CALCULATION OF LONG-RANGE ORIENTATIONAL ORDER PARAMETERS IN IMPURE NEMATIC LIQUID CRYSTALS USING AN EXTENDED VAN DER WAALS MODEL

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For the extended van der Waals model of a binary nematic system consisting of rigid biaxial molecules, we consider the following properties: the relation between the orientational order parameters of a nematic liquid crystal (NLC) $S^{(1)}$ and a nonmesomorphic impurity $S^{(2)}$, the relation between $S^{(2)}$ and the biaxiality parameter $D^{(2)}$ of the impurity, and the lowered clearing temperature of NLC upon dissolution of the nonmesogen. The dependence of these characteristics on the form and size of component molecules and the intermolecular attraction potential is analyzed. The model reproduces the experimental dependence of $S^{(2)}$ and $D^{(2)}$ on temperature and structure of the nematic matrix.

Experimental and theoretical studies of binary and impure systems containing NLC are stimulated by application of these materials in optical electronics, thermography, gas liquid chromatography, and as laser media [1-3]. A special role is played by binary systems containing NLC (a nematic matrix) along with a small amount of a nonmesomorphic component (an impurity). For data processing and displaying devices using impure NLC, important characteristics are the absolute value of $S^{(2)}$ of the impurity molecules, the temperature dependence of $S^{(2)}$, and the relation between the order parameters of NLC and the impurity.

In NMR, ESR, IR, and UV studies of impure NLC, the goal is to establish the relationship between the thermodynamic, optical, and structural properties of NLC and the chemical structure of molecules, as well as peculiarities of intermolecular interaction. Typically a certain aspect of the problem is investigated, for example, the anisotropy of the attraction forces, anisometricity of molecules, or the conformation transformations. Interpretation of experimental data is considerably easier for systems with a low content of the impurity; thus we can avoid the calculation of interaction between the impurity molecules.

Experimental data on the order parameters of components are most frequently analyzed in terms of the medium field Maier-Saupe theory [4-7]. For molecules having no axial symmetry, an extension of this theory to biaxial molecular systems suggested in [8-11] is used. This approach involves investigation of the relation between the order matrix components and parameters of the self-consistent potential for NLC and impurities of different chemical nature, including dyes [10-13]. However, this method does not explicitly allow for the anisotropy of the repulsion forces, which are essential in stabilizing the long-range orientational order [14-17].

Another approach to analyzing the properties of a nematic system uses an extended van der Waals model [16-19] allowing the self-consistent calculation of repulsive and attractive interactions. In the present paper this approach is employed to calculate the order parameters of NLC and impurities in a wide temperature range and to discuss the existing experimental and theoretical dependences. We give data for the nematic-isotropic phase transition ($N$–$I$ PT) for individual NLC, and also data on PT temperature variation upon dissolution of the impurity. The concurrent use of these characteristics expands the potential of a statistical thermodynamic description and allows us to judge about its applicability. The van der Waals model extended to biaxial molecule mixtures was earlier applied in [19] for the analysis of the state diagrams of nematic systems.


MODEL DESCRIPTION

Let us use the van der Waals model in the form applicable to the mixture of biaxial molecules [18, 19]. As a basic system we chose the fluid \( \{N_l\} \) (\( l \) is the index of the component) of rigid molecules having the form of a parallelepiped. In the general case this is a system of species of \( D_{2h} \) symmetry with volume \( v_l \) and dimensions \( A_1 \times A_2 \times A_3 \times a^3 \), where \( a \) is the dimensional length unit.

Let the unit vectors \( \mathbf{e}_{1l}, \mathbf{e}_{2l}, \mathbf{e}_{3l} \) of a molecular coordinate system be directed along the edges \( A_{1l}, A_{2l}, A_{3l} \) of the parallelepiped. As the prevailing orientational (director) axis we choose the \( Z \) axis of the laboratory coordinate system. The orientational order parameters of the component \( l \) in a uniaxial nematic phase are the diagonal elements of the Saupe matrix [20]

\[
S_{ii}^{(l)} = \frac{1}{2} \left\langle 3 \cos^2 \left( Z \hat{\mathbf{e}}_{il} \right) - 1 \right\rangle, \quad i = 1, 2, 3, \tag{1}
\]

where the angular brackets denote the ensemble averaged value.

Since \( \sum_{i=1}^{3} S_{ii}^{(l)} = 0 \), the orientational order of biaxial molecules of type \( l \) is described by two independent values: the parameter \( S^{(l)} = S_{11}^{(l)} \) defining the average orientation degree of \( \mathbf{e}_{il} \) relative to \( Z \) and the biaxiality parameter \( D^{(l)} = S_{22}^{(l)} - S_{33}^{(l)} \) specifying an average projection of the transverse axes \( \mathbf{e}_2, \mathbf{e}_3 \) on \( Z \).

Assume the distribution of molecular axes is discrete, which will essentially simplify the statistical thermodynamic calculations. Let the molecule of \( D_{2h} \) symmetry have a set \( \{\alpha\} \) of six different orientations enumerated in such a way that \( \alpha = 2i - 1, 2i, i = 1, 2, 3 \) if \( |Z \cdot \mathbf{e}_i| = 1 \). We introduce the fraction \( s_{\alpha l} = N_{\alpha l}/N_l \) of species of type \( l \) with orientation \( \alpha \). From (1) we have

\[
S_{\alpha\alpha}^{(l)} = 3s_{2\alpha l} - \frac{1}{2}, \quad \alpha = 1, 2, 3, \tag{2}
\]

since, due to the uniaxial symmetry of the phase on the whole,

\[
s_{1l} = s_{2l}, \quad s_{3l} = s_{4l}, \quad s_{5l} = s_{6l}. \tag{3}
\]

By (2), for \( D^{(l)} \) we have

\[
D^{(l)} = 3 (s_{3l} - s_{5l}). \tag{4}
\]

Let us establish the relation of thermodynamic properties and order parameters of impure NLC with geometrical characteristics of molecules and the intermolecular attraction parameters. From the free Helmholtz energy \( F \) we determine the chemical potentials of molecules of type \( l \) with orientation \( \alpha \) as follows:

\[
\mu_{\alpha l} = \left( \frac{\partial F}{\partial N_{\alpha l}} \right)_{T, V, N_{\alpha}, N_{\beta}}.
\]

With an equilibrium in the orientational distribution of molecules,

\[
\mu_{\alpha l} = \mu_l, \quad \alpha = 1, ..., 6, \tag{5}
\]

where \( \mu_l \) is the chemical potential per \( l \)-species determined by the conventional procedure.

By virtue of (3), there are 4 independent equations (5) for the binary system of biaxial molecules. In the van der Waals model the chemical potential \( \mu_{\alpha l} \) is represented as a sum

\[
\mu_{\alpha l} = \mu_{\alpha l}^{(l)} + \mu_{\alpha l}^{(a)},
\]

where \( \mu_{\alpha l}^{(l)} \) is determined by the properties of a basic system of sterically interacting molecules and \( \mu_{\alpha l}^{(a)} \) denotes the contribution of the intermolecular attraction forces averaged by steric interactions.