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Molecular origin of the heterogeneity in the nematic and smectic liquid crystals: Elastic constants, gradients of order parameters, and visualization of small objects

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The formation of heterogeneous nematic and smectic liquid crystals in the general case of an arbitrary geometry is investigated in the framework of molecular-statistical approach [Emelyanenko and Khokhlov, J. Chem. Phys. **142**, 204905 (2015)]. The molecular aspects of the orientational and translational orderings at the curved surfaces of small solid objects dispersed in liquid crystal are considered, and the differential equations for gradients of the order parameters in vicinities of the small objects are presented in the general form. The five elastic constants are obtained within the same approach, from which we were able to predict that a significant space variations of the order parameters can be observed within the 0.5–0.8 μm area *around* any small object, almost independently of its own dimension. Therefore, the liquid crystals can be a simple tool for the optical visualization of nano-objects. It is also demonstrated that the kind of molecular self-organization (smectic, nematic or conventionally isotropic) at the surfaces of small solid objects can be different from that in the bulk of mesogenic material. Totally we predict eight various combinations of simple states at the surfaces and in the bulk depending on the solid objects' size and temperature. It is also shown that the surfaces of 10 μm-size solid objects and larger act almost as flat surfaces, while the surfaces of 1 μm-size solid objects and smaller act almost as point defects.

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I. INTRODUCTION

One of the most important trends in development of science today is the creation of new materials that can be applied for the recognition of the micron and submicron objects in various liquids or at the surfaces of solids. The submicron objects, even in a minor quantity being present in the natural or artificial functional materials, are often capable either of the enhancement of the principle materials' functions or, vice versa, of worsening.

Topological defects in the liquid crystals are frequently used as the converters of the optical modes of the light beams [1]. This is important for the formation, the so-called, optical vortices and other vector beams, which can be used in the microscopy, nanotechnologies, quantum optics, and information technologies [2–4]. The microparticles with the specified boundary conditions, incorporated into the liquid-crystal matrix, can create different topological structures. The films of nematic liquid crystals containing the nano- and microparticles, are the composite systems, which can be used for the electro-, thermo-, or photoinduced modulation of the light [5]. The suspensions of ferromagnetic or ferroelectric nanoparticles in liquid crystals make the LC's highly sensible to the electric and magnetic fields [6]. A small amount of ferroelectric nanoparticles is known to reorient and hold liquid crystal (LC) molecules in a direction of the orientation of nanoparticles even when an external electric field attempts to orient a liquid crystal in an orthogonal direction [7]. The variable surface anchoring between LC and particles distributed inside makes it possible to use these materials for the detection of impurities [8]. Addition of the nano- and of microparticles into the liquid crystals leads to a change in their viscous and elastic properties [9], and it also improves their luminescent properties [10], that is important for the modern display technologies [11] and other optoelectronic and photonic applications. The use of photosensitive surfactant, adsorbed onto the LC–liquid border, makes it possible to manipulate by the location of particles in the space [12,13].

At the same time, it is known that the occasional micro- and submicron objects can cause the short circuits or destructions of other kinds both in the household devices (displays, solar cells) and in the unique and expensive instruments, utilized in medicine, aviation, power engineering, other areas of human activity, which require the reliable work of different devices. Anyway, it is important, by simple methods and without the loss of time, to recognize the presence and quantity of various micron or submicron objects in different functional materials, and also to know how to manipulate by their positions (or distributions) inside the functional material.

At present, there are no any theories describing the molecular origin of the order parameters variation in the confined geometries. Meanwhile, these variations appear to be intimately related to the elastic constants, because they all originate from the same molecular properties. Our estimations show that in the diameter of 0.5–0.8 μm around the defects or nano- or micro-object related to them, the specific areas with the lowered orientational order parameter arise. Thus, theoretically, these areas themselves can be visible in the optical microscope, even if the nano-objects are located in

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the centers of defects or in the absence of any objects in the centers of defects (but the defects themselves in these cases are realized because of the symmetry of the surrounding structure). Therefore, it is very important to formulate a general molecular approach capable of prediction of the deformed LC structures in various phases, in particular, the elastic constants and the distribution of the orientational and translational order parameters in the space.

Nematic liquid crystals [14] (including chiral or differently deformed nematics [15–18]) are the anisotropic substances, in which the long molecular axes have predominant orientation (locally predominant—in the case when deformation is present), which is called the director (local director). In contrast to the solid crystals, the positions of molecules have no any preference. In other words, the nematic materials have a long-range orientational order (much longer than the range of director deformation), but the long-range translational ordering is absent.

Smectic liquid crystals are the layered structures, in which the translational motion of molecules between the smectic layers is hindered, but there exists a freedom of motion within each two-dimensional layer. The surfaces of all smectic layers are parallel to each other (or locally parallel). The molecules within each smectic layer have a predominant orientation, which is also called the director (local director). Several kinds of smectic phases are known. For example, in the orthogonal smectic Sm-*A* phase the director is parallel to the smectic layer normal in each smectic layer, and therefore the structure of Sm-*A* is optically uniaxial; no spontaneous polarization arises. Many tilted smectic phases are also known, in which the director is not parallel to the smectic layer normal. Tilted smectic phases are mostly known for their ferroelectric properties [19,20]. The anticlinic antiferroelectric phases, and several intermediate phases were discovered in Refs. [21,22]. Some lactic acid derivatives [23,24] are known to possess the reentrant properties (either orthogonal or the ferroelectric phase reappears at lower temperatures) [25–29]. Theoretical investigation of various ferroelectric and antiferroelectric phases was done, for example, in Refs. [30–39].

In Ref. [40] the original translational order parameters were introduces for the smectic materials. In the present paper we are going to take into account the director deformations and the order parameters' gradients. Recently the double nematic-isotropic phase transition was observed [41] and explained theoretically [42]. The one of the transitions was related to the surface and another one was related to the bulk of LC. It was shown that the orientational order parameter is larger at a flat solid surface than in the bulk of LC, and there exists a specific temperature range, at which the orientational order can be observed only near the surface, while apart from the surface the isotropic phase should be observed. Later it was shown [43,44] that, at the curved surfaces, the situation can be opposite because of the deformation of director field, and, as a result, there can exist a specific temperature range, when the orientational order is observed only apart from the surface. Quite recently it was shown that the addition of nanosized fluorinated graphene [45] and shungite carbon [46] affects the phase transition temperatures of mesogenic materials and reduces the nematic-isotropic transition temperature.

Here we present the generalization of our approach to the description of both translational and orientational orderings in a liquid crystal media in the presence of an arbitrary deformation. We are going to follow the idea that smectic layering is similar to the microphase separation in polymers [47–51]. In particular, we demonstrate that there can exist a specific temperature range, at which the translational order can be observed either near the solid surface or apart from the surface depending on the surface curvature. The importance of theoretical consideration of the distorted smectic and nematic substances is well understood from the appearance of new LC phases [52–55] in the presence of director deformation, which cannot be observed in the homogeneous state of LC. This question, however, requires additional consideration. At the same time, any deformed structure of LC can be evolved (or adapted) from basic equations written in the present paper. In addition, we are going to show, how a simple deformed structure can be evolved from the general formulas.

II. STATISTICAL DISTRIBUTIONS OF THE ELONGATED MOLECULES OVER THEIR POSITIONS AND ORIENTATIONS IN THE GENERAL CASE OF AN ARBITRARY GEOMETRY OF A LIQUID CRYSTAL

A. Molecular model

Let us consider the inhomogeneous system of uniaxial elongated molecules having orientational local distribution function $f\{(\mathbf{a}\cdot\mathbf{n}(\mathbf{r})),\mathbf{r}\}$ of their long axes $\mathbf{a}$ with respect to the local nematic director $\mathbf{n}(\mathbf{r})$. In the general case let us assume that molecular concentration distribution $\rho(\mathbf{r})$ is also inhomogeneous. For simplicity let us assume that there is no *direct* correlation between the concentration distribution $\rho(\mathbf{r})$ and the orientational distribution function $f\{(\mathbf{a}\cdot\mathbf{n}(\mathbf{r})),\mathbf{r}\}$. In Ref. [40] the original translational order parameters were introduced for the smectic materials. In the present paper we are going to take into account the director deformations, and therefore the definitions for both the local orientational order parameter and the local translational order parameters will be based on the director $\mathbf{n}_1$ at point 1, where the test molecule (molecule 1), affected by the mean molecular field, is located (see Figs. 1 and 2). As a measure of the orientational ordering one can use the local average Legendre polynomials:

$$S_m(\mathbf{r}_1)\equiv\int f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]P_m(\mathbf{a}_1\cdot\mathbf{n}_1)d^2\mathbf{a}_1, \qquad (1)$$

where $\mathbf{a}_1$ is the orientation of molecule 1 and $\mathbf{r}_1$ denotes the position of molecule 1. In the same manner, let us introduce the local translational order parameters:

$$\sigma_m(\mathbf{r}_1)\equiv V_0\int\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]P_m(\mathbf{u}_{12}\cdot\mathbf{n}_1)d^2\mathbf{u}_{12}, \qquad (2)$$

where $\mathbf{u}_{12}$ is the unit intermolecular vector between the test molecule 1 and a molecule 2 belonging to the surrounding of molecule 1 and participating in the mean molecular field acting on molecule 1. Integration in Eq. (2) is done over the surface of the elementary volume V_0 characteristic to any incompressible media. Here we define the elementary volume as the volume occupied by molecule 1 itself and its nearest surrounding molecules (see discussion below).

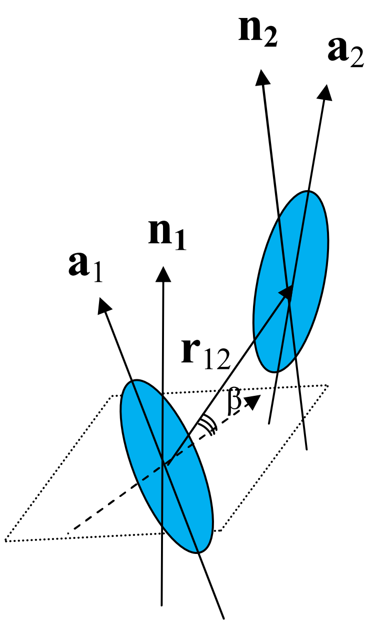

FIG. 1. Pair of neighboring molecules in the inhomogeneous LC (nematic or smectic). The plane perpendicular to director $\mathbf{n}_1$ is shown by dotted line. The projection of intermolecular vector $\mathbf{r}_{12}$ on this plane is shown by dash arrow. Angle β is the angle between $\mathbf{r}_{12}$ and its projection on the plane mentioned above.

Let us introduce the shift angle β between the plane, which is perpendicular to director $\mathbf{n}_1$, and the intermolecular vector $\mathbf{u}_{12}$ (see Fig. 1). Then one can write $\sin\beta = (\mathbf{u}_{12}\cdot\mathbf{n}_1)$, and, in correspondence with definition Eq. (2), the average second and fourth powers of $\sin\beta$ can be written as follows:

$$\langle\sin^2\beta\rangle = \frac{2}{3}\frac{\sigma_2}{\sigma_0} + \frac{1}{3},$$
$$\langle\sin^4\beta\rangle = \frac{8}{35}\frac{\sigma_4}{\sigma_0} + \frac{4}{7}\frac{\sigma_2}{\sigma_0} + \frac{1}{5}. \tag{3}$$

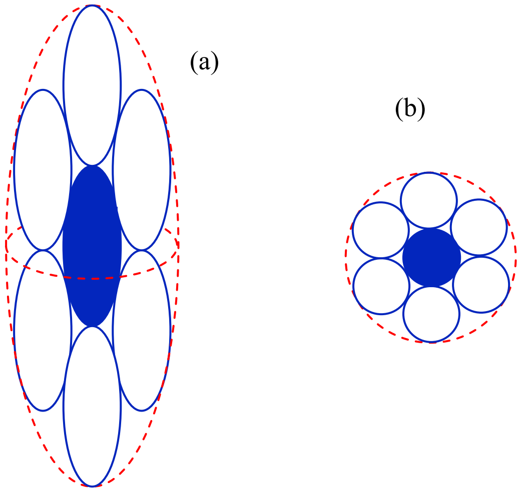

FIG. 2. Model of a liquid crystal molecule (solid ellipsoid) and its nearest surrounding: side view (a) and top view (b). The surrounding molecules are shown by empty ellipsoids. The contours of the whole nearest surrounding are shown by dash lines.

As a measure of the smectic layering we introduce [40] the expected value of the squared deviation from the mean $\sin^2\beta$ (the variance):

$$\begin{aligned}\mathrm{Var}(\sin^2\beta) &\equiv \langle(\sin^2\beta - \langle\sin^2\beta\rangle)^2\rangle\\ &= \langle\sin^4\beta\rangle - \langle\sin^2\beta\rangle^2 = -\frac{4}{9}\left(\frac{\sigma_2}{\sigma_0}-1\right)^2\\ &\quad -\frac{16}{21}\left(\frac{\sigma_2}{\sigma_0}-1\right) + \frac{8}{35}\left(\frac{\sigma_4}{\sigma_0}-1\right),\end{aligned} \tag{4}$$

which should tend to zero at perfect smectic ordering (in both the orthogonal and the tilted smectic phases).

