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Structure, elasticity and phase transitions in liquid crystals with deformations

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ABSTRACT

A molecular-statistical theory describing the nematic liquid crystals (LCs) with spherical inclusions (or point defects) is proposed. At given size of inclusions and nematic order parameters at the surfaces of inclusions (zero in the case of point defects) and far from inclusions (where the nematic LC is almost uniform), the distribution of nematic order parameters in the bulk of LC with inclusions was found to be fully determined by the elastic constants of LC. We have found and explained the two-step heat-driven transformation from the nematic phase into the isotropic phase, with the intermediate phase in between. The nematic order parameters and the elastic constants are evaluated in the framework of a unified approach based on the features of pair interaction potentials of the individual LC molecules. It is shown that, in the case of $K_{33} < K_{11}$, the point defects should destroy the conventional nematic phase.

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1. Introduction

The liquid crystal (LC) structures of various classes near the surfaces were investigated recently.[1,2] In particular, the induction of nematic ordering in the isotropic phase near the surface was investigated and the corresponding memory effect was outlined in [3–6]. The nematic–isotropic phase transition in the presence of a flat surface was studied in the framework of Landau–de Gennes theory [7–12] and in the framework of Onsager approximation.[13,14] Biaxial nematic phase induced by the surface was also predicted theoretically [15] and by computer simulation.[16] However, at the moment, there is no thermodynamic description of the local ordering of the molecules near the distorted surfaces. Such a description is crucial for the investigation of complex topology structures in nematic LCs with inclusions (or defects). In [17], we developed the molecular mean-field theory for the ordering of a nematic LC and its two-step melting near a flat surface, which is in a good agreement with the experiment.[18] In highly sensitive differential scanning calorimetry measurements, a narrow peak corresponding to the transition near a flat surface is observed at higher temperature than the wide peak corresponding to the phase transition in the bulk. Recently, different experiments [19] have found out the two-step melting of nematic materials mixed with spherical nanoparticles (SiO), but the sequence of transitions appeared to be reversed to that at a flat surface, because the splay deformation near the surfaces of nanoparticles reduces the nematic order. In this paper, we propose the molecular-statistical approach, describing a correlation between the elastic constants and the nematic order parameters.

2. Theoretical approach

Let us assume the normal surface conditions at each spherical inclusion. Since the concentration of inclusions in an LC sample is small, let us assume that each inclusion is surrounded by an infinite nematic media, where the deformations of director can be sufficiently large only in the vicinity of inclusions. In this case, the task reduces to consideration of single spherical inclusion in the middle of a spherical droplet filled with nematic LC with free surface conditions at the outer part of the droplet (see Figure 1(a)). One can expect the hedgehog director distribution inside this droplet.

Since any direct intermolecular interaction is of very short range, the surface of inclusion influences directly only the nearest molecules, but this influence is transmitted through the bulk because of the interactions of LC molecules with each other. The bulk free energy of LC per unit solid angle of the sphere can be written in a form of generalized Maier–Saupe theory for inhomogeneous distribution of the nematic order along the radius of the droplet [17]:

$$F = \rho k_B T \int d^2 \mathbf{a}_1 \int r_1^2 dr_1 f((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) \ln f((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) + \frac{1}{2} \rho^2 \int d^2 \mathbf{a}_1 \int d^2 \mathbf{a}_2 \int r_1^2 dr_1 \int d^3 \mathbf{r}_{12} f((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) f((\mathbf{a}_2 \cdot \mathbf{n}_2), r_2) U_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}) + \rho \int d^2 \mathbf{a}_1 \int r_1^2 dr_1 f((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) W((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1), \quad (1)$$

where ρ is the concentration of LC molecules, r_i is the distance of LC molecule i from the center of inclusion. In Equation (1), the orientational distribution function for each molecule $f((\mathbf{a}_i \cdot \mathbf{n}_i), r_i)$ is assumed to depend on the distance r_i , while the director \mathbf{n}_i at a point, where molecule i is located, depends on the angular orientation of vector \mathbf{r}_i , $U_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12})$ is the interaction potential between LC molecules 1 and 2, and $W((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1)$ is the interaction potential of each LC molecule with the surface of inclusion. The first term in Equation (1) is the orientational entropy, the second term is the internal energy, and the third term is the average interaction energy of LC media with the surface of inclusion. Minimizing the free energy functional in Equation (1) with respect to the distribution function $f((\mathbf{a} \cdot \mathbf{n}), r)$ in the bulk of LC (where the third term in Equation (1) can be neglected at this stage, because the bulk interactions dominate), taking into account the normalizing constraint for

