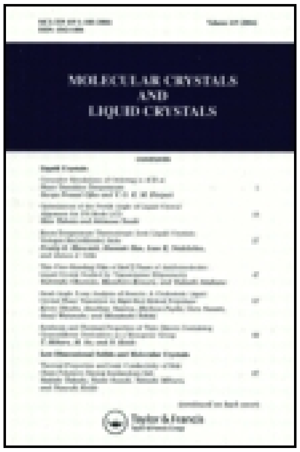

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INFLUENCE OF ANCHORING ENERGY ON ORIENTATIONAL ORDERING AND PHASE TRANSITION IN NEMATIC DROPLETS IN POLYMER MATRIX

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Abstract Analytical expressions are obtained for spatial distribution of the director and the order parameter in a spherical nematic droplet as well as for the shift of the phase transition temperature. The cases of small and large values of anchoring are considered

INTRODUCTION

Great interest has been shown in the last times to nematic liquid crystals (NLC) dispersed in matrices, in particular,to the nematic droplets in polymeric matrix. Optical and other properties of such media depend on both the form, dimensions of droplets and NLC orientational characteristics[1]. The latter also depends on form and dimension of droplets but besides it depends essentially on the conditions at the droplet surface. The orientational ordering in bipolar liquid-crystal spherical droplets is studied in work[2]. Assuming a constant value of the surface order parameter and strong anchoring of the molecules parallel to the surface the spatial distribution of the order parameter is calculated. It is shown the possibility of paranematic phase in the droplet. In work[3] the transformation of the director configuration from a radial-to axial-type structure is observed as the droplet radius, temperature and the strength of an applied electric field are varied. The spatial dependence of the order parameter in spherical droplet is numerically calculated in[4] It is shown that in a droplet with a radial structure the strength of the nematic-polymer interfacial interaction affects the nematic-paranematic phase transition and may induce a boundary-layer nematic phase. The authors of work[5] indicated that a nematic director configuration in cylindrical cavity depends on the surface elastic constant K_{24} if there is weak normal anchoring and reported also the results of the first measurement of K_{24} . In[6] it is shown the existence of orientational order near the cavity wall in the isotropic phase of nematic confined to cylindrical channels. The degree of order at the cavity wall is measured and the surface coupling constant determined for various treatments of the cavity wall.

In the works mentioned above the spatial dependences of the director and the order parameter in the nematic droplets are calculated numerically. In the present work we obtained some the analytical expressions for the spatial distribution of the director and the order parameter in a spherical droplet. Besides it is obtained the simple analytical expressions for the nematic-isotropic liquid phase transition temperature shift if the gradient term in the Landau-de Gennes free energy is small enough.

SPATIAL DISTRIBUTION OF THE DIRECTOR

We consider a spherical nematic droplet in the polymeric matrix with homeotropic conditions on the droplet surface. For generality we suppose that the external static homogeneous electric field $\vec{E}$ is also applied to the sample. The total free energy of the NLC in the droplet is then

$$F_g = F_{el} + F'_{el} + F_{surf} + F_E \tag{1}$$

$$F_{el} = \frac{1}{2} \int dV \; K \; [(div\, \vec{n})^2 + (rot\, \vec{n})^2],$$

$$F'_{el} = - \frac{1}{2} \int dV \; K_{24} \, div\, (\vec{n}\, div\, \vec{n} + [\vec{n}\, rot\, \vec{n}^2]),$$

$$F_{\mathrm{surf}} = -\frac{1}{2} W \int d\sigma \, (\vec{n}\,\vec{e}_r)^2 \ , \ F_E = -\frac{\varepsilon_a}{8\pi} \int dV (\vec{n}\,\vec{E})^2 .$$

The first term in F_g describes the NLC bulk elastic free energy in one-constant approximation, the second term is the part of elastic energy which gives the contribution to the surface free energy of NLC (see for example[5]), the third term describes the surface free energy of the NLC droplet taken in the form suggested in [7] , and the fourth term is present when there is an applied external electric field, K is the Frank elastic constant, ε_a is the anisotropy of NLC dielectric constant, $\vec{e}_r$ is the unit vector directed along the droplet radius, the parameter W >0. We'd like to note that we excluded in the Expr.(1) the term containing the elastic constant K_{13} because the presence of this term is open to question.

Taking into account the condition $n^2=1$, the minimization of Expr.(1) leads to the following differential equation:

$$-\frac{1}{2} K \Delta\vec{n} - \frac{\varepsilon_a}{8\pi} (\vec{n}\,\vec{E})\,\vec{E} = \chi\,\vec{n} \qquad (2)$$

and boundary condition to it on the droplet surface ($r = R$, where R is the droplet radius)

$$\frac{K-K_{24}}{2}\left(\vec{e}_r \operatorname{div}\vec{n} - [\vec{e}_r \operatorname{rot}\vec{n}\,]\right) - \vec{e}_r \frac{W}{2} (\,\vec{n}\vec{e}_r) + K_{24} (\vec{e}\nabla)\vec{n} = \mu\vec{n} \quad (3)$$

Here χ , μ are found using the equality $n^2=1$.