B. Free energy of a liquid crystal having the orientational and translational correlations between molecules

Let us apply the Maier-Saupe mean-field theory [56,57] for the description of both nematic and smectic states with the presence of director deformation and the order parameter gradients. The free energy of the molecular system generalized for the case of inhomogeneous liquid crystals (both nematic and smectic) can be written in the following form:

$$\begin{aligned}F &= k_BT\iint d^3\mathbf{r}_1 d^2\mathbf{a}_1\rho(\mathbf{r}_1)f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\\ &\quad\times\ln\{\rho(\mathbf{r}_1)f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\}\\ &\quad+\frac{1}{2}\iiiint d^3\mathbf{r}_1 d^2\mathbf{a}_1 d^3\mathbf{r}_2 d^2\mathbf{a}_2\rho(\mathbf{r}_1)f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\\ &\quad\times\rho(\mathbf{r}_2)f[(\mathbf{a}_2\cdot\mathbf{n}_2),\mathbf{r}_2]U^{\mathrm{ef}}_{12}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}),\end{aligned} \tag{5}$$

where $\mathbf{r}_i$ $(i = 1, 2)$ are the coordinates of points 1 and 2, where molecules 1 and 2 are located, $\mathbf{r}_{12}$ is the vector connecting points 1 and 2, k_B is the Boltzmann constant, T is the temperature, $U^{\mathrm{ef}}_{12}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})$ is the effective pair interaction potential for two molecules with long axes $\mathbf{a}_1$ and $\mathbf{a}_2$ located at points 1 and 2, respectively, while $\mathbf{n}_1$ is the director at point 1 and $\mathbf{n}_2$ is the director at point 2. The first term in Eq. (5) is the entropy, and the second term is the internal energy. At any point $\mathbf{r}$ the orientational distribution function $f[(\mathbf{a}\cdot\mathbf{n}),\mathbf{r}]$ in Eq. (5) satisfies the normalizing constraint:

$$\int d^2\mathbf{a}f\{(\mathbf{a}\cdot\mathbf{n}(\mathbf{r})),\mathbf{r}\} = 1. \tag{6}$$

Substituting constraint Eq. (6) into Eq. (5) one can write the free-energy density in the vicinity of point 1 in the following form:

$$\begin{aligned}\left.\frac{\partial F}{\partial V}\right|_{\mathbf{r}=\mathbf{r}_1} &= k_BT\rho(\mathbf{r}_1)\ln\rho(\mathbf{r}_1) + k_BT\rho(\mathbf{r}_1)\\ &\quad\times\int d^2\mathbf{a}f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\ln f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\\ &\quad+\frac{1}{2}\rho(\mathbf{r}_1)\iiint d^3\mathbf{r}_{12}d^2\mathbf{a}_1 d^2\mathbf{a}_2\rho(\mathbf{r}_2)\\ &\quad\times f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]f[(\mathbf{a}_2\cdot\mathbf{n}_2),\mathbf{r}_{12}]U^{\mathrm{ef}}_{12}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}),\end{aligned} \tag{7}$$

where location 2 is now counted from location 1. To obtain the normalizing constraint for concentration $\rho(\mathbf{r})$, and then to separate functions $\rho(\mathbf{r})$ and $f[(\mathbf{a}\cdot\mathbf{n}),\mathbf{r}]$ in the free energy Eq. (7), let us take into account that the total average number of nearest neighbors of molecule 1 is constant in the condensed incompressible medium:

$$V_0\int d^2\mathbf{u}_{12}\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]=\sigma_0, \tag{8}$$

where V_0 is the average elementary volume occupied by some molecule 1 and all its nearest neighbors, vector $\mathbf{u}_{12}$ is the unit vector between molecule 1 and its nearest neighbor 2 counted from director $\mathbf{n}_1$ for simplicity, $\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]$ is the concentration of neighboring molecules at the surface of contact with molecule 1, and parameter σ_0 is the average number of the nearest neighbors. Taking into account that all averages and densities use the elementary volume as a minimal space that cannot be split furthermore without violation of the local uniformity, but, on the other hand, the V_0 volume is sufficiently large for determination of all local averages and densities (before consideration of the director deformation and gradients of the order parameters), let us change over from $\rho(\mathbf{r}_1)$ in Eq. (7) to its average Eq. (8) by integrating Eq. (7) with respect to $\mathbf{r}_1$ assuming that molecule 1 is the neighbor of some other molecule (let us say, molecule 0). Taking into account that, totally, in the same manner, the energy density Eq. (7) can be integrated within the same spaces around σ_0 different molecules with the same result of integration, one should divide the result of integration by σ_0 to obtain the free energy $V_0\partial F/\partial V$ per volume V_0:

$$\begin{aligned}4\pi\sigma_0V_0\left.\frac{\partial F}{\partial V}\right|_{\mathbf{r}=\mathbf{r}_1} &= k_BT\int d^2\mathbf{u}_{12}\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]V_0\ln\{\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]V_0\}+k_BT\sigma_0\int d^2\mathbf{a}_1 f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\ln f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\\ &\quad+\frac{1}{2}\sigma_0\iint d^2\mathbf{u}_{12}d^2\mathbf{a}_1\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\int d^2\mathbf{a}_2\int dr_{12}r_{12}^2 f[(\mathbf{a}_2\cdot\mathbf{n}_2),\mathbf{r}_2]U_{12}^{\text{ef}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}),\end{aligned} \tag{9}$$

where in the second and third terms we have taken into account the normalizing constraint Eq. (8). Minimizing the free energy Eq. (9) independently with respect to orientational distribution function $f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]$ and concentration distribution $\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]$ under constraint Eqs. (6) and (8), one obtains the following set of equations:

$$\begin{aligned}f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]&=\frac{1}{I_0^f(\mathbf{r}_1)}\exp\left\{-\frac{U_{\text{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]}{k_BT}\right\},\\ \rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]&=\frac{\sigma_0}{V_0}\frac{1}{I_0^\rho(\mathbf{r}_1)}\exp\left\{-\frac{U_{\text{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]}{k_BT}\right\},\end{aligned} \tag{10}$$

where $U_{\text{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]$ is the mean—over all locations $\mathbf{r}_{12}$ and all orientations $\mathbf{a}_2$ of the second molecule—molecular field acting on molecule 1 located at point $\mathbf{r}_1$ and having orientation $\mathbf{a}_1$ of its long axis:

$$U_{\text{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\equiv\int d^2\mathbf{u}_{12}\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]\int d^2\mathbf{a}_2\int dr_{12}r_{12}^2 f[(\mathbf{a}_2\cdot\mathbf{n}_2),\mathbf{r}_2]U_{12}^{\text{ef}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}), \tag{11}$$

and correlation function $U_{\text{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]$ is the average over all orientations of molecules 1 and 2 interaction between them at orientation $\mathbf{u}_{12}$ of the intermolecular vector:

$$U_{\text{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]\equiv\frac{1}{2}\frac{\sigma_0}{V_0}\int d^2\mathbf{a}_1 f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]\int d^2\mathbf{a}_2\int dr_{12}r_{12}^2 f[(\mathbf{a}_2\cdot\mathbf{n}_2),\mathbf{r}_2]U_{12}^{\text{ef}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}), \tag{12}$$

while integrals $I_m^f(\mathbf{r}_1)$ and $I_m^\rho(\mathbf{r}_1)$ [including the normalizing integrals $I_0^f(\mathbf{r}_1)$ and $I_0^\rho(\mathbf{r}_1)$ in Eq. (10)] are defined as follows:

$$\begin{aligned}I_m^f(\mathbf{r}_1)&=\int P_m(\mathbf{a}_1\cdot\mathbf{n}_1)\exp\left\{-\frac{U_{\text{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]}{k_BT}\right\}d^2\mathbf{a}_1,\\ I_m^\rho(\mathbf{r}_1)&=\int P_m(\mathbf{u}_{12}\cdot\mathbf{n}_1)\exp\left\{-\frac{U_{\text{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]}{k_BT}\right\}d^2\mathbf{u}_{12},\end{aligned} \tag{13}$$

where P_m is the mth Legendre polynomial. Then from Eq. (13), in particular, the recurrent equations for determination of the order parameters follow:

$$S_m(\mathbf{r})=\frac{I_m^f(\mathbf{r})}{I_0^f(\mathbf{r})},\qquad\frac{\sigma_m(\mathbf{r})}{\sigma_0}=\frac{I_m^\rho(\mathbf{r})}{I_0^\rho(\mathbf{r})}, \tag{14}$$

where σ_0 is constant. From analysis of Eqs. (11) and (12) it follows that at any point $\mathbf{r}_1$,

$$V_0\int d^2\mathbf{u}_{12}\rho((\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1)U_{\text{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]=\frac{1}{2}\sigma_0\int d^2\mathbf{a}_1 f((\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1)U_{\text{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]. \tag{15}$$

Taking this into account and substituting Eqs. (10)–(13) into Eq. (9), one obtains the following expression for the equilibrium free-energy density:

$$4\pi V_0 \frac{\partial F_{\mathrm{eq}}}{\partial V}\bigg|_{\mathbf{r}=\mathbf{r}_1} = -k_B T \ln I_0^{\rho}(\mathbf{r}_1) I_0^{f}(\mathbf{r}_1) - \int d^2\mathbf{a}_1 \times f[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1] U_{\mathrm{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1)], \quad (16)$$

where V_0 is the bulk of a molecule and its nearest surrounding. Approximately, the bulk of a molecule with its surrounding exceeds the bulk of the molecule itself tree times in each dimension, and totally 27 times in 3D space (see illustration in Fig. 2). In particular, for a molecule of cyanobiphenyl having 4.1×10^{-26} m^3 bulk, one obtains $V_0 \approx 1.1 \times 10^{-24}$ m^3.

C. Gradients of the mean field and of the correlation function

Let us approximate the effective intermolecular interaction $U_{12}^{\mathrm{ef}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})$ by spherical invariants $T_{\ell L\lambda}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2)$ [40,44]:

$$U_{12}^{\mathrm{ef}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}) = -\sum_{\ell,L,\lambda} J_{\ell L\lambda}(r_{12}) T_{\ell L\lambda}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2), \quad (17)$$

where we take into account the following few spherical invariants, which is enough for the description of inhomogeneous nematic and smectic states:

$$\begin{aligned}
T_{000}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2) &= 1,\\
T_{202}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2) &= P_2(\mathbf{a}_1\cdot\mathbf{a}_2) = \tfrac{3}{2}(\mathbf{a}_1\cdot\mathbf{a}_2)^2 - \tfrac{1}{2},\\
T_{404}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2) &= P_4(\mathbf{a}_1\cdot\mathbf{a}_2)\\
&= \tfrac{35}{8}(\mathbf{a}_1\cdot\mathbf{a}_2)^4 - \tfrac{15}{4}(\mathbf{a}_1\cdot\mathbf{a}_2)^2 + \tfrac{3}{8},\\
T_{222}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2) &= \tfrac{9}{2}(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12}) - \tfrac{3}{2}(\mathbf{a}_1\cdot\mathbf{a}_2)^2 - \tfrac{3}{2}(\mathbf{a}_1\cdot\mathbf{u}_{12})^2 - \tfrac{3}{2}(\mathbf{a}_2\cdot\mathbf{u}_{12})^2 + 1,\\
T_{242}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2) &= \tfrac{35}{8}(\mathbf{a}_1\cdot\mathbf{u}_{12})^2(\mathbf{a}_2\cdot\mathbf{u}_{12})^2 - \tfrac{5}{2}(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12}) + \tfrac{1}{4}(\mathbf{a}_1\cdot\mathbf{a}_2)^2\\
&\quad - \tfrac{5}{8}(\mathbf{a}_1\cdot\mathbf{u}_{12})^2 - \tfrac{5}{8}(\mathbf{a}_2\cdot\mathbf{u}_{12})^2 + \tfrac{1}{8},
\end{aligned} \quad (18)$$

and their analogs corresponding to a permutation of the ℓ, L and λ indexes. Here we assume that the ordering of the long molecular axes is nonpolar (i.e., invariants with odd indexes ℓ and λ are absent) and neglect the small chirality terms (i.e., spherical invariants with odd indexes L). One notes that the average of any spherical invariant $T_{\ell L\lambda}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2)$ with respect to any of its arguments is proportional to the order parameter of kinds (14) (ℓth for $\mathbf{a}_1$, Lth for $\mathbf{u}_{12}$, and λth for $\mathbf{a}_2$) with appropriate distribution function. For both vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ the distribution function is $f[(\mathbf{a}\cdot\mathbf{n}),\mathbf{r}]$, while for vector $\mathbf{u}_{12}$ the distribution function is $\rho[(\mathbf{u}_{12}\cdot\mathbf{n}),\mathbf{r}]$. Let us also note that implementation of the higher order spherical invariants will not bring us any new information about the structure of a liquid crystal considered here. In other words, let us take into account only those spherical invariants, which result in the appearance of the S_2 and S_4 orientational order parameters and σ_2/σ_0 and σ_4/σ_0 translational order parameters in the free energy. Introducing coefficients

$$J_{\ell L\lambda}^{(i)} \equiv \frac{1}{V_0}\int_0^{\infty} dr_{12} r_{12}^{i+2} J_{\ell L\lambda}(r_{12}), \quad (19)$$

using the gradient expansion for the orientational order parameters and director:

$$\begin{aligned}
S_\lambda(\mathbf{r}_2) &\approx S_\lambda(\mathbf{r}_1) + \tfrac{1}{2}(\mathbf{r}_{12}\cdot\nabla)^2 S_\lambda(\mathbf{r}_1),\\
\mathbf{n}_2 &\approx \mathbf{n}_1 + (\mathbf{r}_{12}\cdot\nabla)\mathbf{n}_1 + \tfrac{1}{2}(\mathbf{r}_{12}\cdot\nabla)^2\mathbf{n}_1,
\end{aligned} \quad (20)$$

and considering only up to the square gradients either in S or in $\mathbf{n}$, one obtains from Eqs. (11) and (12) the following expressions for the mean field and correlation function:

$$U_{\mathrm{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1] = U_{\mathrm{MF}}^{(0)}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1] + \Delta U_{\mathrm{MF}}^{S}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1] + \Delta U_{\mathrm{MF}}^{\mathbf{n}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1], \quad (21)$$

$$U_{\mathrm{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1] = U_{\mathrm{corr}}^{(0)}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1] + \Delta U_{\mathrm{corr}}^{S}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1] + \Delta U_{\mathrm{corr}}^{\mathbf{n}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1], \quad (22)$$

where the first terms in both Eqs. (21) and (22) are expressed in the same form as in the homogeneous state:

$$U_{\mathrm{MF}}^{(0)}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1] = -\sum_{\ell,L,\lambda} J_{\ell L\lambda}^{(0)} \sigma_L(\mathbf{r}_1) S_\lambda(\mathbf{r}_1) P_\ell(\mathbf{a}_1\cdot\mathbf{n}_1), \quad (23)$$

$$U_{\mathrm{corr}}^{(0)}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1] = -\frac{1}{2}\sigma_0 \sum_{\ell,L,\lambda} J_{\ell L\lambda}^{(0)} S_\ell(\mathbf{r}_1) S_\lambda(\mathbf{r}_1) P_L(\mathbf{u}_{12}\cdot\mathbf{n}_1), \quad (24)$$

the second terms reflect the gradients of the orientational order parameters [see Appendix A]:

$$\begin{aligned}
\Delta U_{\mathrm{MF}}^{S}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1] &= -\frac{1}{2} V_0 \sum_{\ell L\lambda} J_{\ell L\lambda}^{(2)} P_\ell(\mathbf{a}_1\cdot\mathbf{n}_1) \int d^2\mathbf{u}_{12}\, \rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1] P_L(\mathbf{u}_{12}\cdot\mathbf{n}_1)(\mathbf{u}_{12}\cdot\nabla)^2 S_\lambda(\mathbf{r}_1)\\
&= -\frac{1}{2}\sum_{\ell L\lambda} J_{\ell L\lambda}^{(2)} P_\ell(\mathbf{a}_1\cdot\mathbf{n}_1)\hat{g}_L(\{\sigma_k\}) S_\lambda(\mathbf{r}_1),
\end{aligned} \quad (25)$$

$$\begin{aligned}\Delta U^{S}_{\text{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1] &= -\frac{1}{4}\sigma_0\sum_{\ell L\lambda} J^{(2)}_{\ell L\lambda} S_\ell(\mathbf{r}_1) P_L(\mathbf{u}_{12}\cdot\mathbf{n}_1)(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2 S_\lambda(\mathbf{r}_1)\\ &= -\frac{1}{4}\sigma_0\sum_{\ell L\lambda} J^{(2)}_{\ell L\lambda} S_\ell(\mathbf{r}_1)\hat{g}_L(\{P_k(\mathbf{u}_{12}\cdot\mathbf{n}_1)\}) S_\lambda(\mathbf{r}_1),\end{aligned}\tag{26}$$

where operators $\hat{g}_L(\{\sigma_k\})$ and $\hat{g}_L(\{P_k(\mathbf{u}_{12}\cdot\mathbf{n}_1)\})$ acting on the orientational order parameters $S_\lambda(\mathbf{r}_1)$ are expressed as follows [either translational order parameters σ_k in the case of Eq. (25) or Legendre polynomials $P_k(\mathbf{u}_{12}\cdot\mathbf{n}_1)$ in the case of Eq. (26) should be substituted instead of x_k]:

$$\begin{aligned}&\hat{g}_0(\{x_k\}) \equiv \tfrac{1}{3}(x_0 - x_2)\boldsymbol{\nabla}^2 + x_2(\mathbf{n}_1\cdot\boldsymbol{\nabla})^2,\\ &\hat{g}_2(\{x_k\}) \equiv \left(-\tfrac{1}{15}x_0 + \tfrac{5}{21}x_2 - \tfrac{6}{35}x_4\right)\boldsymbol{\nabla}^2 + \left(\tfrac{1}{5}x_0 + \tfrac{2}{7}x_2 + \tfrac{18}{35}x_4\right)(\mathbf{n}_1\cdot\boldsymbol{\nabla})^2,\end{aligned}\tag{27}$$

while consideration of $L = 4$ yields the appearance of σ_6/σ_0 translational order parameter in the free energy, which is beyond our agreement made above. The third terms in both Eqs. (21) and (22) are responsible for the deformation of director [see Appendix B]:

$$\begin{aligned}\Delta U^{\mathbf{n}}_{\text{MF}}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1] &= -V_0\sum_{\ell L\lambda} J^{(2)}_{\ell L\lambda} P_\ell(\mathbf{a}_1\cdot\mathbf{n}_1) S_\lambda(\mathbf{r}_1)\int d^2\mathbf{u}_{12}\,\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1][T_{\ell L\lambda}(\mathbf{n}_1,\mathbf{u}_{12},\mathbf{n}_2) - T_{\ell L\lambda}(\mathbf{n}_1,\mathbf{u}_{12},\mathbf{n}_1)]\\ &= \frac{1}{2}k_{11}(\boldsymbol{\nabla}\cdot\mathbf{n})^2 + \frac{1}{2}k_{22}(\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2 + \frac{1}{2}k_{33}[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2 + k_{13}\boldsymbol{\nabla}\cdot\{\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})\}\\ &\quad - k_{24}\boldsymbol{\nabla}\cdot\{\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}) + [\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]\},\end{aligned}\tag{28}$$

$$\begin{aligned}\Delta U^{\mathbf{n}}_{\text{corr}}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1] &= -\frac{1}{2}\sigma_0\sum_{\ell L\lambda} J^{(2)}_{\ell L\lambda} S_\ell(\mathbf{r}_1) S_\lambda(\mathbf{r}_1)[T_{\ell L\lambda}(\mathbf{n}_1,\mathbf{u}_{12},\mathbf{n}_2) - T_{\ell L\lambda}(\mathbf{n}_1,\mathbf{u}_{12},\mathbf{n}_1)]\\ &= \frac{1}{2}\sigma_0\left(\frac{1}{2}\tilde{k}_{11}(\boldsymbol{\nabla}\cdot\mathbf{n})^2 + \frac{1}{2}\tilde{k}_{22}(\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2 + \frac{1}{2}\tilde{k}_{33}[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2 + \tilde{k}_{13}\boldsymbol{\nabla}\cdot\{\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})\}\right.\\ &\quad\left. - \tilde{k}_{24}\boldsymbol{\nabla}\cdot\{\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}) + [\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]\}\right),\end{aligned}\tag{29}$$

where coefficients $k_{ij} = k_{ij}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]$ are similar to the elastic constants and are expressed in terms of the interaction symmetry constants $J^{(2)}_{\ell L\lambda}$ and order parameters $S_\lambda = S_\lambda(\mathbf{r}_1)$ and $\sigma_L = \sigma_L(\mathbf{r}_1)$ as follows (the expressions take into account the commutation of indexes ℓ and λ, since the interacting molecules are indistinguishable):

$$\begin{aligned}k_{11} &= \tfrac{9}{14}(\sigma_2 - \sigma_4)\left[J^{(2)}_{220}P_2(\mathbf{a}_1\cdot\mathbf{n}_1) + J^{(2)}_{022}S_2\right] + \left[(\sigma_0 - \sigma_2)J^{(2)}_{202} + \left(\tfrac{1}{5}\sigma_0 + \tfrac{4}{7}\sigma_2 - \tfrac{27}{35}\sigma_4\right)J^{(2)}_{222}\right]\\ &\quad\times P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 - \left(\tfrac{1}{2}\sigma_0 - \tfrac{29}{14}\sigma_2 + \tfrac{11}{7}\sigma_4\right)\left[J^{(2)}_{422}P_4(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 + J^{(2)}_{224}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_4\right],\\ k_{22} &= \tfrac{3}{14}(\sigma_2 - \sigma_4)\left[J^{(2)}_{220}P_2(\mathbf{a}_1\cdot\mathbf{n}_1) + J^{(2)}_{022}S_2\right] + \left[(\sigma_0 - \sigma_2)J^{(2)}_{202} - \left(\tfrac{2}{5}\sigma_0 - \sigma_2 + \tfrac{3}{5}\sigma_4\right)J^{(2)}_{222}\right]\\ &\quad\times P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 - \left(\tfrac{1}{6}\sigma_0 - \tfrac{7}{6}\sigma_2 + \sigma_4\right)\left[J^{(2)}_{422}P_4(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 + J^{(2)}_{224}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_4\right],\\ k_{33} &= \left(\tfrac{9}{14}\sigma_2 + \tfrac{12}{14}\sigma_4\right)\left[J^{(2)}_{220}P_2(\mathbf{a}_1\cdot\mathbf{n}_1) + J^{(2)}_{022}S_2\right] + \left[(\sigma_0 + 2\sigma_2)J^{(2)}_{202} + \left(\tfrac{1}{5}\sigma_0 + \tfrac{10}{7}\sigma_2 + \tfrac{48}{35}\sigma_4\right)J^{(2)}_{222}\right]\\ &\quad\times P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 + \left(\tfrac{2}{3}\sigma_0 + \tfrac{137}{42}\sigma_2 + \tfrac{18}{7}\sigma_4\right)\left[J^{(2)}_{422}P_4(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 + J^{(2)}_{224}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_4\right],\\ k_{13} &= -\left(\tfrac{1}{10}\sigma_0 + \tfrac{1}{14}\sigma_2 - \tfrac{6}{35}\sigma_4\right)\left[J^{(2)}_{220}P_2(\mathbf{a}_1\cdot\mathbf{n}_1) + J^{(2)}_{022}S_2 + J^{(2)}_{222}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 + J^{(2)}_{422}P_4(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 + J^{(2)}_{224}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_4\right],\\ k_{24} &= \tfrac{1}{2}(\sigma_0 - \sigma_2)J^{(2)}_{202}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 - \left(\tfrac{1}{20}\sigma_0 - \tfrac{5}{28}\sigma_2 + \tfrac{9}{70}\sigma_4\right)\left[J^{(2)}_{220}P_2(\mathbf{a}_1\cdot\mathbf{n}_1) + J^{(2)}_{022}S_2 + 2J^{(2)}_{222}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_2\right]\\ &\quad - \left(\tfrac{13}{60}\sigma_0 - \tfrac{65}{84}\sigma_2 + \tfrac{39}{70}\sigma_4\right)\left[J^{(2)}_{422}P_4(\mathbf{a}_1\cdot\mathbf{n}_1)S_2 + J^{(2)}_{224}P_2(\mathbf{a}_1\cdot\mathbf{n}_1)S_4\right],\end{aligned}\tag{30}$$

while coefficients $\tilde{k}_{ij}[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]$ should by written in a similar way as coefficients $k_{ij}[(\mathbf{a}_1\cdot\mathbf{n}_1),\mathbf{r}_1]$ [Eq. (30)], where, however, all polynomials $P_\ell(\mathbf{a}_1\cdot\mathbf{n}_1)$ should be replaced with the corresponding orientational order parameters $S_\ell(\mathbf{r}_1)$ and all translational order parameters σ_L should be replaced with the corresponding polynomials $P_L(\mathbf{u}_{12}\cdot\mathbf{n}_1)$.

D. Gradients of the orientational and translational order parameters

Substituting Eqs. (23)–(26) and (28)–(29) into Eqs. (21)–(22), and then Eq. (21)–(22) into Eq. (13), one obtains the following expressions for the integrals $I_\ell^f(\mathbf{r})$ and $I_\ell^\rho(\mathbf{r})$ participating in the recurrent Eq. (14) for the order parameters:

$$\begin{aligned} I_m^f(\mathbf{r}) &= \int_{-1}^{1} dt P_m(t)\exp\left\{\frac{1}{k_BT}\sum_{\ell L\lambda}\left[J^{(0)}_{\ell L\lambda}P_\ell(t)\sigma_L(\mathbf{r})S_\lambda(\mathbf{r})+\frac{1}{2}J^{(2)}_{\ell L\lambda}P_\ell(t)\hat{g}_L(\{\sigma_k(\mathbf{r})\})S_\lambda(\mathbf{r})\right]-\frac{\Delta U^{\mathbf{n}}_{\mathrm{MF}}(t,\mathbf{r})}{k_BT}\right\},\\ I_m^\rho(\mathbf{r}) &= \int_{-1}^{1} dt P_m(t)\exp\left\{\frac{\sigma_0}{2k_BT}\sum_{\ell L\lambda}\left[J^{(0)}_{\ell L\lambda}S_\ell(\mathbf{r})P_L(t)S_\lambda(\mathbf{r})+\frac{1}{2}J^{(2)}_{\ell L\lambda}S_\ell(\mathbf{r})\hat{g}_L(\{P_k(t)\})S_\lambda(\mathbf{r})\right]-\frac{\Delta U^{\mathbf{n}}_{\mathrm{corr}}(t,\mathbf{r})}{k_BT}\right\}, \end{aligned} \tag{31}$$

where $t\equiv(\mathbf{a}_1\cdot\mathbf{n}_1)$ in the first line of Eq. (31), $t\equiv(\mathbf{u}_{12}\cdot\mathbf{n}_1)$ in the second line of Eq. (31), $\mathbf{r}\equiv\mathbf{r}_1$. Equations (14) and (31) determine the equilibrium equation of state for any complex nematic or smectic LC, including the director deformation and the order parameters gradients. One notes that differential Eqs. (14) and (31) are difficult to solve directly, because the gradients are in the power of exponents. For this purpose, let us expand the exponents in the first line of Eq. (31) in Taylor series with respect to the small gradients in S_λ. Then one obtains the following simple differential equation from the first part of Eq. (14):

$$\frac{1}{2k_BT}\sum_{\ell L\lambda}J^{(2)}_{\ell L\lambda}[I_{0\ell}(\mathbf{r})S_m(\mathbf{r})-I_{\ell m}(\mathbf{r})]\hat{g}_L(\{\sigma_k(\mathbf{r})\})S_\lambda(\mathbf{r})\approx -I_{00}(\mathbf{r})S_m(\mathbf{r})+I_{0m}(\mathbf{r}), \tag{32}$$

where

$$I_{nm}(\mathbf{r})=\int_{-1}^{1}dt P_n(t)P_m(t)\exp\left\{\frac{1}{k_BT}\sum_{\ell L\lambda}J^{(0)}_{\ell L\lambda}P_\ell(t)\sigma_L(\mathbf{r})S_\lambda(\mathbf{r})-\frac{\Delta U^{\mathbf{n}}_{\mathrm{MF}}(t,\mathbf{r})}{k_BT}\right\}. \tag{33}$$

Let us introduce the following functions:

$$\begin{aligned} \Phi_2^{(0)}(\{S_k\},\{\sigma_k\}) &\equiv 2\big(J^{(2)}_{422}+J^{(2)}_{224}\big)^{-1}\frac{I_{22}(S_4I_{00}-I_{04})-I_{24}(S_2I_{00}-I_{02})-I_{02}(S_4I_{02}-S_2I_{04})}{I_{24}(S_4I_{02}-I_{24})-I_{44}(S_2I_{02}-I_{22})-I_{04}(S_4I_{22}-S_2I_{24})},\\ \Phi_4^{(0)}(\{S_k\},\{\sigma_k\}) &\equiv 2\big(J^{(2)}_{422}+J^{(2)}_{224}\big)^{-1}\frac{I_{24}(S_4I_{00}-I_{04})-I_{44}(S_2I_{00}-I_{02})-I_{04}(S_4I_{02}-S_2I_{04})}{I_{24}(S_4I_{02}-I_{24})-I_{44}(S_2I_{02}-I_{22})-I_{04}(S_4I_{22}-S_2I_{24})}, \end{aligned} \tag{34}$$

Then the solution of differential Eq. (32) can be written as follows:

$$\begin{aligned} \hat{g}_2(\{\sigma_k(\mathbf{r})\})S_2(\mathbf{r}) &= 2k_BT\,\Phi_2(\{S_k(\mathbf{r})\},\{\sigma_k(\mathbf{r})\}),\\ \hat{g}_2(\{\sigma_k(\mathbf{r})\})S_4(\mathbf{r}) &= 2k_BT\,\Phi_4(\{S_k(\mathbf{r})\},\{\sigma_k(\mathbf{r})\}), \end{aligned} \tag{35}$$

where

$$\begin{aligned} \Phi_2(\{S_k\},\{\sigma_k\}) &\equiv \Phi_2^{(0)}\big[1-\big(J^{(2)}_{220}+J^{(2)}_{022}\big)\Phi_2^{(0)}/2\big]^{-1},\\ \Phi_4(\{S_k\},\{\sigma_k\}) &\equiv -\big\{\Phi_4^{(0)}+2\big(J^{(2)}_{422}+J^{(2)}_{224}\big)^{-1}\big[J^{(2)}_{202}\hat{g}_0(\{\sigma_k\})/\hat{g}_2(\{\sigma_k\})+J^{(2)}_{222}\big]\Phi_2^{(0)}\big\}\big[1-\big(J^{(2)}_{220}+J^{(2)}_{022}\big)\Phi_2^{(0)}/2\big]^{-1}, \end{aligned} \tag{36}$$

where the differential operators $\hat{g}_0(\{\sigma_k(\mathbf{r})\})$ and $\hat{g}_2(\{\sigma_k(\mathbf{r})\})$ acting on $S_2(\mathbf{r})$ or $S_4(\mathbf{r})$ are determined by Eq. (27). In the same manner, one could expand the second line of Eq. (31) in Taylor series with respect to the small gradients in S_λ. However, taking into account that Eqs. (31) do not contain any explicit gradients in $\{\sigma_k\}$, one can farther simplify the second line of Eq. (31) neglecting gradients in $\{S_k\}$ as well:

$$\frac{\sigma_m(\mathbf{r})}{\sigma_0}=\frac{1}{I^\rho_{00}(\mathbf{r})}\int_{-1}^{1}dt P_m(t)\exp\left\{\frac{\sigma_0}{2k_BT}\sum_{\ell L\lambda}J^{(0)}_{\ell L\lambda}P_L(t)S_\ell(\mathbf{r})S_\lambda(\mathbf{r})-\frac{\Delta U^{\mathbf{n}}_{\mathrm{corr}}(t,\mathbf{r})}{k_BT}\right\}, \tag{37}$$

where $I^\rho_{00}(\mathbf{r})$ is the normalizing integral in the same approximation:

$$I^\rho_{00}(\mathbf{r})=\int_{-1}^{1}dt\exp\left\{\frac{\sigma_0}{2k_BT}\sum_{\ell L\lambda}J^{(0)}_{\ell L\lambda}P_L(t)S_\ell(\mathbf{r})S_\lambda(\mathbf{r})-\frac{\Delta U^{\mathbf{n}}_{\mathrm{corr}}(t,\mathbf{r})}{k_BT}\right\}, \tag{38}$$

where, however, the orientational order parameters at each coordinate $\mathbf{r}$ should be substituted from differential Eqs. (35). Functions $\Phi_2(\{S_k\},\{\sigma_k\})$ and $\Phi_4(\{S_k\},\{\sigma_k\})$ defined in Eq. (36) describe the capability of propagation of the order parameters through the inhomogeneous LC. One notes, that both of them are inversely proportional to coefficients $J^{(2)}_{422}=J^{(2)}_{224}$, which are themselves proportional to the difference between the bend and splay elastic constants $K^N_{33}-K^N_{11}$ in the nematic state in the absence of positional correlations of molecules (i.e., at $\sigma_2=\sigma_4=0$), see Eq. (30).