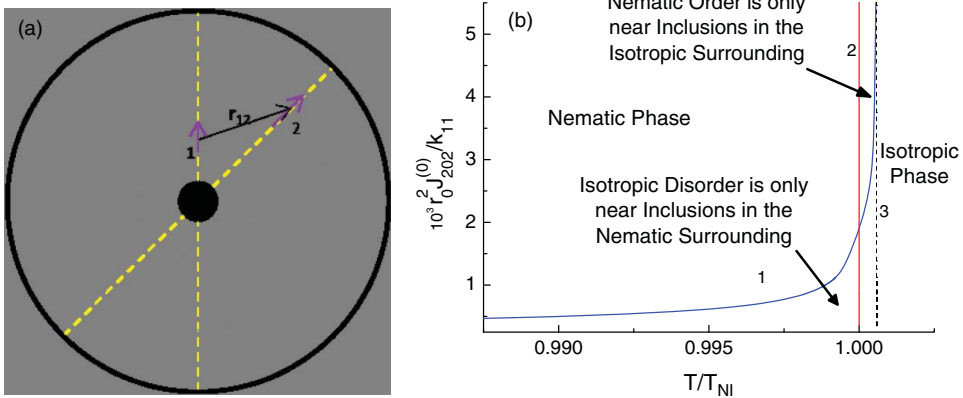


Figure 1. (a) Spherical inclusion in the center of a large spherical nematic droplet with free boundary conditions on the outer boundary of a droplet; r_{12} is the vector connecting the two LC molecules located at points 1 and 2; (b) phase diagram, where Curve 1 corresponds to a transition from nematic phase to the isotropic phase near the surface of inclusion; Curve 2 corresponds to the phase transition in the bulk; Curve 3 is an asymptote for the surface transition temperature in the case of a flat surface. Here, $J_{202}^{(0)}/k_B = 1440$ K; $J_{404}^{(0)}/k_B = 144$ K; $J_{22}^{(0)}/k_B = 2.95$ K; $J_{44}^{(0)}/k_B = 2.6$ K; $(k_{33} - k_{11})/(J_{202}^{(0)2} J_0^2) = 6.3 \times 10^{-4}$; $g_2/(J_{202}^{(0)2} J_0^2) = 4 \times 10^{-3}$. The homeotropic anchoring at the surface of inclusion is supposed.

the distribution function and introducing the local nematic order parameters

$$S_\ell(r) \equiv \int d^2\mathbf{a} f((\mathbf{a} \cdot \mathbf{n}), r) P_\ell(\mathbf{a} \cdot \mathbf{n}), \quad (2)$$

depending on the separation r from the center of inclusion, one obtains

$$S_\ell(r) = I_\ell(r)/I_0(r), \quad \text{where} \quad I_\ell \equiv \int_{-1}^1 d^2\mathbf{a} P_\ell(\mathbf{a} \cdot \mathbf{n}) \exp\left\{-\frac{U_{MF}((\mathbf{a} \cdot \mathbf{n}), r)}{k_B T}\right\}, \quad (3)$$

P_ℓ is the ℓ -th Legendre polynomial, and the mean field potential acting on a molecule located at point \mathbf{r}_1 , where nematic director has orientation \mathbf{n}_1 , is expressed as follows:

$$U_{MF}((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) = \rho \int d^2\mathbf{a}_2 \int d^3\mathbf{r}_{12} f((\mathbf{a}_2 \cdot \mathbf{n}_2), r_2) U_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}), \quad (4)$$

