)–(68) for $S_1^{AB}, S_{11}^{AB} S_2^{AB}, S_3^{AB}$. These expressions should be in agreement with the requirement that vanishing of parameters S_i^A and S_i^B implicates vanishing of S_i^{AB}.

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