E. Equilibrium free energy of the deformed liquid crystal and elastic constants

Substituting Eq. (21) for the mean field energy into Eq. (16) and introducing the normalizing integrals for the orientational and translational distribution functions disregarding any gradients (either in the order parameters or in the director):

$$I^{f}_{000}(\mathbf{r}) = \int_{-1}^{1} dt\, \exp\left\{\frac{\sigma_0}{k_B T}\sum_{\ell L\lambda} J^{(0)}_{\ell L\lambda} P_\ell(t) S_\lambda(\mathbf{r})\sigma_L(\mathbf{r})/\sigma_0\right\},$$

$$I^{\rho}_{000}(\mathbf{r}) = \int_{-1}^{1} dt\, \exp\left\{\frac{\sigma_0}{2k_B T}\sum_{\ell L\lambda} J^{(0)}_{\ell L\lambda} P_L(t) S_\ell(\mathbf{r}) S_\lambda(\mathbf{r})\right\}, \tag{39}$$

one obtains the following expression for the equilibrium free-energy density:

$$\frac{\partial F_{\mathrm{eq}}(\mathbf{r})}{\partial V} = \frac{\partial F_0(\mathbf{r})}{\partial V} + \frac{\partial F_S(\mathbf{r})}{\partial V} + \frac{\partial F_{\mathbf{n}}(\mathbf{r})}{\partial V}, \tag{40}$$

where

$$\begin{aligned} 4\pi V_0 \frac{\partial F_0(\mathbf{r})}{\partial V} &= -k_B T \ln I^{\rho}_{000}(\mathbf{r}) I^{f}_{000}(\mathbf{r}) \\ &\quad + \sum_{\ell,L,\lambda} J^{(0)}_{\ell L\lambda} S_\ell(\mathbf{r})\sigma_L(\mathbf{r}) S_\lambda(\mathbf{r}) \end{aligned} \tag{41}$$

is the equilibrium homogeneous free-energy density multiplied by $4\pi V_0$,

$$4\pi V_0 \frac{\partial F_S(\mathbf{r})}{\partial V} = -\frac{1}{2}\sum_{\ell L\lambda} J^{(2)}_{\ell L\lambda} S_\ell(\mathbf{r})\hat{g}_L(\{\sigma_k(\mathbf{r})\}) S_\lambda(\mathbf{r}) \tag{42}$$

is the equilibrium free-energy density (multiplied by $4\pi V_0$) related to the inhomogeneity of the order parameters, and

$$\begin{aligned} \frac{\partial F_{\mathbf{n}}(\mathbf{r})}{\partial V} &= \frac{1}{2}K_{11}(\mathbf{r})(\nabla\cdot\mathbf{n})^2 + \frac{1}{2}K_{22}(\mathbf{r})(\mathbf{n}\cdot[\nabla\times\mathbf{n}])^2 + \frac{1}{2}K_{33}(\mathbf{r})[\mathbf{n}\times[\nabla\times\mathbf{n}]]^2 + K_{13}(\mathbf{r})\nabla\cdot\{\mathbf{n}(\nabla\cdot\mathbf{n})\} \\ &\quad - K_{24}(\mathbf{r})\nabla\cdot\{\mathbf{n}(\nabla\cdot\mathbf{n}) + [\mathbf{n}\times[\nabla\times\mathbf{n}]]\} \end{aligned} \tag{43}$$

is the equilibrium free-energy density related to the inhomogeneity of director, where the elastic constants $K_{ij}(\mathbf{r})$ should be obtained from the functions $k_{ij}[(\mathbf{a}_1\cdot\mathbf{n}_1), \mathbf{r}_1]$ [Eq. (30)] by replacements of polynomials $P_\ell(\mathbf{a}_1\cdot\mathbf{n}_1)$ with the corresponding order parameters $S_\ell(\mathbf{r})$:

$$\begin{aligned} 4\pi V_0 K_{11} &= \tfrac{9}{14}(\sigma_2-\sigma_4)\big[J^{(2)}_{220}+J^{(2)}_{022}\big]S_2 + \big[(\sigma_0-\sigma_2)J^{(2)}_{202} + \big(\tfrac{1}{5}\sigma_0+\tfrac{4}{7}\sigma_2-\tfrac{27}{35}\sigma_4\big)J^{(2)}_{222}\big]S_2^2 \\ &\quad - \big(\tfrac{1}{2}\sigma_0-\tfrac{29}{14}\sigma_2+\tfrac{11}{7}\sigma_4\big)\big[J^{(2)}_{422}+J^{(2)}_{224}\big]S_2S_4, \\ 4\pi V_0 K_{22} &= \tfrac{3}{14}(\sigma_2-\sigma_4)\big[J^{(2)}_{220}+J^{(2)}_{022}\big]S_2 + \big[(\sigma_0-\sigma_2)J^{(2)}_{202} - \big(\tfrac{2}{5}\sigma_0-\sigma_2+\tfrac{3}{5}\sigma_4\big)J^{(2)}_{222}\big]S_2^2 \\ &\quad - \big(\tfrac{1}{6}\sigma_0-\tfrac{7}{6}\sigma_2+\sigma_4\big)\big[J^{(2)}_{422}+J^{(2)}_{224}\big]S_2S_4, \\ 4\pi V_0 K_{33} &= \big(\tfrac{9}{14}\sigma_2+\tfrac{12}{14}\sigma_4\big)\big[J^{(2)}_{220}+J^{(2)}_{022}\big]S_2 + \big[(\sigma_0+2\sigma_2)J^{(2)}_{202} + \big(\tfrac{1}{5}\sigma_0+\tfrac{10}{7}\sigma_2+\tfrac{48}{35}\sigma_4\big)J^{(2)}_{222}\big]S_2^2 \\ &\quad + \big(\tfrac{2}{3}\sigma_0+\tfrac{137}{42}\sigma_2+\tfrac{18}{7}\sigma_4\big)\big[J^{(2)}_{422}+J^{(2)}_{224}\big]S_2S_4, \\ 4\pi V_0 K_{13} &= -\big(\tfrac{1}{10}\sigma_0+\tfrac{1}{14}\sigma_2-\tfrac{6}{35}\sigma_4\big)\big\{\big[J^{(2)}_{220}+J^{(2)}_{022}\big]S_2 + J^{(2)}_{222}S_2^2 + \big[J^{(2)}_{422}+J^{(2)}_{224}\big]S_2S_4\big\}, \\ 4\pi V_0 K_{24} &= \tfrac{1}{2}(\sigma_0-\sigma_2)S_2^2 - \big(\tfrac{1}{20}\sigma_0-\tfrac{5}{28}\sigma_2+\tfrac{9}{70}\sigma_4\big)\big\{\big[J^{(2)}_{220}+J^{(2)}_{022}\big]S_2 + 2J^{(2)}_{222}S_2^2\big\} \\ &\quad - \big(\tfrac{13}{60}\sigma_0-\tfrac{65}{84}\sigma_2+\tfrac{39}{70}\sigma_4\big)\big[J^{(2)}_{422}+J^{(2)}_{224}\big]S_2S_4. \end{aligned} \tag{44}$$

One notes from Eq. (44) that each elastic constant essentially depends on the orientational and translational order parameters, and thus, can be different in various geometries of the same material, where the gradients of the order parameters takes place. They also vary essentially with the variation of temperature. The temperature dependencies of all five elastic constants in the case of the homogeneous LC are presented in Fig. 3. All the elastic constants are different from zero in the nematic (N) and smectic (Sm) phases. Initially, the values of $J^{(2)}_{\ell L\lambda}$ (totally four constants) were taken so that the elastic constants fit the experimental data (solid lines in Fig. 3). In particular, at $T = 342.74$ K, the data for $K_{11} \approx 5$ pN, $K_{22} \approx 3$ pN, and $K_{33} \approx 8$ pN fit well the experimental data for the same parameters measured in 5CB material at $T \approx T_{NI} - 5\,K$ in Refs. [58–60], while the K_{13}/K_{11} ratio in the nematic phase is about −0.2 (solid lines in Fig. 3) similar to that in [61]. Here we are using the experimental data for the elastic constants in 5CB for tuning the $J^{(2)}_{\ell L\lambda}$ constants because of the two reasons. The first one is that the data for K_{11}, K_{22}, and K_{33} in 5CB are the most familiar in the scientific community and are well reproduced by different experimental methods. The second reason is that the value of K_{13} is measured only in 5CB to our best knowledge. What concerns the K_{24} elastic constant, at the first glance it appears about twice lower than that observed experimentally (we have already taken into account that in many publications the corresponding term in the elastic energy is written with 1/2 multiplier, differently from presentation here and in Ref. [61]). However in all publications, where the K_{24} elastic constant is measured, the splaybend elastic term (proportional to K_{13}) is not written explicitly. Meanwhile, for instance, in the case of a pure splay, the disregarded splaybend term would contribute with positive sign into the saddle-splay

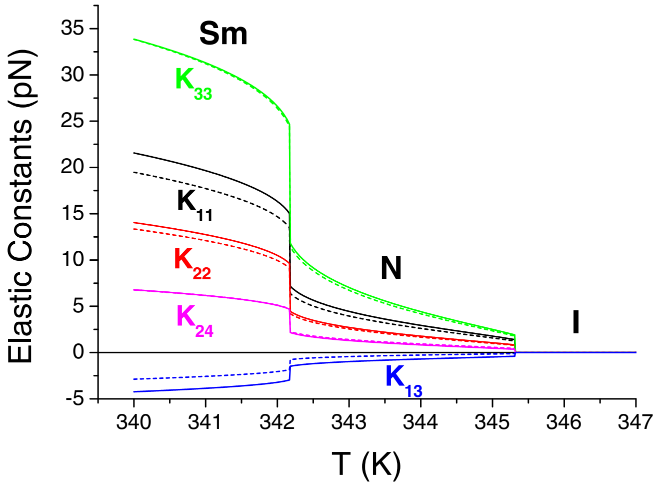

FIG. 3. The temperature dependencies of the elastic constants in the homogeneous LC at $\sigma_0 J^{(0)}_{202}/k_B = 1100\,\mathrm{K}$, $\sigma_0 J^{(0)}_{220}/k_B = \sigma_0\, J^{(0)}_{022}/k_B = 1023\,\mathrm{K}$, $\sigma_0 J^{(0)}_{222}/k_B = -1122\,\mathrm{K}$, $\sigma_0 J^{(0)}_{242}/k_B = -3080\,\mathrm{K}$, $\sigma_0\, J^{(0)}_{404}/k_B = -55\,\mathrm{K}$, $\sigma_0 J^{(2)}_{202}/k_B = 51\,\mathrm{K}\,\mu\mathrm{m}^2$, $\sigma_0 J^{(2)}_{222}/k_B = 39\,\mathrm{K}\,\mu m^2$, $\sigma_0 J^{(2)}_{422}/k_B = \sigma_0 J^{(2)}_{224}/k_B = 35\,\mathrm{K}\,\mu\mathrm{m}^2$, $\sigma_0 J^{(2)}_{220}/k_B = \sigma_0 J^{(2)}_{022}/k_B = 9\,\mathrm{K}\,\mu\mathrm{m}^2$ (solid lines) or $\sigma_0 J^{(2)}_{220}/k_B = \sigma_0 J^{(2)}_{022}/k_B = 0\,\mathrm{K}\,\mu\mathrm{m}^2$ (dash lines), and all other constants participating in approximation Eq. (17) equal to zero. Here $V_0 \approx 1.1 \times 10^{-24}\,\mathrm{m}^3$ (see discussion at the end of Sec. II B).

term. Taking this into account one ascertains the quantitative correspondence of our theoretical value of the K_{24} elastic term to the experimental observations [68–71]. At the same time, any reasonable values of the elastic constants (positive K_{11}, K_{22}, K_{33}, K_{24} and negative K_{13} within the piconewton range; $K_{22} < K_{11} < K_{33}$) can be obtained by a slight variation of parameters $J^{(2)}_{\ell L\lambda}$. In particular, we can easily model the elastic constants in 8CB or different LC materials, and the results will be automatically in a good correlation with experimental measurements [62–65]. Our results are also in a good agreement with different molecular modeling approaches [66,67].

Why it is important to know the values of the $J^{(2)}_{\ell L\lambda}$ constants? One notes from comparison of Eqs. (34)–(36) and (44) that the same $J^{(2)}_{\ell L\lambda}$ constants are responsible for the gradients of order parameters, which are considered below, and this is the prime target of the present paper to find out these gradients. We would also like to mention that, in our theory, the temperature ranges of all phases and the values of order parameters $\{S_k\}$ and $\{\sigma_k\}$ are regulated by $J^{(0)}_{\ell L\lambda}$ constants [with zero upper index, see definition in Eq. (19)], while the direct correlation between $J^{(0)}_{\ell L\lambda}$ and $J^{(2)}_{\ell L\lambda}$ constants is not evident. Therefore we consider some typical $J^{(0)}_{\ell L\lambda}$ constants from Refs. [40,72], at which both the smectic and nematic phases can exist, and both the smectic-nematic and nematic-isotropic phase transitions are the well-pronounced first-order phase transitions. This does not automatically mean that this particular combination of $J^{(0)}_{\ell L\lambda}$ and $J^{(2)}_{\ell L\lambda}$ constants corresponds to any particular material. At the same time, consideration of some model material with well-pronounced nematic and smectic phases gives us an opportunity to answer the question, how large the typical elastic constants and the gradients of the order parameters should be in the smectic phase in comparison with the same characteristics in the nematic phase, while different phase sequences (in particular, without smectic phase or without nematic phase) are considered in Refs. [40,72]. At given choice of parameters, all the elastic constants change step-wise at the transition from nematic to smectic (at $T \approx 342.17\,\mathrm{K}$, see Fig. 3). The splay elastic constant K_{11} immediately changes from 7.17 to 15.02 pN, and farther increases within the smectic phase. In particular, at $T = 340\,\mathrm{K}$ it already reaches 21.57 pN. The twist elastic constant K_{22} immediately changes from 4.46 to 9.62 pN, and farther increases within the smectic phase. In particular, at $T = 340\,\mathrm{K}$ it reaches 14.05 pN. The bend elastic constant K_{33} immediately changes from 11.83 to 24.65 pN, and farther increases within the smectic phase. In particular, at $T = 340\,\mathrm{K}$ it reaches 33.86 pN. The same order of increase is characteristic to the absolute values of the splaybend and saddle-splay elastic constants, K_{13} and K_{24}, respectively.