where $\mathbf{u}_{12} \equiv \mathbf{r}_{12}/|\mathbf{r}_{12}|$ is the unit intermolecular vector. Minimizing the free energy functional in Equation (1) with respect to the distribution function $f((\mathbf{a} \cdot \mathbf{n}), r)$ at the surface of inclusion (at $r = r_0$), one obtains recurrent equation in the same form (3) with the only difference that the surface potential $W((\mathbf{a} \cdot \mathbf{n}), r_0)$ should be added to the mean field potential $U_{MF}((\mathbf{a} \cdot \mathbf{n}), r_0)$. Let us approximate the intermolecular potential $U_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12})$ by spherical invariants [20,21] and the surface potential $W((\mathbf{a} \cdot \mathbf{n}), r_0)$ by Legendre polynomials:

$$U_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}) = - \sum_{\ell L \lambda} J_{\ell L \lambda}(r_{12}) T_{\ell L \lambda}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2), \quad W((\mathbf{a} \cdot \mathbf{n}), r_0) = - \sum_{\ell} J_{\ell}^s P_{\ell}(\mathbf{a} \cdot \mathbf{n}), \quad (5)$$

where the following spherical invariants are used for approximation:

$$\begin{aligned} T_{000}(\mathbf{x}, \mathbf{z}, \mathbf{y}) &= 1, & T_{202}(\mathbf{x}, \mathbf{z}, \mathbf{y}) &= P_2(\mathbf{x} \cdot \mathbf{y}) = \frac{3}{2}(\mathbf{x} \cdot \mathbf{y})^2 - \frac{1}{2}, \\ T_{222}(\mathbf{x}, \mathbf{z}, \mathbf{y}) &= \frac{9}{2}(\mathbf{x} \cdot \mathbf{y})(\mathbf{x} \cdot \mathbf{z})(\mathbf{y} \cdot \mathbf{z}) - \frac{3}{2}(\mathbf{x} \cdot \mathbf{y})^2 - \frac{3}{2}(\mathbf{x} \cdot \mathbf{z})^2 - \frac{3}{2}(\mathbf{y} \cdot \mathbf{z})^2 + 1, \\ T_{404}(\mathbf{x}, \mathbf{z}, \mathbf{y}) &= P_4(\mathbf{x} \cdot \mathbf{y}) = \frac{35}{8}(\mathbf{x} \cdot \mathbf{y})^4 - \frac{15}{4}(\mathbf{x} \cdot \mathbf{y})^2 + \frac{3}{8}, \\ T_{242}(\mathbf{x}, \mathbf{z}, \mathbf{y}) &= \frac{35}{8}(\mathbf{x} \cdot \mathbf{z})^2(\mathbf{y} \cdot \mathbf{z})^2 - \frac{5}{2}(\mathbf{x} \cdot \mathbf{y})(\mathbf{x} \cdot \mathbf{z})(\mathbf{y} \cdot \mathbf{z}) \\ &+ \frac{1}{4}(\mathbf{x} \cdot \mathbf{y})^2 - \frac{5}{8}(\mathbf{x} \cdot \mathbf{z})^2 - \frac{5}{8}(\mathbf{y} \cdot \mathbf{z})^2 + \frac{1}{8}, \end{aligned} \quad (6)$$

and also the spherical invariants $T_{L\ell\lambda}(\mathbf{x}, \mathbf{z}, \mathbf{y}) = T_{\ell L\lambda}(\mathbf{z}, \mathbf{x}, \mathbf{y})$ and $T_{\ell\lambda L}(\mathbf{x}, \mathbf{z}, \mathbf{y}) = T_{\ell\lambda L}(\mathbf{x}, \mathbf{y}, \mathbf{z})$ corresponding to commutation of the indexes in invariants (6). Each vector \mathbf{a}_1 , \mathbf{a}_2 , or \mathbf{u}_{12} can be substituted instead by one of each argument \mathbf{x} , \mathbf{y} , or \mathbf{z} . One notes that the average of any spherical invariant $T_{\ell L \lambda}(\mathbf{x}, \mathbf{z}, \mathbf{y})$ with respect to any of its arguments is the order parameter of kind (2) (ℓ -th for \mathbf{x} , L -th for \mathbf{y} and λ -th for \mathbf{z}) with appropriate distribution function. For both vectors \mathbf{a}_1 and \mathbf{a}_2 , the distribution function is $f((\mathbf{a} \cdot \mathbf{n}), r)$, while for vector \mathbf{u}_{12} , the distribution function is $1/(4\pi)$, because distribution of vector \mathbf{u}_{12} is isotropic in the nematic state. In particular, in the homogeneous nematic state, where the order parameters S_ℓ and director \mathbf{n} are uniform, only spherical invariants $T_{\ell 0 \ell}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2)$ (with index L equal to zero and with index λ equal to index ℓ) contribute in average. On the contrary, in the deformed nematic and/or in the nematic with gradients of the order parameters, the other spherical invariants will also contribute. Coefficients $J_{\ell L \lambda}(r_{12})$ depend only on distance