In the general case of arbitrary values of the anchoring energy W , equations (2) and (3) can be solved only numerically. Here we consider the cases of large and small enough values of energy W , when the solution can be obtained in the analytical form.

Let the anchoring energy of the W is sufficiently small so that the director distribution $\vec{n}(\vec{r})$ in a droplet is close to the homogeneous distribution ($\vec{n}_0$ = const.) in an infinite NLC in the constant electric field $E(\vec{n}_0 \parallel \vec{E} \parallel Oz\,]$.

Then, eliminating multipliers λ and μ from Eqs. (2), (3) and supposing $\vec{n} = \vec{n}_0 + \delta\vec{n}$, where $|\delta\vec{n}| \ll 1$, we obtain the equation linearized relative to $\delta\vec{n}$. Its solution satisfying boundary condition (3) takes the form

$$\delta\vec{n} = A \sqrt{\frac{\pi}{2t}} \; J_{5/2}(t) \; \sin 2\theta \; \vec{e}_\rho \; , \qquad (4)$$

$$A = \frac{WR}{2K}\Big[- \frac{3sht}{t} \Big(\frac{2}{t^2} + 1 \Big) + \Big(1 + \frac{6}{t^2} \Big) cht - \frac{K_{24}}{K}\Big[\Big(1 + \frac{3}{t}\Big) \frac{sht}{t} - \frac{3}{t^2} cht\Big) \Big]^{-1}_{t=t_0} \; .$$

$$t = r \left\{ \frac{\varepsilon_a E^2}{4\pi K} \right\}^{1/2} , \; t_0 = t/_{r=R}$$

where $J_{5/2}(t)$ is the modified spherical Bessel's function, $\vec{e}_\rho$ is the unit vector of the cylindrical coordinate system ($\vec{e}_\rho \perp \vec{e}_z$), θ is the polar angle.

If the external field $\vec{E}$ is absent, then, the solution of linearized Eq.(2),(3) will be as follows:

$$\vec{n} = \vec{e}_z + \frac{WR}{K}(6 - 2K_{24}/K)^{-1} \Big(\frac{r}{R} \Big)^2 \sin 2\theta \; \vec{e}_\rho \qquad (5)$$

So long as $|\delta\vec{n}| \ll 1$, the obtained expressions (4), (5) are valid if the parameter $\frac{WR}{K} \ll 1$.

If the anchoring energy W of the director with the droplet surface is large enough so that $\frac{WR}{K} \gg 1$ then $\delta\vec{n}$ cannot be considered small. In this case, as it is shown in[1] the spatial director distribution takes the radial configuration $\vec{n} = \vec{e}_r$.

SPATIAL DISTRIBUTION OF THE ORDER PARAMETER

To consider the contribution of the degree of molecular orientational ordering to the NLC droplet free energy one should add the Landau-de Gennes free energy to Expr.(1)

$$F_1 = \int\Big[\frac{1}{2} \lambda(\vec{\nabla} S)^2 + \frac{1}{2} a'(T - T_0^*) S^2 + \frac{1}{3} b S^3 + \frac{1}{4} c S^4\Big] dV \quad (6)$$

where temperature T_0^*, a', b, c, λ are material parameters.

We must also take into account in Expr.(1) that K and W depend on the order parameter $S=S(\vec{r})$

According to [8] and other papers $K=\alpha S^2$ The experimental measurements carried out for several nematics in [9-10] show that $W\sim S^2$ in a wide temperature range and therefore, following these results, we put $W = wS^2$.

We restrict ourselves to the case when the influence of the droplet surface is the most essential and the director has the radial configuration.

Then from the condition of free energy F_g+F_1 minimum we obtain the following differential equation for the order parameter S in the absence of external electric field (see also[4])

$$\frac{\partial^2 S}{\partial r^2} + \frac{2}{r}\frac{\partial S}{\partial r} - \frac{4\alpha}{\lambda r^2}S - \Phi(S) = 0 \qquad (7)$$

$$\Phi(S) = \frac{1}{\lambda}\,[a'(T - T_0^*)S + bS^2 + cS^3]$$

and a boundary condition to it

$$\left[\frac{w}{\lambda}S - \frac{\partial S}{\partial r}\right]_{r=R} = 0 \qquad (8)$$

The last equation differs from the boundary condition in work[4] because we put here $W\sim S^2$

In an infinite nematic the order parameter is independent of coordinates and is the solution of equation $\Phi(S) = 0$. We denote the root of the latter, corresponding to a nematic phase, as S_0