At the same time, all tendencies related to the choice of the $J^{(0)}_{\ell L\lambda}$ constants also correlate with the experimental observations. In particular, the temperature range of nematic phase in a material, where the smectic phase is also observed, is usually not as large as in a material, where the smectic phase is not observed (compare, for example, the data for 7CB and 8CB materials in Ref. [62]). Comparison of the phase sequences at various combinations of the $J^{(0)}_{\ell L\lambda}$ constants in Refs. [40,72] leads to a conclusion that the smectic phase arises rather *instead* of a part of nematic phase than *in addition* to it, while the smectic phase itself does not look as something *completely* different from nematic phase, but rather as a phase with much better translational and orientational order. This also correlates with speculations about the close translational order in nematics and long-range translational order in smectics, because the range of the order obviously depends on its magnitude.

F. How many elastic constants are independent and what is their molecular origin?

One notes from Eq. (30) [and it is discussed in a more detailed in Appendix B] that there exists the following relation between the elastic constants, reducing their independent number:

$$K_{24}(\mathbf{r}) = \tfrac{1}{2}K_{13}(\mathbf{r}) + \tfrac{1}{4}K_{11}(\mathbf{r}) + \tfrac{1}{4}K_{22}(\mathbf{r}), \qquad (45)$$

and thus, only four elastic constants appear to be independent on the molecular level. One can outline the meaning of each $J^{(2)}_{\ell L\lambda}$ constant on the macroscopic level in the *idealized* case of the homogeneous nematic (where $\sigma_2 = \sigma_4 = 0$):

$$\begin{aligned}
\frac{1}{4\pi V_0} J^{(2)}_{202} S_2^2 &= \overline{K}^N, \quad \overline{K}^N \equiv \left(K^N_{11} + K^N_{22} + K^N_{33}\right)/3,\\
\frac{1}{4\pi V_0} J^{(2)}_{222} S_2^2 &= \frac{25}{21}\left(K^N_{11} - K^N_{22}\right) + \frac{10}{21}\left(K^N_{33} - K^N_{22}\right),\\
\frac{1}{4\pi V_0} J^{(2)}_{422} S_2 S_4 = \frac{1}{4\pi V_0} J^{(2)}_{224} S_2 S_4 &= \frac{3}{7}\left(K^N_{33} - K^N_{11}\right),\\
\frac{1}{4\pi V_0} J^{(2)}_{220} S_2 = \frac{1}{4\pi V_0} J^{(2)}_{022} S_2 &= -5K^N_{13} - \frac{1}{6}\left(K^N_{11} - K^N_{22}\right)\\
&\quad - \frac{2}{3}\left(K^N_{33} - K^N_{22}\right). \qquad (46)
\end{aligned}$$

From Eq. (46), in particular, it follows that the $J^{(2)}_{202}$ constant describes only the so-called one-constant approximation, the $J^{(2)}_{222}$ constant describes the difference between the bend/splay constants and the twist constant, the $J^{(2)}_{422}$ and $J^{(2)}_{224}$ constants describe the difference between the bend and splay elastic constants, and, finally, the $J^{(2)}_{220}$ and $J^{(2)}_{022}$ constants mostly determine the splaybend elastic constant (compare also the solid and dash lines in Fig. 3).

III. APPLICATION OF THEORY TO THE CASE OF RADIAL DISTRIBUTION OF THE DIRECTOR FIELD IN THE SPHERE

A. Change over from the differential equations of the second order to the ones of the first order

One notes that spherical droplet with spherical particle in the center can model the low concentration of impurity particles in the bulk (see Fig. 4). As a simple example of application of our theory, let us therefore consider the radial distribution of director in the sphere with a small spherical solid particle of radius r_0 placed in the center (see Fig. 4). Let us also suppose that mesogenic material has a homeotropic anchoring at the surface of solid particle. In the limit case of $r_0 = 0$ there will be a point defect in the center of the sphere (see Ref. [44]), so that the geometry is not restricted by the presence of the spherical particle. In this geometry $(\mathbf{n}_1 \cdot \nabla)^2 = \nabla^2$, and one obtains instead of Eq. (27):

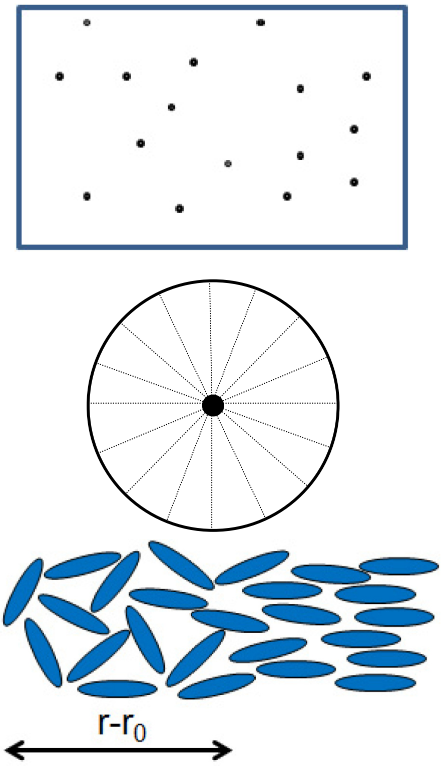

FIG. 4. Liquid crystal media with solid particles dispersed inside; spherical LC droplet with radial director distribution (shown by dotted lines) and solid spherical particle in the center; an illustration of the orientational order parameter variation with distance from a small particle. Here the radius of each particle is r_0; LC exhibits homeotropic anchoring at each sphere.

$$\hat{g}_0(\{x_k\}) \equiv \tfrac{1}{3}(x_0 + 2x_2)\nabla^2,$$
$$\hat{g}_2(\{x_k\}) \equiv \left(\tfrac{2}{15}x_0 + \tfrac{11}{21}x_2 + \tfrac{12}{35}x_4\right)\nabla^2, \tag{47}$$

and only three elastic deformations (square splay $(\nabla \cdot \mathbf{n})^2 = 4/r_1^2$, the splaybend $\nabla \cdot \{\mathbf{n}(\nabla \cdot \mathbf{n})\} = 2/r_1^2$ and the saddle-splay $-\nabla \cdot \{\mathbf{n}(\nabla \cdot \mathbf{n}) - (\mathbf{n} \cdot \nabla)\mathbf{n}\} = -2/r_1^2$) are present in Eqs. (28), (29), and (43).

In a number of simple geometries (including the one considered in the present section) it is possible to change over from the second order differential Eq. (35) to the first-order differential equations. For this purpose let us consider the complete differential of the order parameters $S_2(\mathbf{r})$ and $S_4(\mathbf{r})$:

$$dS(\mathbf{r}) = \frac{\partial S}{\partial x}dx + \frac{\partial S}{\partial y}dy + \frac{\partial S}{\partial z}dz = d\mathbf{r} \cdot \nabla S, \tag{48}$$

where either $S_2(\mathbf{r})$ or $S_4(\mathbf{r})$ can be substituted instead of $S(\mathbf{r})$. Here and below let us agree that the dot means the scalar product of the two vectors, while vector ∇ acts only on S, which is written just after the ∇ symbol. Applying Eq. (48) twice (after each equality sign in the line below), one obtains

$$\int \nabla^2 S dS(\mathbf{r}) = \int \nabla^2 S \nabla S \cdot d\mathbf{r} = \int \nabla S \cdot d(\nabla S)$$
$$= \frac{1}{2}[\nabla S(\mathbf{r})]^2. \tag{49}$$

Thus, integrating both parts of the first expression in Eq. (35) with respect to S_2 and integrating both parts of the second expression in Eq. (35) with respect to S_4, one obtains

$$\frac{\partial S_2(r)}{\partial r} = \pm\left\{\frac{4k_BT}{\sigma_0}\left[\frac{2}{15} + \frac{11}{21}\frac{\sigma_2(r)}{\sigma_0} + \frac{12}{35}\frac{\sigma_4(r)}{\sigma_0}\right]^{-1} \times \int_{S_2(r)}^{S_2(\infty)} \Phi_2(S_2(r), S_4(r), \sigma_2(r), \sigma_4(r))dS_2\right\}^{1/2},$$
$$\frac{\partial S_4(r)}{\partial r} = \pm\left\{\frac{4k_BT}{\sigma_0}\left[\frac{2}{15} + \frac{11}{21}\frac{\sigma_2(r)}{\sigma_0} + \frac{12}{35}\frac{\sigma_4(r)}{\sigma_0}\right]^{-1} \times \int_{S_4(r)}^{S_4(\infty)} \Phi_4(S_2(r), S_4(r), \sigma_2(r), \sigma_4(r))dS_4\right\}^{1/2}, \tag{50}$$

where functions Φ_2 and Φ_4 are determined by Eq. (36). Here we also assume that at the outer sphere (which is the border of LC droplet) the structure is already homogeneous, therefore the infinity sign is used in the upper limits in Eqs. (50). Thus, knowing also the orientational order parameters $S_2(r_0)$ and $S_4(r_0)$ on the particle's surface (at r_0), one can evolve Eqs. (50) step by step to any larger distance r. The solutions $S_2(r)$ and $S_4(r)$ [and therefore $\sigma_2(r)$ and $\sigma_4(r)$, in correspondence with Eqs. (37)–(38)] will obviously depend on the particle's size r_0.

B. Orientational and translational order parameters of LC at the particle's surface and in the homogeneous bulk of LC

To solve the differential Eqs. (50), one needs to know the values of the orientational $\{S_k(r_0)\}$ and the translational

$\{\sigma_k(r_0)\}$ order parameters at the inner border (at the surface between the solid particle in the center of the sphere and the surrounding LC), and also the values of the order parameters in the homogeneous LC (in the infinity). To determine the order parameters at the particle's surface, one should take explicitly into account the anisotropic interaction of the LC molecules with the surface, for instance, in the form of a sequence of Legendre polynomials:

$$U_{\mathrm{MF}}\{(\mathbf{a}\cdot\mathbf{n}(r_0)), r_0\} \longrightarrow U_{\mathrm{MF}}\{(\mathbf{a}\cdot\mathbf{n}(r_0)), r_0\} - \sum_{\ell} J_{\ell}^{\mathrm{surf}} P_{\ell}(\mathbf{a}\cdot\mathbf{k}), \tag{51}$$

where $\mathbf{k}$ is the surface normal coinciding with director $\mathbf{n}(r_0)$ in the case of homeotropic anchoring at the surface of a particle. In order to provide the sharp radial distribution at the particle's surface, let us consider positive J_2^{surf} and J_4^{surf} constants and neglect the higher order terms in approximation Eq. (51). At r_0 one obtains in the mean field approximation neglecting the small gradients in order parameters [compare to Eq. (14)]:

$$S_m(r_0) = I_m^f(r_0)/I_0^f(r_0),\ \sigma_m(r_0)/\sigma_0 = I_m^{\rho}(r_0)/I_0^{\rho}(r_0), \tag{52}$$

where

$$I_m^f(r_0) = \int_{-1}^{1} dt P_m(t) \exp\left\{\frac{1}{k_B T}\left[\sum_{\ell L\lambda} J_{\ell L\lambda}^{(0)} P_{\ell}(t) S_{\lambda}(r_0)\sigma_L(r_0) + \sum_{\ell} J_{\ell}^{\mathrm{surf}} P_{\ell}(t) - 2\frac{k_{11}(t,r_0) + k_{13}(t,r_0) - k_{24}(t,r_0)}{r_0^2}\right]\right\},$$

$$I_m^{\rho}(r_0) = \int_{-1}^{1} dt P_m(t) \exp\left\{\frac{\sigma_0}{2k_B T}\left[\sum_{\ell L\lambda} J_{\ell L\lambda}^{(0)} P_L(t) S_{\ell}(r_0) S_{\lambda}(r_0) - 2\frac{\tilde{k}_{11}(t,r_0) + \tilde{k}_{13}(t,r_0) - \tilde{k}_{24}(t,r_0)}{r_0^2}\right]\right\}, \tag{53}$$

where parameters $k_{11}(t, r_0)$, $k_{13}(t, r_0)$ and $k_{24}(t, r_0)$ are determined in the first, fourth and fifth line of Eq. (30), respectively, while the explanations how to obtain parameters $\tilde{k}_{11}(t, r_0)$, $\tilde{k}_{13}(t, r_0)$ and $\tilde{k}_{24}(t, r_0)$ is presented in the paragraph following Eq. (30). Similar to that in Eq. (31), $t = (\mathbf{a}_1 \cdot \mathbf{n}_1)$ in the first line of Eq. (53), while $t = (\mathbf{u}_{12} \cdot \mathbf{n}_1)$ in the second line of Eq. (53). The first expression in Eq. (52) is the recurrent equation for determination of the orientational order parameters at r_0, while the second expression in Eq. (52) should be used for the calculation of the translational order parameters at each turn of recurrence. After an appropriate number of recurrences, one obtains $\{S_k(r_0)\}$ and $\{\sigma_k(r_0)\}$ with particular accuracy. In the infinity (at the outer border of LC droplet) the following equations, analogous to Eqs. (52) and (53) can be obtained (in the absence of the anchoring at the outer border):

$$S_m(\infty) = I_m^f(\infty)/I_0^f(\infty),\ \sigma_m(\infty)/\sigma_0 = I_m^{\rho}(\infty)/I_0^{\rho}(\infty), \tag{54}$$

where

$$I_m^f(\infty) = \int_{-1}^{1} dt P_m(t) \times \exp\left\{\frac{1}{k_B T}\sum_{\ell L\lambda} J_{\ell L\lambda}^{(0)} P_{\ell}(t) S_{\lambda}(\infty)\sigma_L(\infty)\right\},$$

$$I_m^{\rho}(\infty) = \int_{-1}^{1} dt P_m(t) \times \exp\left\{\frac{\sigma_0}{2k_B T}\sum_{\ell L\lambda} J_{\ell L\lambda}^{(0)} P_L(t) S_{\ell}(\infty) S_{\lambda}(\infty)\right\}. \tag{55}$$

Several temperature dependencies of the orientational order parameter S_2 and of the variance of $\sin^2\beta$ [see definitions in Eqs. (1) and (4)] are presented in Fig. 5. The black thick lines correspond to the temperature dependencies of the mentioned parameters in the homogeneous LC, while the thin lines of various colors and with different numbers correspond to the temperature dependencies of the same parameters of LC at the surfaces of the particles of various radii (from 1.25 to 10 μm). The molecular parameters are chosen so that the two first-order phase transitions (smectic-nematic and nematic-isotropic) are realized in each case. It was discussed in Refs. [40,72] that one or both transitions can be of the second order or continuous, or a direct smectic-isotropic phase transition can be realized at different choice of the molecular parameters. The smectic phase (Sm) is characterized by a low variance of $\sin^2\beta$ tending to farther decreasing down to zero with the temperature tending to zero, which means that the molecules tend to be located within the planes (see Fig. 1). The $\mathrm{Var}(\sin^2\beta)$ parameter is not sensitive to the molecular tilt in smectic layers, so that we cannot predict, whether the smectic phase is tilted or not within the framework of a model considered in this paper. The orientational order parameter in the smectic phase appears to be rather high and tends to one with the temperature tending to zero. In the homogeneous media (far from any particles) the isotropic phase (I) corresponds to $S_2 = 0$ and $\mathrm{Var}(\sin^2\beta) = 4/45$, and these two parameters describe the equiprobable distribution over the sphere as for the molecular axes, as for the intermolecular vectors. In the presence of the particles (or any surfaces at all), the phase with very small S_2 and $\mathrm{Var}(\sin^2\beta)$ close to $4/45$ at these surfaces arises at high temperatures. Let us call this phase "conventionally isotropic." The nematic phase (N) arises between the smectic phase and the isotropic (or conventionally isotropic) phase in the temperature scale. The prime orientational order parameter S_2 in the nematic phase is also high, but can be several times smaller than that in the smectic phase. The main parameter distinguishing the nematic phase from the smectic phase is $\mathrm{Var}(\sin^2\beta)$, which does not have any pronounced tendency to decrease with the decreasing temperature in the nematic phase. Usually $\mathrm{Var}(\sin^2\beta)$ is even larger than $4/45$ in the nematic phase. This is a well-known property of variance, which increases first, when a distribution function becomes