r_{12} between molecules 1 and 2. Substituting Equation (5) into Equation (4), one obtains

$$U_{MF}((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) = -\rho \int d^3 \mathbf{r}_{12} \sum_{\ell L \lambda} J_{\ell L \lambda}(r_{12}) S_\lambda(r_2) T_{\ell L \lambda}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{n}_2), \quad (7)$$

where \mathbf{n}_2 is the nematic director at point \mathbf{r}_2 . One can use the gradient expansion for the order parameters and director:

$$S_\lambda(r_2) \approx S_\lambda(r_1) + \frac{1}{2}(\mathbf{r}_{12} \cdot \nabla)^2 S_\lambda(r_1), \quad \mathbf{n}_2 \approx \mathbf{n}_1 + (\mathbf{r}_{12} \cdot \nabla) \mathbf{n}_1 + \frac{1}{2}(\mathbf{r}_{12} \cdot \nabla)^2 \mathbf{n}_1. \quad (8)$$

Taking into account that the order parameters and the director distribution weakly depend on the distance r_{12} between molecules in comparison with functions $J_{\ell L \lambda}(r_{12})$, one can estimate the integral over distance r_{12} in Equation (7) by the saddle point method.[22] Introducing coefficients

$$J_{\ell L \lambda}^{(i)} \equiv \int_0^\infty dr_{12} r_{12}^{i+2} J_{\ell L \lambda}(r_{12}), \quad (9)$$

and considering only up to the square gradients either in S or in \mathbf{n} , one obtains

$$U_{MF}((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) = -4\pi\rho \sum_{\ell=2,4} J_{\ell 0 \ell}^{(0)} S_\ell(r_1) P_\ell(\mathbf{a}_1 \cdot \mathbf{n}_1) + \Delta U_{MF}^S((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) + \Delta U_{MF}^n((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1), \quad (10)$$

where the first term is the mean field of the homogeneous nematic state. The second term in Equation (10) reflects the gradients of the nematic order parameters:

$$\begin{aligned} \Delta U_{MF}^S((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) &= -\frac{1}{2}\rho \sum_{\ell L \lambda} J_{\ell L \lambda}^{(2)} \int d^2 \mathbf{u}_{12} T_{\ell L \lambda}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{n}_1) (\mathbf{u}_{12} \cdot \nabla)^2 S_\lambda(r_1) \\ &= -4\pi\rho \{S_2''(r_1)[g_2 P_2(\mathbf{a}_1 \cdot \mathbf{n}_1) + g_4 P_4(\mathbf{a}_1 \cdot \mathbf{n}_1)] + S_4''(r_1)g_4 P_4(\mathbf{a}_1 \cdot \mathbf{n}_1)\}, \end{aligned} \quad (11)$$

where $S_\ell''(r_1) \equiv \partial^2 S_\ell / \partial r^2|_{r=r_1}$, and the propagation constants g_2 and g_4 in the case of spherical symmetry are expressed as follows:

$$g_2 = \frac{1}{6}J_{202}^{(2)} + \frac{1}{15}J_{222}^{(2)}, \quad g_4 = \frac{1}{30} \left[J_{422}^{(2)} + J_{224}^{(2)} \right]. \quad (12)$$