Supposing that $S = S_0 + f(r)$ one can solve equation (7) with boundary condition (8) analytically if $f(r)$ is small. Then

$$S = S_0 + \frac{1}{\sqrt{\rho}}\,[B\,I_\nu(\rho) + \sum_n D_n Y_n(\rho)] \qquad (9)$$

$$B = \frac{\varepsilon S_o \sqrt{\rho}}{I_{\nu+1}(\rho_R) + \left(\frac{\nu}{\rho_R} - \varepsilon - \frac{1}{\sqrt{\rho}} \right) I_\nu(\rho_R)} \qquad (10)$$

$$D_n = \frac{4\alpha}{\lambda\mu_n} S_o \int_0^{\rho} \rho_1^{-1/2} Y_n^*(\rho_1) d\rho_2 \left(\int_0^{\rho_R} |Y_n^*(\rho_1)^2| \, \rho_1 d\rho_1 \right)^{-1} \qquad (11)$$

$$\rho = r/r_c \, , \; \rho_R = R/r_c \, , \; \varepsilon = w r_c/\lambda \, , \; \nu = 4\alpha/\lambda + 1/4 \, ,$$

$$r_c^2 = 1/\left(\frac{\partial\Phi}{\partial S} \right)_{S=S_o}$$

$$Y_n(\rho) = \begin{cases} I_n(\sqrt{\mu_n + 1} \;\; \rho) & ,\text{if} \;\; \mu_n + 1 > 0 \\ J_n(\sqrt{|\mu_n + 1|} \;\; \rho) & ,\text{if} \;\; \mu_n + 1 < 0 \end{cases}$$

where I_ν is the modified Bessel's function, J_ν is the Bessel's function of a real argument and μ_n are the solutions of the equation

$$\left[\left(\varepsilon + \frac{1}{2\rho_R} \right) Y_n - \frac{\partial Y_n}{\partial \rho_R} \right]_{\rho=\rho_R} = 0 \qquad (12)$$

In Expr.(9) the summation is taken with respect to all roots of Eq.(12).

If we put (as it was done for example in [4]) $W = wS$, then instead of Eq.(8) we have the next boundary condition

$$\left(\frac{w}{\lambda} - \frac{\partial S}{\partial r} \right)_{r=R} = 0 \qquad (13)$$

The solution of Eq.(7) in this case is describing by the formula (9) as well as above but in Exprs.(10),(12) the quantities $\varepsilon I_\nu(\rho_R)$ and εY_n must be replaced by the quantity ε, respectively.

PHASE TRANSITION TEMPERATURE SHIFT

If the order parameter S weakly depends on coordinates and the parameter λ is sufficiently small, than we can neglect the gradient term in the expression for F_l .

The condition of small contribution of this term compared to the contribution of the Frank energy, in the case of the radial director configuration leads to the inequality

$$\frac{\alpha}{\lambda} \gg \frac{1}{4}\left(\frac{\Delta S}{S}\right)^2 \frac{R}{l} \qquad (14)$$

where ΔS is the order parameter variation over the characteristic length l .

The condition of the small contribution of the gradient term in comparison with the contribution of the anchoring energy of the director

$$\frac{wR}{\lambda} \gg \left(\frac{\Delta S}{S}\right)^2 \frac{R}{l} \qquad (15)$$

If $\Delta S/S \approx 0.1$ and, $l \approx R$ then the inequality (14) is fulfilled because $\alpha/\lambda \approx 3$ [4]. If we put $\lambda \approx 4 \times 10^{-11} N$ [11], $R=0.1$ mkm the condition (15) may be satisfied for $w \gg 4 \times 10^{-6}$ J/m^2.

Supposing that the above inequalities are fulfilled, we omit the gradient term in the expression for the droplet free energy $F=F_{el}+F'_{el}+F_{surf}+F_{l}$, and consider the order parameter S to be independent of coordinates. Then, collecting the terms at S^2 , we obtain that

$$\frac{F}{\frac{4}{3}\pi R^3} = \frac{1}{2}\,a(T-T^{*})S^2 + \frac{1}{3}\,bS^3 + \frac{1}{4}\,cS^4 \qquad (16)$$

where

$$T^{*} = T_0^{*} + \frac{3w}{aR} \qquad (17)$$

An analogous calculation for the director configuration (5) gives

$$T^{*} = T_0^{*} + \frac{w}{aR} \qquad (18)$$

In obtaining expressions (17) and (18) small terms $\left(\frac{wR}{a}\right)^{-1}$ and $\frac{wR}{a}$, respectively, appearing due to the terms F_{el}, F'_{el} are neglected compared to the unity. It is obvious that the same temperature shift will take place for the temperature of nematic-isotropic liquid phase transition and for the temperature T^{*}.

If we put $w= 10^{-3}$ J/m^2, $a= 6.\times 10^4$ J/(m^{3}K) [11,12], than for the droplets of radius $R=0.1$ mkm the parameter $\frac{wR}{a} \gg 1$

and the phase transition temperature shift is determined by Expr.(17) and has the order $\frac{3w}{aR} \approx 0.5^{\circ}$ that may be easily checked experimentally.

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