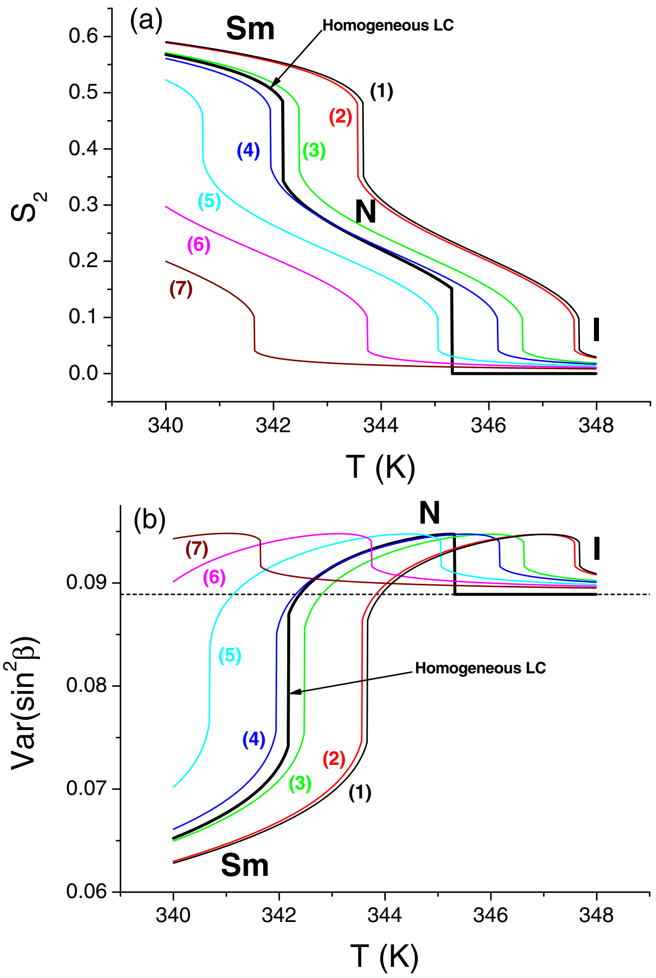

FIG. 5. The temperature dependencies of the prime orientational order parameter (a) and of the variance of $\sin^2\beta$ (b) at $\sigma_0 J^{(0)}_{202}/k_B = 1100\,\mathrm{K}$, $\sigma_0 J^{(0)}_{220}/k_B = \sigma_0 J^{(0)}_{022}/k_B = 1023\,\mathrm{K}$, $\sigma_0 J^{(0)}_{222}/k_B = -1122\,\mathrm{K}$, $\sigma_0 J^{(0)}_{242}/k_B = -3080\,\mathrm{K}$, $\sigma_0 J^{(0)}_{404}/k_B = -55\,\mathrm{K}$, $J^{\mathrm{surf}}_2/k_B = 0.55\,\mathrm{K}$, $J^{\mathrm{surf}}_4/k_B = 5.5\,\mathrm{K}$, $\sigma_0 J^{(2)}_{202}/k_B = 51\,\mathrm{K}\,\mu\mathrm{m}^2$, $\sigma_0 J^{(2)}_{222}/k_B = 39\,\mathrm{K}\,\mu\mathrm{m}^2$, $\sigma_0 J^{(2)}_{422}/k_B = \sigma_0 J^{(2)}_{224}/k_B = 35\,\mathrm{K}\,\mu\mathrm{m}^2$, and all other constants participating in approximation Eqs. (17) and (51) equal to zero. The black thick line corresponds to the homogeneous LC (far from any particles), while the thin lines with different numbers correspond to the LC at the surfaces of spherical particles of various radii: (1) $r_0 = \infty$ [flat surface]; (2) 10; (3) 3; (4) 2.5; (5) 1.9; (6) 1.55; (7) 1.25 μm.

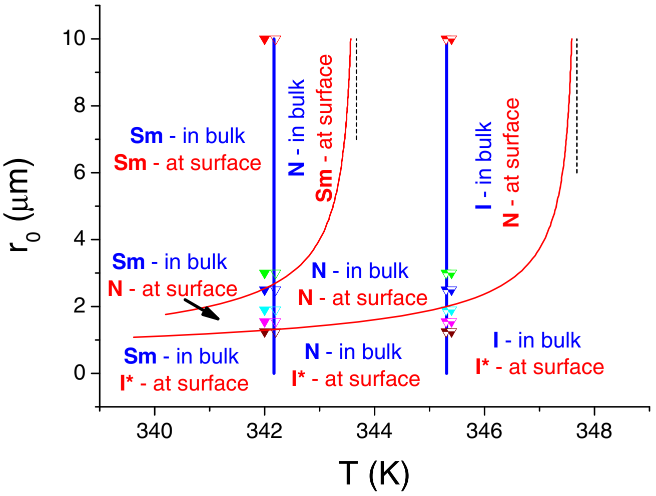

FIG. 6. The r_0-T phase diagram at the same molecular parameters [constants participating in approximation Eqs. (17) and (51)] as in Fig. 5. The blue thick lines correspond to the structure transitions in the bulk of LC, while the red thin lines correspond to the structure transitions at the surfaces of particles of diameter r_0. The dash lines correspond to the structure transitions at a flat surface. The triangles correspond to the points in the diagram, at which the r-dependence of the S_2 and Var($\sin^2\beta$) parameters is presented in Figs. 7 and 8. The color of each triangle corresponds to the color of particular lines in Figs. 7 and 8.

nonuniform (a broad maximum of the distribution function arises), and then decreases again, when the distribution function maximum becomes higher and narrower. That is the reason why the value of Var($\sin^2\beta$) exhibits some maximum in the nematic phase. One notes from Fig. 5 that generally the more ordered phases exist up to the higher temperatures at larger radii particles, while, on the contrary, the less ordered phases exist down to the lower temperatures at lower radii particles. The r_0-T phase diagram is presented in Fig. 6 at the same molecular parameters [constants participating in approximation Eqs. (17) and (51)] as in Fig. 5. The blue thick vertical lines correspond to the structure transitions in the bulk of LC, while the red thin lines correspond to the structure transitions at the surfaces of particles of diameter r_0. The dash lines correspond to the structure transitions at a flat surface (the limits of red curves in Fig. 6 at $r_0 \to \infty$). One notes that the 10 μm and higher-radii particles affect the LC media almost as a flat surface, while the 1 μm and lower-radii particles affect the LC media rather as point defects, because both the smectic-nematic and the nematic-isotropic phase transition borders of a liquid crystal at the particle's surface shift dramatically to the lower temperatures when r_0 farther decreases. In particular, in the case of a point defect, the isotropic liquid will arise in the center of sphere. Eight different phases are present in the diagram, and each solid line corresponds to the first-order phase transition border. Each phase is characterized by a combination of particular structure kinds [smectic (Sm), nematic (N) or isotropic (I or I^*)] in the bulk of LC and at the surfaces of spherical particles. Here I^* designates the conventionally isotropic phase arising at the particles' surfaces. At a given choice of molecular parameters the smectic structure arises in the bulk of LC at $T \lesssim 342.17\,\mathrm{K}$. At $T \approx 342.17\,\mathrm{K}$, the smectic structure arises also at the particles' surfaces at $r_0 \gtrsim 2.67\,\mu\mathrm{m}$, while the nematic and conventionally isotropic structures arise at the particles' surfaces at $1.31\,\mu\mathrm{m} \lesssim r_0 \lesssim 2.67\,\mu\mathrm{m}$ and $r_0 \lesssim 1.31\,\mu\mathrm{m}$, respectively. The nematic structure arises in the bulk of LC at $342.17 \lesssim T \lesssim 345.31\,\mathrm{K}$. At $T \gtrsim 343.67\,\mathrm{K}$, the smectic structure cannot arise at the particles' surfaces anymore at any particles' size. The $T \approx 343.67\,\mathrm{K}$ temperature corresponds to the limit smectic-nematic transition border at $r_0 \to \infty$. At $T \approx 343.67\,\mathrm{K}$, the nematic structure arises at the particles' surfaces at $r_0 \gtrsim 1.53\,\mu\mathrm{m}$, while the conventionally isotropic phase arises at the particles' surfaces at $r_0 \lesssim 1.53\,\mu\mathrm{m}$. Finally, the isotropic structure arises in the bulk of LC at $T \gtrsim 345.31\,\mathrm{K}$. At $T \approx 345.31\,\mathrm{K}$, the nematic structure arises at the particles' surfaces at $r_0 \gtrsim 2.00\,\mu\mathrm{m}$, while the conventionally isotropic phase arises at the particles' surfaces at $r_0 \lesssim 2.00\,\mu\mathrm{m}$. At $T \gtrsim 347.68\,\mathrm{K}$, the nematic structure cannot arise at the particles' surfaces anymore at any particles' size, and only conventionally isotropic structure arises. The $T \approx 347.68\,\mathrm{K}$ temperature corresponds to the limit nematic-isotropic transition border at $r_0 \to \infty$. Below we are going to consider the dependencies of the prime orientational order parameter S_2 and the main parameter $\mathrm{Var}(\sin^2\beta)$ characterizing the layering of molecules on the distance r–r_0 from the particle's surface at several particular points in the diagram presented in Fig. 6, which are shown by triangles.

C. Variation of the LC order parameters in the space near the spherical particles with homeotropic boundary conditions

Once both the orientational and translational order parameters are obtained at r_0 from Eqs. (52)–(53) and in the infinity from Eqs. (54)–(55), they can be substituted into the differential Eq. (50) as the integration limits at zero step, from where the whole $\{S_k(r)\}$ and $\{\sigma_k(r)\}$ dependencies could be obtained using a simple numerical scheme. The plus or minus signs in Eq. (50) should be chosen from comparison of the order parameters at r_0 and in the infinity, to fulfill the increasing or decreasing orientational order parameters in an appropriate way. The only new problem arising in this scheme (which does not arise in the case of the uniform LC), is that both $S_2(r)$ and $S_4(r)$ dependencies participate now in both functions Φ_2 and Φ_4 in Eq. (50). More exactly, it is not known from the beginning, how $S_2(r)$ and $S_4(r)$ are correlated. As a simple approximation, since the explicit correlation is not too much important, we are using a model where $S_2(r)$ and $S_4(r)$ are linearly dependent of each other.

Knowing the orientational and translational order parameters at the surface of a particle r_0, one obtains the gradients of the orientational order parameters at the surface of a particle from Eq. (50), and thus, the orientational and translational order parameters at the next step of integration [the translational order parameters at the next step of integration should be directly substituted from Eqs. (37)–(38) after the substitution of the orientational order parameters at the same step into them]. Step by step, one can find out the whole evolution of the orientational and translational order parameters up to any distance from the spherical particle.

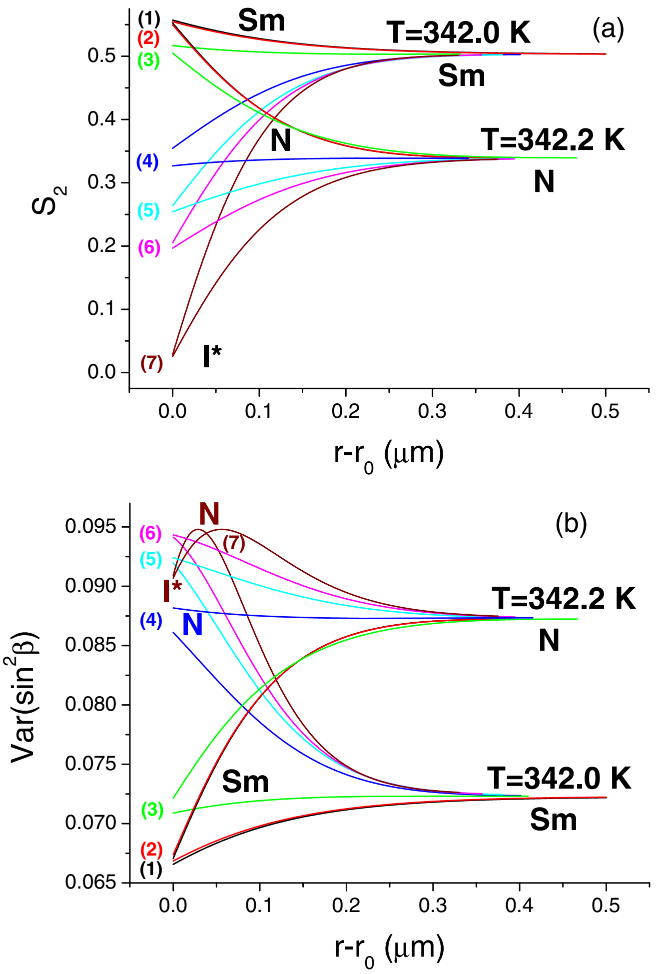

FIG. 7. The dependencies of the prime orientational order parameter (a) and of the variance of $\sin^2\beta$ (b) on the distance $r - r_0$ from the particle's surface just below (at $T = 342.0\,\mathrm{K}$, solid triangles in Fig. 6) and just above (at $T = 342.2\,\mathrm{K}$, hollow triangles in Fig. 6) the smectic-nematic transition temperature in the bulk of LC at various sizes of the particles: (1) $r_0 = \infty$ [flat surface]; (2) 10; (3) 3; (4) 2.5; (5) 1.9; (6) 1.55; (7) $1.25\,\mu\mathrm{m}$. Molecular parameters [constants participating in approximation Eqs. (17) and (51)] are the same as in Figs. 5 and 6. The color of each curve corresponds to the color of particular triangle in Fig. 6.