The third term in Equation (10) is responsible for the deformation of director:

$$\begin{aligned} \Delta U_{MF}^n((\mathbf{a}_1 \cdot \mathbf{n}_1), r_1) &= -\frac{1}{2}\rho \sum_{\ell L \lambda} J_{\ell L \lambda}^{(2)} S_\lambda(r_1) \int d^2 \mathbf{u}_{12} \{T_{\ell L \lambda}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{n}_2) - T_{\ell L \lambda}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{n}_1)\}, \\ &= \frac{2\pi}{7}\rho (\text{div } \mathbf{n}_1)^2 \left\{ (11k_{11} + 3k_{33})S_2(r_1)P_2(\mathbf{a}_1 \cdot \mathbf{n}_1) - 3(k_{33} - k_{11})\frac{S_2^2(r_1)}{S_4(r_1)}P_4(\mathbf{a}_1 \cdot \mathbf{n}_1) \right\}, \end{aligned} \quad (13)$$

where only the splay deformation $\text{div } \mathbf{n}_1 \equiv 1/r_1$ is present in the case of the hedgehog structure, while, in the general case, the three reduced elastic constants $k_{11} \equiv K_{11}/S_2^2$, $k_{22} \equiv K_{22}/S_2^2$ and

$k_{33} \equiv K_{33}/S_2^2$ are expressed as follows:

$$\begin{aligned} k_{11} &= \frac{1}{4}J_{202}^{(2)} + \frac{1}{20}J_{222}^{(2)} - \frac{1}{8}\left[J_{422}^{(2)} + J_{224}^{(2)}\right]\frac{S_4}{S_2}, \\ k_{22} &= \frac{1}{4}J_{202}^{(2)} - \frac{1}{10}J_{222}^{(2)} - \frac{1}{24}\left[J_{422}^{(2)} + J_{224}^{(2)}\right]\frac{S_4}{S_2}, \\ k_{33} &= \frac{1}{4}J_{202}^{(2)} + \frac{1}{20}J_{222}^{(2)} + \frac{1}{6}\left[J_{422}^{(2)} + J_{224}^{(2)}\right]\frac{S_4}{S_2}. \end{aligned} \quad (14)$$

One notes that the average of Equation (13) with respect to vector \mathbf{a}_1 contains only one elastic constant k_{11} , as it should be in the case of pure splay deformation. Since the propagation constants (12) and the elastic constants (14) are expressed in terms of the same interaction constants $J_{\ell L}^{(2)}$, they appear to be linearly dependent of each other:

$$g_2 = \frac{2}{3}\bar{k} + \frac{4}{9}\left(\frac{5}{7}k_{11} - k_{22} + \frac{2}{7}k_{33}\right), \quad g_4 = \frac{4}{35}(k_{33} - k_{11})\frac{S_2}{S_4}, \quad (15)$$

where $\bar{k} \equiv (k_{11} + k_{22} + k_{33})/3$ is the average elastic constant. Substituting Equations (11)–(14) into Equation (10), one obtains the following expression for the integrals in Equation (3):

$$\begin{aligned} I_\ell(r) &\equiv \int_{-1}^1 dt P_\ell(t) \exp\left\{\frac{\rho}{k_B T} \left[J_2(r)S_2(r)P_2(t) + J_4(r)S_4(r)P_4(t) + S_2''(r)(g_2P_2(t) \right. \right. \\ &\quad \left. \left. + g_4P_4(t)) + S_4''(r)g_4P_2(t) \right] \right\}, \quad \text{where } t \equiv (\mathbf{a} \cdot \mathbf{n}) \end{aligned} \quad (16)$$

$$J_2(r) \equiv J_{202}^{(0)} - \frac{k_{11}}{r^2} - \frac{3}{14r^2}(k_{33} - k_{11}), \quad J_4(r) \equiv J_{404}^{(0)} + \frac{3}{14r^2}(k_{33} - k_{11})\frac{S_2^2(r)}{S_4^2(r)}, \quad (17)$$

where elastic constants k_{11} and k_{33} are in correspondence with Equation (14). Taking into account that gradients terms S_2'' and S_4'' are small with respect to the other terms in Equation (16), the exponent can be expanded in Taylor series with respect to them, and one can take into account only the first terms in these expansions explicitly depending on S_2'' and S_4'' . Then, instead of recurrent Equation (3), one obtains

$$S_2''(r) = \frac{\rho}{k_B T} \Phi_2(S_2(r), S_4(r)), \quad S_4''(r) = \frac{\rho}{k_B T} \Phi_4(S_2(r), S_4(r)), \quad (18)$$

where

$$\begin{aligned} \Phi_2(S_2, S_4) &\equiv \frac{1}{g_4} \frac{I_{22}(S_4 I_{00} - I_{04}) - I_{24}(S_2 I_{00} - I_{02}) - I_{02}(S_4 I_{02} - S_2 I_{04})}{I_{24}(S_4 I_{02} - I_{24}) - I_{44}(S_2 I_{02} - I_{22}) - I_{04}(S_4 I_{22} - S_2 I_{24})}, \\ \Phi_4(S_2, S_4) &\equiv -\frac{1}{g_4} \frac{I_{24}(S_4 I_{00} - I_{04}) - I_{44}(S_2 I_{00} - I_{02}) - I_{04}(S_4 I_{02} - S_2 I_{04})}{I_{24}(S_4 I_{02} - I_{24}) - I_{44}(S_2 I_{02} - I_{22}) - I_{04}(S_4 I_{22} - S_2 I_{24})} - \frac{g_2}{g_4} \Phi_2(S_2(r), S_4(r)), \end{aligned} \quad (19)$$

where integrals $I_{mn}(S_2, S_4)$ are defined as follows:

$$I_{mn}(S_2, S_4) \equiv \int_{-1}^1 dt P_m(t) P_n(t) \exp \left\{ \frac{\rho}{k_B T} [J_2(r) S_2(r) P_2(t) + J_4(r) S_4(r) P_4(t)] \right\}. \quad (20)$$

The second-order differential equations (18) determine the dependence of the order parameters S_2 and S_4 on the distance r from the center of inclusion. These equations can be reduced to the following first-order differential equations:

$$S'_2(r) = \pm \sqrt{2 \int_{S_2(r)}^{S_2(\infty)} \Phi_2(S_2, S_4(r)) dS_2}, \quad S'_4(r) = \pm \sqrt{2 \int_{S_4(r)}^{S_4(\infty)} \Phi_4(S_2(r), S_4) dS_4}, \quad (21)$$

and the latter ones can be solved numerically to obtain the dependencies $S_2(r)$ and $S_4(r)$ at a given temperature. From Equation (1), one obtains the following approximate expression (without gradients in S_2 and S_4) for the free energy:

$$F = -\rho k_B T \int_{r_0}^{\infty} r^2 dr \ln I_{00}\{S_2(r), S_4(r)\} + \frac{1}{2} \rho^2 \int_{r_0}^{\infty} r^2 dr \left\{ \left[J_{202}^{(0)} - \frac{1}{r^2} k_{11} \right] S_2^2(r) + J_{404}^{(0)} S_4^2 \right\}, \quad (22)$$

which can be used for determination of the phase transition temperatures. The values of the order parameters $S_2(\infty)$ and $S_4(\infty)$ far from inclusion can be obtained by solving Maier–Saupe Equations (3)–(4) numerically, where the mean field can also be estimated without gradients in S_2 and S_4 (the first and third terms in Equation (10)). The values of the order parameters $S_2(r_0)$ and $S_4(r_0)$ at the surface of inclusion can be obtained in the same manner, but the surface potential $W(\mathbf{a} \cdot \mathbf{n}, r_0)$ in the form of approximation (5) should be added to the mean field potential in Equation (3).

3. Discussion of the results

The system of differential equations (21) was solved numerically, and the phase diagram presented in Figure 1(b) was obtained. The heat-driven transformation from nematic state to the isotropic state occurs by means of two successive phase transitions, one related to the surface effects (line 1) and another one related to the bulk effects (line 2). The bulk-related transition temperature T_{NI} is independent of parameter $J_{202}^{(0)} r_0^2 / k_{11}$, while the surface-related transition temperature greatly depends on this parameter and has the asymptotic value (dashed line 3) at large $J_{202}^{(0)} r_0^2 / k_{11}$ coinciding with the phase transition temperature at a flat surface. The four phases are present in the diagram: the nematic phase, the isotropic phase and one of the intermediate phases in between: either the phase in which the nematic order exists only near the inclusions (in the case of large inclusions), or, vice versa, the phase in which the nematic order exists only apart from the inclusions (in the case of small inclusions). In the case of small inclusions, when the splay deformation near the surfaces of inclusions is large, the sequence of transitions appears to be reversed to that at a flat surface. The temperature range of the intermediate phase expands greatly, when r_0 decreases, therefore expansion (8) appears to be autocorrelated. The dependencies $S_2(r/r_0)$ and $S_4(r/r_0)$ at $k_{33} > k_{11}$ are presented in Figure 2(a,b), respectively, for different temperatures. Curve 1 in both figures corresponds to a temperature below both transition temperatures (at the surface and in the bulk), Curves 2 and 3 correspond to a temperature between the transition temperatures at the surface and in the bulk, and