Since all the gradients of the orientational and translational order parameters are intimately related to the elastic constants (because they depend on the same coefficients $J^{(2)}_{\ell L\lambda}$ [see Eqs. (19), (34)–(36), and (44)] of the expansion of the pair intermolecular potential in spherical invariants), and since all the elastic constants are believed to be known from the experiment, one can evolve all possible variations of the LC orientational and translational order parameters in the space near the spherical particles with homeotropic boundary conditions. Several dependencies of the prime orientational order parameter S_2 and of the main parameter $\mathrm{Var}(\sin^2\beta)$ characterizing the smectic layering on the distance r–r_0 from the particle's surface are presented in Figs. 7 and 8. Molecular parameters [constants participating in approximation Eqs. (17) and (51)] are the same as in Figs. 5 and 6. Let us first consider the structures just below (at $T = 342.0\,\mathrm{K}$, solid triangles in Fig. 6) and just above (at $T = 342.2\,\mathrm{K}$, hollow triangles in Fig. 6) the smectic-nematic transition temperature in the bulk of LC. The corresponding r-dependencies of parameters S_2 and $\mathrm{Var}(\sin^2\beta)$ are presented in Fig. 7. At a flat surface $r_0 = \infty$ [curve (1)] and at the surfaces of large particles [$r_0 = 10$ and $3\,\mu\mathrm{m}$; curves (2) and (3), respectively] the smectic structure is realized, which is characterized by the high orientational order parameter S_2 and low $\mathrm{Var}(\sin^2\beta)$. At the surfaces of smaller particles [$r_0 = 2.5$, 1.9 and $1.55\,\mu\mathrm{m}$; curves (4), (5), and (6), respectively] the nematic structure is realized, which is characterized by the lower orientational order parameter S_2 and sufficiently higher $\mathrm{Var}(\sin^2\beta)$. Finally, at the surfaces of very small particles [$1.25\,\mu\mathrm{m}$, curve (7)] the conventionally isotropic structure is realized, which is characterized by the orientational order parameter S_2 close to zero, while the value $\mathrm{Var}(\sin^2\beta)$ does not differ from that

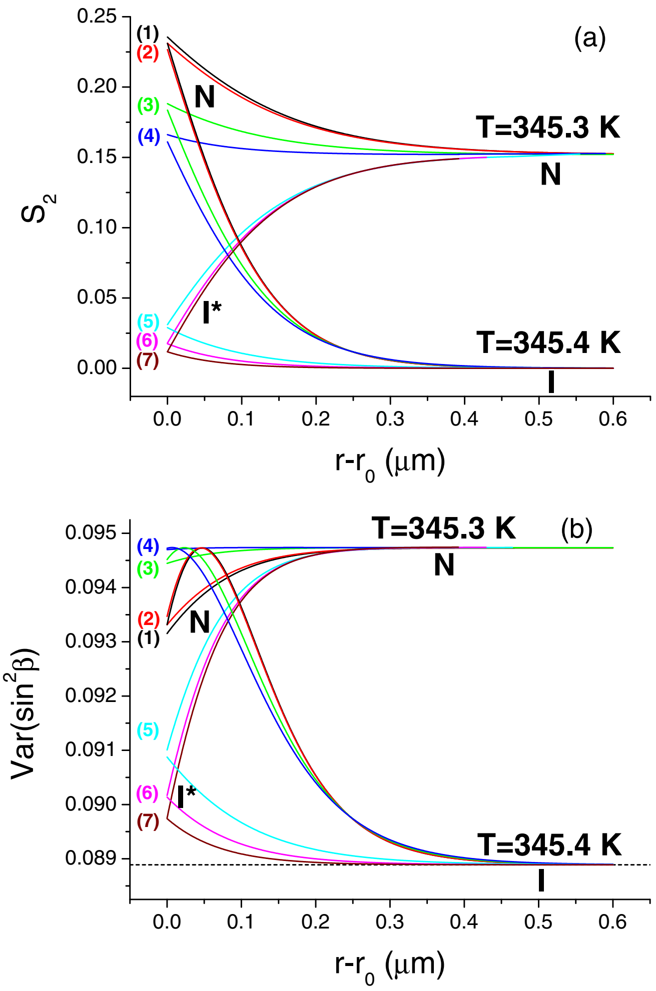

FIG. 8. The dependencies of the prime orientational order parameter (a) and of the variance of $\sin^2\beta$ (b) on the distance r–r_0 from the particle's surface just below (at $T = 345.3$ K, half up triangles in Fig. 6) and just above (at $T = 343.4$ K, half down triangles in Fig. 6) the nematic-isotropic transition temperature in the bulk of LC at various sizes of the particles: (1) $r_0 = \infty$ [flat surface]; (2) 10; (3) 3; (4) 2.5; (5) 1.9; (6) 1.55; (7) 1.25 μm. Molecular parameters [constants participating in approximation Eqs. (17) and (51)] are the same as in Figs. 5 and 6. The color of each curve corresponds to the color of particular triangle in Fig. 6. The 4/45 level of $\text{Var}(\sin^2\beta)$, corresponding to the uniform distribution of the intermolecular vectors, is shown by the dash line.

in the nematic phase very much, because the distribution of the intermolecular vectors in both isotropic and nematic phases is close to random. When the distance from the particle increases, all the structures evolve continuously either into the smectic structure [at $T = 342.0$ K] or into the nematic structure [at $T = 342.2$ K]. In particular, the conventionally isotropic phase [curve (7) at $T = 342.0$ K] can first evolve into the nematic structure, and then into the smectic structure. The information about that can be withdrawn from the fact that the value of $\text{Var}(\sin^2\beta)$ grows first and then decreases, while the value of S_2 monotonously increases with the increasing distance r, similarly to the evolution of S_2 and $\text{Var}(\sin^2\beta)$ [but continuously] with the decreasing temperature (Fig. 5).

Let us now consider the structures just below (at $T = 345.3$ K, half up triangles in Fig. 6) and just above (at $T = 345.4$ K, half down triangles in Fig. 6) the nematic-isotropic transition temperature in the bulk of LC. The corresponding r-dependencies of parameters S_2 and $\text{Var}(\sin^2\beta)$ are presented in Fig. 8. At a flat surface $r_0 = \infty$ [curve (1)] and at the surfaces of large particles [$r_0 = 10$, 3, and 2.5 μm; curves (2), (3), and (4), respectively] the nematic structure is realized, which is characterized by the moderate orientational order parameter S_2. At the surfaces of smaller particles [$r_0 = 1.9$, 1.55 and 1.25 μm; curves (5), (6), and (7), respectively] the conventionally isotropic structure is realized, which is characterized by the very low orientational order parameter S_2. The value of $\text{Var}(\sin^2\beta)$ does not differ in the nematic and conventionally isotropic structures very much [compared to that in the smectic structure, see Fig. 7(b)], because the distribution of the intermolecular vectors in both isotropic and nematic phases is close to random. However, in the nematic structure, it appears to be a little bit higher than in the conventionally isotropic structure. When the distance from the particle increases, all the structures evolve continuously either into the nematic structure [at $T = 345.3$ K] or into the isotropic structure [at $T = 345.4$ K]. A part of the curves in Fig. 8(b) reach their maxima at some distance r, when a pronounced broad intermolecular vectors distribution function peak arises, similarly to that in Fig. 5(b) and curve (7) in Fig. 7(b). The level 4/45 corresponding to the perfect random distribution of the intermolecular vectors is presented by the dash line in Fig. 8(b).

IV. CONCLUSION

The molecular-statistical theory reflecting both the orientational and translational order parameters inhomogeneity, as well as the director inhomogeneity, was derived in the present paper. An arbitrary configuration of the heterogeneous liquid crystal (LC) was considered. Our previous approach published in Ref. [40] was generalized for the case of inhomogeneous director distribution and inhomogeneous distribution of the order parameters. The self-consistent equations for determination of the orientational and translational order parameters have been obtained in the form of specific Boltzmann distributions, where the mean molecular field is in the exponent indicator of the orientational distribution function of the principal molecular axes $\mathbf{a}$ with respect to the local director $\mathbf{n}$, while the correlation function is in the exponent indicator of the translational distribution function of the unit intermolecular vectors $\mathbf{u}_{12}$ with respect to the local director $\mathbf{n}$. The local orientational and translational order parameters are introduced as $S_m \equiv \langle P_m(\mathbf{a}\cdot\mathbf{n})\rangle_{\mathbf{a}}$ and $\sigma_m/\sigma_0 \equiv \langle P_m(\mathbf{u}_{12}\cdot\mathbf{n})\rangle_{\mathbf{u}_{12}}$, where σ_0 is the average number of the nearest neighbors of a liquid crystal molecule, which is constant in the case of incompressible media. For the description of space inhomogeneity in both nematic and smectic states it is enough to consider the S_2 and S_4 orientational order parameters and the σ_2/σ_0 and σ_4/σ_0 translational order parameters. As a measure of smectic layering, the $\text{Var}(\mathbf{u}_{12}\cdot\mathbf{n})^2$ parameter was introduced that can be written in terms of the σ_2/σ_0 and σ_4/σ_0 order parameters. One readily notes that $\text{Var}(\mathbf{u}_{12}\cdot\mathbf{n})^2$ should tend to zero when all the $\mathbf{u}_{12}$ intermolecular vectors tend to be oriented within their plains. At random distribution of the $\mathbf{u}_{12}$ vectors over the sphere, $\mathrm{Var}(\mathbf{u}_{12}\cdot\mathbf{n})^2$ is equal to $4/45$. From our equations for the order parameters it follows that $\mathrm{Var}(\mathbf{u}_{12}\cdot\mathbf{n})^2$ is exactly equal to $4/45$ in the isotropic phase, and it is close to $4/45$ in the nematic phase. At the nematic to smectic phase transition, $\mathrm{Var}(\mathbf{u}_{12}\cdot\mathbf{n})^2$ reduces dramatically and further tends to zero, when the temperature further decreases.

The molecular pair potential was approximated by a set of spherical invariants $T_{\ell L\lambda}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2)$, which is complete orthogonal set of functions. The average of $T_{\ell L\lambda}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2)$ over the $\mathbf{a}_1$, $\mathbf{u}_{12}$ and $\mathbf{a}_2$ vectors is equal to $S_\ell(\mathbf{r}_1)\sigma_L(\mathbf{r}_1)S_\lambda(\mathbf{r}_2)P_\lambda(\mathbf{n}_1\cdot\mathbf{n}_2)$, where $\mathbf{n}_1$ is director at point $\mathbf{r}_1$ and $\mathbf{n}_2$ is director at point $\mathbf{r}_2$, and therefore the gradient expansions of the orientational order parameter $S_\lambda(\mathbf{r}_2)$ and of director $\mathbf{n}_2$ at point $\mathbf{r}_1$ have been used to obtain the self-consistent equations for the orientational and translational order parameters. The gradient expansion of director results in the appearance of the Frank elastic terms in the free energy, molecular field and correlation function, with the detailed molecular information about all five Frank elastic constants, while the gradient expansion of the orientational order parameter results in the differential equations of the second order for S_2 and S_4. Both expansions are expressed in terms of the same constants of approximation of the pair potential in spherical invariants. Knowing the values of elastic constants from the experiments, we have estimated the approximation constants, and thus, all quantitative characteristics participating in differential equations for the orientational order parameters have been fully defined.

The differential equations for the orientational order parameters have been solved numerically in the case of the radial distribution of director in spherical droplet with the solid particle placed in the center, which can be considered as a simple model of a liquid crystal composite with addition of low concentration of solid particles. As a result, the dependencies of the orientational S_2 and S_4 order parameters and of the translational σ_2/σ_0 and σ_4/σ_0 order parameters on the distance from spherical particles have been obtained at various temperatures and various sizes of the particles. Generally, the order parameters at the surface of a particle and on the periphery of a droplet (in the bulk of mesogenic material) are different, because of the two competing effects. The first effect is the direct anisotropic interaction of the LC molecules with solid surface. This effect enlarges the orientational (and thus, the translational) order parameters in the vicinity of the surface. The second effect is the deformation of director field in the vicinity of the curved surfaces, which diminishes the order parameters. As a result of this competition, the orientational and translational order parameters either appear to be higher than in the bulk (in the case of the large particles), or they appear to be lower than in the bulk (in the case of the small particles). It is also demonstrated that the kind of molecular self-organization (smectic, nematic or conventionally isotropic) at the surfaces of solid particles can be different from that in the bulk of mesogenic material. In the case of the large particles, the lower symmetry structures can be observed within particular temperature ranges at the surfaces of solid particles than those in the bulk of mesogenic material (the nematic areas near the surfaces of particles inside of the isotropic bulk, or the smectic areas near the surfaces of particles inside of the nematic bulk). On the contrary, in the case of the small particles, the higher symmetry structures can be observed within particular temperature ranges at the surfaces of solid particles than those in the bulk of mesogenic material (the almost isotropic areas near the surfaces of particles inside of the nematic or smectic bulk, or the nematic areas near the surfaces of particles inside of the smectic bulk). In these two cases, a significant space variations of the order parameters is observed within the 0.5–0.8 μm area *around* each particle, and the dimensions of these specific areas are almost independent of the particles' size. In any case, the material exhibits the double smectic-nematic phase transition and the double nematic-isotropic phase transition. The one of each duplet is related to a structure transition near the surfaces of particles, while another one is related to a structure transition in the bulk of mesogenic material. Totally we have found eight various combinations of states at the surfaces and in the bulk depending on the solid particles' size and temperature. It is also shown that the surfaces of 10 μm-radii solid particles and larger act almost as flat surfaces, while the surfaces of 1 μm-radii solid particles and smaller act almost as point defects. Therefore, the liquid crystals can be a simple tool for the optical visualization of nano-objects, around which the almost micrometer-size isotropic area should be observed inside of the nematic or smectic media.

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APPENDIX A: MEAN FIELD AND CORRELATION FUNCTION CONTRIBUTIONS RESPONSIBLE FOR THE GRADIENTS OF ORDER PARAMETERS

The same specific $(\mathbf{u}_{12}\cdot\nabla)^2$ operator acts on the orientational order parameters under the integrals in both Eqs. (25) and (26). Let us average this term over the azimuthal orientation of vector $\mathbf{u}_{12}$ and then collect the projections on the director $\mathbf{n}_1$ and on the *xy*-plane perpendicular to director:

$$\frac{1}{2\pi}\int_0^{2\pi} d\varphi_{\mathbf{u}_{12}}(\mathbf{u}_{12}\cdot\nabla)^2=\frac{1}{2\pi}\int_0^{2\pi} d\varphi_{\mathbf{u}_{12}}\big[(\mathrm{u}_{12})_n^2\nabla_n^2+(\mathrm{u}_{12})_x^2\nabla_x^2+(\mathrm{u}_{12})_y^2\nabla_y^2\big]$$

$$
\begin{aligned}
&= \frac{1}{2\pi}\int_0^{2\pi} d\varphi_{\mathbf{u}_{12}}\{(\mathbf{u}_{12}\cdot\mathbf{n}_1)^2\nabla_n^2 + [1-(\mathbf{u}_{12}\cdot\mathbf{n}_1)^2][\cos^2\varphi_{\mathbf{u}_{12}}\nabla_x^2 + \sin^2\varphi_{\mathbf{u}_{12}}\nabla_y^2]\}\\
&= \frac{1}{2}[1-(\mathbf{u}_{12}\cdot\mathbf{n}_1)^2]\boldsymbol{\nabla}^2 + \left[\frac{3}{2}(\mathbf{u}_{12}\cdot\mathbf{n}_1)^2 - \frac{1}{2}\right](\mathbf{n}_1\cdot\boldsymbol{\nabla})^2\\
&= \frac{1}{3}[1-P_2(\mathbf{u}_{12}\cdot\mathbf{n}_1)]\boldsymbol{\nabla}^2 + P_2(\mathbf{u}_{12}\cdot\mathbf{n}_1)(\mathbf{n}_1\cdot\boldsymbol{\nabla})^2. \qquad \text{(A1)}
\end{aligned}
$$

Multiplication of Eq. (A1) by Legendre polynomials $P_L(\mathbf{u}_{12}\cdot\mathbf{n}_1)$ yields Eqs. (26) and (27) for the part of the correlation function related to the gradients of order parameters. If one further integrates the obtained expressions over zenithal orientation of vector $\mathbf{u}_{12}$ with $\rho\,[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]$ weight using definition (2) for the translational order parameters, then one obtains Eq. (25) for the mean field related to the gradients of order parameters.

APPENDIX B: MEAN FIELD AND CORRELATION FUNCTION CONTRIBUTIONS RESPONSIBLE FOR THE DIRECTOR DEFORMATION

To obtain the mean field Eq. (28) and correlation function Eq. (29) contributions responsible for the director deformation, one should substitute the second part of expansion from Eq. (20) into all spherical invariants $T_{\ell L\lambda}(\mathbf{n}_1,\mathbf{u}_{12},\mathbf{n}_2)$ Eq. (18). In the case of the mean field [Eq. (28)] one should also integrate the result over the unit intermolecular vector $\mathbf{u}_{12}$ with $\rho\,[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]$ weight using definition Eq. (2) for the translational order parameters. Let us make these calculations for each spherical invariant. Integrations will result in the appearance of the following four independent values in various combinations:

$$
\begin{aligned}
-n_\alpha\,\boldsymbol{\nabla}^2 n_\alpha &= (\nabla_\alpha n_\beta)^2 = (\boldsymbol{\nabla}\cdot\mathbf{n})^2 + (\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2 + [\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2 - \boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}) - (\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n}),\\
(\boldsymbol{\nabla}\cdot\mathbf{n})^2 + (\nabla_\beta n_\alpha)(\nabla_\alpha n_\beta) + (\nabla_\alpha n_\beta)^2 &= 3(\boldsymbol{\nabla}\cdot\mathbf{n})^2 + (\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2 + [\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2 - 2\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}) - (\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n}),\\
-n_\alpha\nabla_\alpha\nabla_\beta n_\beta &= (\boldsymbol{\nabla}\cdot\mathbf{n})^2 - \boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})),\\
-n_\alpha n_\beta n_\gamma\nabla_\alpha\nabla_\beta n_\gamma &= [\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2. \qquad \text{(B1)}
\end{aligned}
$$

One notes that the square splay $(\boldsymbol{\nabla}\cdot\mathbf{n})^2$, the square twist $(\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2$, the square bend $[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2$, the saddle-splay $-\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}) - (\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n})$ and the splaybend $\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}))$ can be written in terms of the four independent values Eq. (B1). Using constraint Eq. (8), let us define for any function $Q(\mathbf{n}_2)$ its average increment $\langle\Delta Q(\mathbf{n}_2)\rangle \equiv V_0/\sigma_0\int d^2\mathbf{u}_{12}\rho[(\mathbf{u}_{12}\cdot\mathbf{n}_1),\mathbf{r}_1]\{Q(\mathbf{n}_2) - Q(\mathbf{n}_1)\}$. The following universal rules for the averages of multiplications of projections of vector $\mathbf{u}_{12}$ on the Cartesian axes should be used:

$$
\langle u_\alpha u_\beta\rangle = \frac{1}{3}\delta_{\alpha\beta}(1-\sigma_2/\sigma_0) + n_\alpha n_\beta\sigma_2/\sigma_0, \qquad \text{(B2)}
$$

$$
\begin{aligned}
\langle u_\alpha u_\beta u_\gamma u_\delta\rangle = {}& (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\alpha\delta} + \delta_{\beta\delta}\delta_{\alpha\gamma})\left\{\frac{1}{15} - \frac{2}{21}\frac{\sigma_2}{\sigma_0} + \frac{1}{35}\frac{\sigma_4}{\sigma_0}\right\} + \frac{1}{7}(n_\alpha n_\beta\delta_{\gamma\delta} + n_\alpha n_\gamma\delta_{\beta\delta}\\
&+ n_\alpha n_\delta\delta_{\beta\gamma} + n_\beta n_\gamma\delta_{\alpha\delta} + n_\beta n_\delta\delta_{\alpha\gamma} + n_\gamma n_\delta\delta_{\alpha\beta})(\sigma_2-\sigma_4)/\sigma_0 + n_\alpha n_\beta n_\gamma n_\delta\sigma_4/\sigma_0, \qquad \text{(B3)}
\end{aligned}
$$

where δ is the Kronecker symbol. Using Eqs. (B1)–(B3) and expansion Eq. (20) up to the square term in $\boldsymbol{\nabla}$, one obtains

$$
\begin{aligned}
\langle\Delta(\mathbf{n}_1\cdot\mathbf{n}_2)^2\rangle &= \langle\mathbf{n}_1\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}_1\rangle = \langle n_\alpha u_\beta\nabla_\beta u_\gamma\nabla_\gamma n_\alpha\rangle\\
&= \frac{1}{3}(1-\sigma_2/\sigma_0)n_\alpha\boldsymbol{\nabla}^2 n_\alpha + \sigma_2/\sigma_0 n_\alpha n_\beta n_\gamma\nabla_\alpha\nabla_\beta n_\gamma\\
&= -\frac{1}{3}\left(1-\frac{\sigma_2}{\sigma_0}\right)\{(\boldsymbol{\nabla}\cdot\mathbf{n})^2 + (\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2 - \boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})\\
&\quad - (\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n})\} - \frac{1}{3}(1+2\sigma_2/\sigma_0)[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n})]]^2, \qquad \text{(B4)}
\end{aligned}
$$

$$
\langle\Delta(\mathbf{n}_1\cdot\mathbf{u}_{12})^2\rangle = 0, \qquad \text{(B5)}
$$

$$
\begin{aligned}
\langle\Delta(\mathbf{n}_2\cdot\mathbf{u}_{12})^2\rangle &= \langle(\mathbf{u}_{12}\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})\mathbf{n}_1)^2 + (\mathbf{u}_{12}\cdot\mathbf{n}_1)(\mathbf{u}_{12}\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}_1)\rangle\\
&= \langle(u_\alpha u_\beta\nabla_\beta n_\alpha)(u_\gamma u_\delta\nabla_\delta n_\gamma) + u_\alpha n_\alpha u_\beta u_\gamma\nabla_\gamma u_\delta\nabla_\delta n_\beta\rangle\\
&= \left(\frac{1}{15} - \frac{2}{21}\frac{\sigma_2}{\sigma_0} + \frac{1}{35}\frac{\sigma_4}{\sigma_0}\right)[(\boldsymbol{\nabla}\cdot\mathbf{n})^2 + (\nabla_\alpha n_\beta)^2 + (\nabla_\beta n_\alpha)(\nabla_\alpha n_\beta)]
\end{aligned}
$$

$$
\begin{aligned}
&+\left(\frac{1}{15}+\frac{1}{21}\frac{\sigma_2}{\sigma_0}-\frac{4}{35}\frac{\sigma_4}{\sigma_0}\right)(n_\alpha\nabla^2 n_\alpha+2n_\alpha\nabla_\alpha\nabla_\beta n_\beta)+\frac{2\sigma_2+5\sigma_4}{7\sigma_0}n_\alpha n_\beta n_\gamma\nabla_\alpha\nabla_\beta n_\gamma\\
&=-\frac{\sigma_2-\sigma_4}{7\sigma_0}\{3(\boldsymbol{\nabla}\cdot\mathbf{n})^2+(\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2\}-\frac{3\sigma_2+4\sigma_4}{7\sigma_0}[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2\\
&-\left(\frac{1}{15}-\frac{5}{21}\frac{\sigma_2}{\sigma_0}+\frac{6}{35}\frac{\sigma_4}{\sigma_0}\right)\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})-(\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n})+\left(\frac{2}{15}+\frac{2}{21}\frac{\sigma_2}{\sigma_0}-\frac{8}{35}\frac{\sigma_4}{\sigma_0}\right)\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})),
\end{aligned}
\tag{B6}
$$

$$
\begin{aligned}
&\langle\Delta\{(\mathbf{n}_1\cdot\mathbf{n}_2)(\mathbf{n}_1\cdot\mathbf{u}_{12})(\mathbf{n}_2\cdot\mathbf{u}_{12})\}\rangle\\
&=\langle(\mathbf{u}_{12}\cdot\mathbf{n}_1)(\mathbf{u}_{12}\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}_1)+(\mathbf{u}_{12}\cdot\mathbf{n}_1)^2(\mathbf{n}_1\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}_1)\rangle/2\\
&=\langle u_\alpha n_\alpha u_\beta u_\gamma\nabla_\gamma u_\delta\nabla_\delta n_\beta+u_\alpha n_\alpha u_\beta n_\beta n_\mu u_\gamma\nabla_\gamma u_\delta\nabla_\delta n_\mu\rangle/2\\
&=\left(\frac{1}{15}+\frac{1}{21}\frac{\sigma_2}{\sigma_0}-\frac{4}{35}\frac{\sigma_4}{\sigma_0}\right)(n_\alpha\nabla^2 n_\alpha+n_\alpha\nabla_\alpha\nabla_\beta n_\beta)+\left(\frac{1}{15}+\frac{10}{21}\frac{\sigma_2}{\sigma_0}+\frac{16}{35}\frac{\sigma_4}{\sigma_0}\right)n_\alpha n_\beta n_\gamma\nabla_\alpha\nabla_\beta n_\gamma\\
&=-\left(\frac{1}{15}+\frac{1}{21}\frac{\sigma_2}{\sigma_0}-\frac{4}{35}\frac{\sigma_4}{\sigma_0}\right)\{2(\boldsymbol{\nabla}\cdot\mathbf{n})^2+(\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2-\boldsymbol{\nabla}\cdot(2\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})-(\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n})\}\\
&-\left(\frac{2}{15}+\frac{11}{21}\frac{\sigma_2}{\sigma_0}+\frac{12}{35}\frac{\sigma_4}{\sigma_0}\right)[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2,
\end{aligned}
\tag{B7}
$$

$$
\begin{aligned}
\langle\Delta\{(\mathbf{n}_1\cdot\mathbf{n}_2)^2(\mathbf{n}_1\cdot\mathbf{u}_{12})^2\}\rangle&=\langle(\mathbf{u}_{12}\cdot\mathbf{n}_1)^2(\mathbf{n}_1\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}_1)\rangle\\
&=\langle u_\alpha n_\alpha u_\beta n_\beta n_\mu u_\gamma\nabla_\gamma u_\delta\nabla_\delta n_\mu\rangle\\
&=\left(\frac{1}{15}+\frac{1}{21}\frac{\sigma_2}{\sigma_0}-\frac{4}{35}\frac{\sigma_4}{\sigma_0}\right)n_\alpha\nabla^2 n_\alpha+\left(\frac{2}{15}+\frac{11}{21}\frac{\sigma_2}{\sigma_0}+\frac{12}{35}\frac{\sigma_4}{\sigma_0}\right)n_\alpha n_\beta n_\gamma\nabla_\alpha\nabla_\beta n_\gamma\\
&=-\left(\frac{1}{15}+\frac{1}{21}\frac{\sigma_2}{\sigma_0}-\frac{4}{35}\frac{\sigma_4}{\sigma_0}\right)\{(\boldsymbol{\nabla}\cdot\mathbf{n})^2+(\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2-\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})-(\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n})\}\\
&-\left(\frac{1}{5}+\frac{4}{7}\frac{\sigma_2}{\sigma_0}+\frac{8}{35}\frac{\sigma_4}{\sigma_0}\right)[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2,
\end{aligned}
\tag{B8}
$$

$$
\begin{aligned}
\langle\Delta\{(\mathbf{n}_1\cdot\mathbf{n}_2)^2(\mathbf{n}_2\cdot\mathbf{u}_{12})^2\}\rangle&=\langle(\mathbf{u}_{12}\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})\mathbf{n}_1)^2+(\mathbf{u}_{12}\cdot\mathbf{n}_1)^2(\mathbf{n}_1\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}_1)+(\mathbf{u}_{12}\cdot\mathbf{n}_1)(\mathbf{u}_{12}\cdot(\mathbf{u}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}_1)\rangle\\
&=\langle(u_\alpha u_\beta\nabla_\beta n_\alpha)(u_\gamma u_\delta\nabla_\delta n_\gamma)+u_\alpha n_\alpha u_\beta n_\beta n_\mu u_\gamma\nabla_\gamma u_\delta\nabla_\delta n_\mu+u_\alpha n_\alpha u_\beta u_\gamma\nabla_\gamma u_\delta\nabla_\delta n_\beta\rangle\\
&=\left(\frac{1}{15}-\frac{2}{21}\frac{\sigma_2}{\sigma_0}+\frac{1}{35}\frac{\sigma_4}{\sigma_0}\right)((\boldsymbol{\nabla}\cdot\mathbf{n})^2+(\nabla_\alpha n_\beta)^2+(\nabla_\beta n_\alpha)(\nabla_\alpha n_\beta))\\
&+\left(\frac{2}{15}+\frac{2}{21}\frac{\sigma_2}{\sigma_0}-\frac{8}{35}\frac{\sigma_4}{\sigma_0}\right)(n_\alpha\nabla^2 n_\alpha+n_\alpha\nabla_\alpha\nabla_\beta n_\beta)+\left(\frac{2}{15}+\frac{17}{21}\frac{\sigma_2}{\sigma_0}+\frac{37}{35}\frac{\sigma_4}{\sigma_0}\right)n_\alpha n_\beta n_\gamma\nabla_\alpha\nabla_\beta n_\gamma\\
&=-\left(\frac{1}{15}+\frac{10}{21}\frac{\sigma_2}{\sigma_0}-\frac{19}{35}\frac{\sigma_4}{\sigma_0}\right)(\boldsymbol{\nabla}\cdot\mathbf{n})^2-\left(\frac{1}{15}+\frac{4}{21}\frac{\sigma_2}{\sigma_0}-\frac{9}{35}\frac{\sigma_4}{\sigma_0}\right)(\mathbf{n}\cdot[\boldsymbol{\nabla}\times\mathbf{n}])^2\\
&-\left(\frac{1}{5}+\frac{\sigma_2}{\sigma_0}+\frac{4}{5}\frac{\sigma_4}{\sigma_0}\right)[\mathbf{n}\times[\boldsymbol{\nabla}\times\mathbf{n}]]^2+\frac{2}{7\sigma_0}(\sigma_2-\sigma_4)\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})-(\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n})\\
&+\left(\frac{2}{15}+\frac{2}{21}\frac{\sigma_2}{\sigma_0}-\frac{8}{35}\frac{\sigma_4}{\sigma_0}\right)\boldsymbol{\nabla}\cdot(\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})).
\end{aligned}
\tag{B9}
$$

One notes that Eqs. (B5), (B6), (B8), and (B9) appeared to be nonsymmetrical with respect to the replacement of indexes 1 and 2. This happened, because we selected molecule 1 as a test molecule and molecule 2 belonging to the "molecular surrounding" affecting molecule 1. Obviously, we could do just in an opposite way, while, in fact, molecules 1 and 2 are in the same conditions. Therefore the final expressions for the gradients of spherical invariants $T_{\ell L\lambda}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2)$ should be symmetrical with respect to replacement of indexes 1 and 2. Since the replacement of indexes 1 and 2 in spherical invariants Eq. (18) is equivalent to the replacement of indexes ℓ and λ, the final expressions for the gradients should be averaged with respect to this replacement. Taking this into account, substituting Eqs. (B4)–(B9) into the definitions of spherical invariants Eq. (18) and collecting the similar terms, one obtains mean field energy Eq. (28) responsible for the director deformation. To obtain the correlation function Eq. (29) one should take into account that all the averages with respect to the *azimuthal* orientation of vector $\mathbf{u}_{12}$ are the same as in Eqs. (B5)–(B9), while all the translational order parameters σ_L ($L = 0$, 2, and 4) should be replaced with the corresponding Legendre polynomials $P_L(\mathbf{u}_{12}\cdot\mathbf{n}_1)$ (which are the corresponding expressions before integration with respect to vector $\mathbf{u}_{12}$ over the sphere).

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