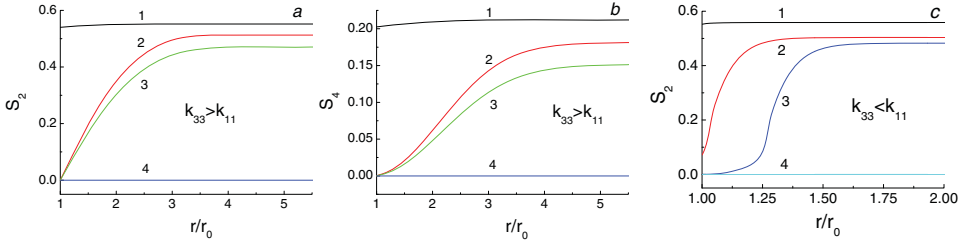


Figure 2. Dependencies of the order parameters on the distance from inclusion $S_2(r/r_0)$ (a,c) and $S_4(r/r_0)$ (b), where r_0 is the radius of inclusion, for $T = 310$ K (1); $T = 315$ K (2); $T = 319$ K (3); $T = 322$ K (4). Here, $f_{202}^{(0)}/k_B = 1440$ K; $f_{404}^{(0)}/k_B = 144$ K; $f_2/k_B = 2.95$ K; $f_4/k_B = 2.6$ K; $k_{11}/(J_{202}^{(0)}/r_0^2) = 1.82 \times 10^{-3}$; $g_2/(J_{202}^{(0)}/r_0^2) = 4 \times 10^{-3}$; $(k_{33} - k_{11})/(J_{202}^{(0)}/r_0^2) = 6.3 \times 10^{-4}$ in (a) and $(k_{33} - k_{11})/(J_{202}^{(0)}/r_0^2) = -6.3 \times 10^{-4}$ in (c).

Curve 4 corresponds to a temperature above both transition temperatures. From Equations (18) and (19), it follows that the sign of parameter g_4 determines the sign of the second derivative $S''_2(r_0)$. In the conventional case of $k_{33} > k_{11}$, $S''_2(r_0)$ is negative below the temperature of complete loss of the isotropic phase in the bulk, and the nematic order parameter S_2 grows greatly with the increasing distance r/r_0 in the intermediate phase. At the same time, in the case $k_{33} < k_{11}$ (which is abnormal for the conventional nematics, but is found in twist-bend nematics), the parameter g_4 is negative, and therefore the second derivative $S''_2(r_0)$ is positive. In this case, the isotropic disorder in the intermediate phase penetrates deeply from inclusion into the bulk of LC, as shown in Figure 2(c). We expect that any point defect ($r_0 \rightarrow 0$) can destroy the conventional nematic order in the case $k_{33} < k_{11}$. This could be an explanation for why k_{33} is usually larger than k_{11} .

At given volume fraction ϕ of the inclusions in LC material, one can estimate the average order parameters $\langle S_2 \rangle$ and $\langle S_4 \rangle$ in the sample. For this purpose, let us consider one spherical inclusion of radius r_0 in the center of spherical LC droplet of radius $R = r_0/\sqrt[3]{\phi}$ and integrate numerically $S_2(r)$ and $S_4(r)$ from r_0 to R . Temperature dependencies of $\langle S_2 \rangle$ and $\langle S_4 \rangle$ are shown in Figures 3 and 4. From Figure 3, one can see that parameter $k_{11}/[J_{202}^{(0)}/r_0^2]$ mainly regulates the surface-related transition temperature, while the order parameters distribution within each phase remains almost unchanged. On the contrary, from Figure 4, it follows that parameter $(k_{33} - k_{11})/[J_{202}^{(0)}/r_0^2]$ mainly regulates the order parameters distribution in the intermediate phase, while both transition temperatures remain almost unchanged.

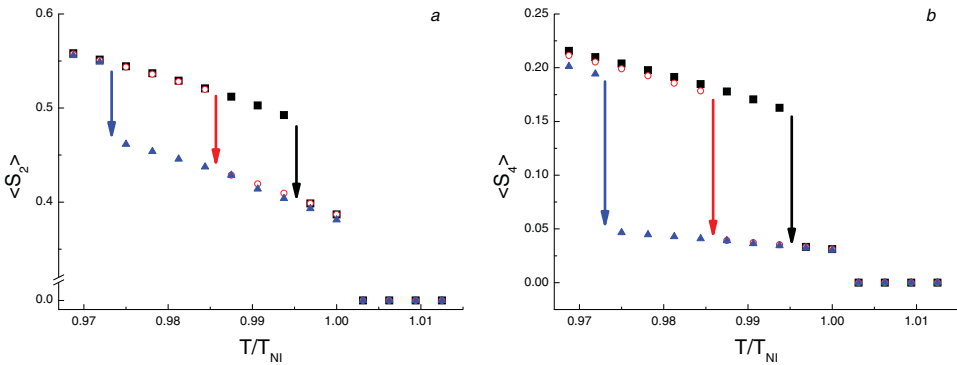


Figure 3. Temperature dependencies of the average values of the order parameters $\langle S_2 \rangle$ (a) and $\langle S_4 \rangle$ (b) in a spherical droplet of radius $R = 5r_0$ with inclusion of radius r_0 in its center at $k_{11}/(J_{202}^{(0)}/r_0^2) = 0.91 \times 10^{-3}$ (squares); 1.82×10^{-3} (circles); and 3.64×10^{-3} (triangles). Other parameters are the same as in Figure 2.

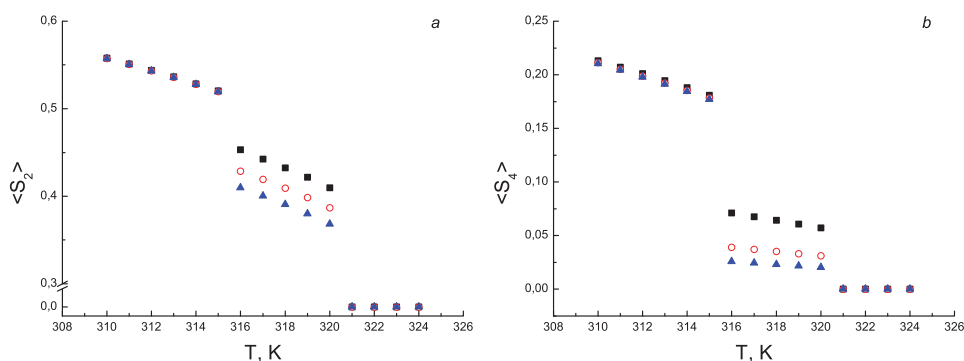


Figure 4. Temperature dependencies of the average values of the order parameters $\langle S_2 \rangle$ (a) and $\langle S_4 \rangle$ (b) in a spherical droplet of radius $R = 5r_0$ with inclusion of radius r_0 in its center at $(k_{33} - k_{11})/(J_{202}^0/r_0^2) = 3.15 \times 10^{-4}$ (squares); 6.3×10^{-4} (circles); and 12.6×10^{-4} (triangles). Other parameters are the same as in Figure 2.

4. Conclusions

A molecular-statistical theory describing the nematic LCs with spherical inclusions (or point defects) is proposed. It is shown that, at given size of inclusions and nematic order parameters at the surfaces of inclusions and far from inclusions, the distribution of nematic order parameters in the bulk of LC with inclusions is fully determined by the elastic constants of LC. The two-step heat-driven transformation from the nematic phase into the isotropic phase, with the intermediate phase in between, is explained. The nematic order parameters and the elastic constants are evaluated in the framework of a unified approach based on the features of pair interaction potentials of the individual LC molecules. It is outlined that the difference between the elastic constants $k_{33} - k_{11}$ regulates the depth of penetration of the nematic order/isotropic disorder from inclusions into the bulk of LC. It is shown that at $k_{33} < k_{11}$, the conventional nematic phase becomes unstable in the presence of point defects. The theory developed in the present paper can be helpful in understanding the structure and behavior of nanocomposite LC systems with nanoparticles, which are extensively studied these days.

Disclosure statement

No potential conflict of interest was reported by the authors.

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