Physics

ONSAGER THEORY OF NEMATIC LIQUID CRYSTALS DOPED WITH FERROELECTRIC NANOPARTICLES

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The Onsager virial theory for the isotropic-nematic phase transition of thin rod-like nematic molecules doped with ferroelectric nanoparticles is treated comprehensively. An expression for free energy of the system as a whole is received. By applying the Lagrange multiplier method for variation of free energy expression the orientational distribution function of nematics in the presence of nanoparticles is obtained.

Keywords: ferroelectric nanoparticles, free energy, Onsager theory, orientational distribution function.

Introduction. Although liquid crystals (LC) have been known for more than a century [1], a real upsurge in interest may be traced especially for the last 50 years. It is partly due to the application of LC in devices such as displays. Another reason for an increased study of LC is the wealth of different possible phases with orientational and/or partial positional order that rise in addition to the more common gaseous, liquid and crystalline phases. These LC phases give an opportunity of studying all types of subtle problems in the theory of phase transitions, in particular, of critical phenomena [2].

The statistical-mechanical theory of phase transitions in LC was described by Onsager in an original work [3], where it was exhibited that in contrast to the gas-liquid transition the isotropic-nematic phase transition for solid elastic particles is treatable within the virial expansion of free energy. For very thin, rigid, hard particles the transition occurs at very low volume fraction and the virial expansion may be truncated after the second virial term, leading to an exact theory for infinitely thin particles.

The rapid increase in the interest in portable devices with liquid crystal displays has created a demand for higher-performance LC materials. This lead to heightened requirements to the design and synthesis of new LC materials. Long-range forces between ultrafine particles embedded in LC matrices produced intriguing colloids [4–8]. For example, dispersed ferromagnetic particles greatly enhance the magnetic properties of LC [4, 5]. Large ($\gg \mu m$) colloidal particles form defects in LC

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matrices producing large director deformations. Ensembles of these particles and defects can form complex structures [6]. High concentrations (>2–3% by weight) of submicron particles can create almost rigid LC suspensions [7–8].

In [9–14] it was shown that at low concentrations LC colloids behave as pure LC with no evidence of dissolved particles, but have enhanced properties. These dilute suspensions are stable, because the nanoparticles do not significantly perturb the director field in the LC, and interaction between the particles is weak. Importantly, the nanoparticles share their intrinsic properties with the LC matrix due to the alignment with LC. In particular, the doping a nematic LC matrix with ferroelectric nanoparticles produces enhanced dielectric anisotropy, introduces the ferroelectric properties inherent to the nanoparticles, increases the parameter of orientational order of the host liquid crystal and the isotropic nematic transition temperature, and decreases the switching voltage for the Frederick's transition.

The present paper aims at deeper understanding of physical properties and consideration of the thermodynamics of a nematic liquid crystal (NLC) dispersed with ferroelectric nanoparticles. The potential energy and free energy of the interaction of nanoparticles and LC molecules have been obtained taking into consideration nanoparticles orientational distribution. We have disseminated Onsager theory to such a composite material.

Interaction Potential Energy. Let us consider a NLC elongated cylindrical molecules with length L and diameter D ($L \gg D$). In NLC there are some dispersed spherical ferroelectric nanoparticles with radius R and dipole moment $\vec{p}$. The concentration of ferroelectric particles suspended in the LC host system is very low (<1%). In our theoretical model each nanoparticle interacts with the LC order tensor $Q_{\alpha\beta}^{\mathrm{LC}}$ by means of its electric field $\vec{E}$:

$$\vec{E}(\vec{r}) = \frac{1}{\varepsilon}\left(\frac{3\vec{r}(\vec{r}\vec{p})}{r^5} - \frac{\vec{p}}{r^3}\right).\tag{1}$$

The interaction potential energy may be written in the form

$$U_{\mathrm{int}} = \frac{1}{12\pi}\Delta\varepsilon\int d^3 r\, Q_{\alpha\beta}^{\mathrm{LC}}(\vec{r}) E_\alpha(\vec{r}) E_\beta(\vec{r}) ,\tag{2}$$

where $\Delta\varepsilon$ is the dielectric permittivity anisotropy of fully aligned NLC. In the electric field of ferroelectric particle the higher multipoles due to the dielectric anisotropy of NLC are neglected. Near the nanoparticle the electric field is a rapidly varying function of position, but LC order tensor cannot follow those variations because that would require much more elastic energy. In our case the nanoparticles are so small that a homogenous LC order tensor is predictable. So, we can integrate interaction potential energy

$$U_{\mathrm{int}} = \frac{\Delta\varepsilon}{45\varepsilon^2 R^3} Q_{\alpha\beta}^{\mathrm{LC}}\left\langle p_\alpha p_\beta \right\rangle,\tag{3}$$

averaging over the nanoparticle orientation distribution. The distribution can be expressed by defining nanoparticles order tensor analogous to that for LC:

$$Q_{\alpha\beta}^{n} = \frac{3}{2}\frac{\left\langle p_\alpha p_\beta \right\rangle}{p^2} - \frac{1}{2}\delta_{\alpha\beta}.\tag{4}$$

Thus, the interaction potential energy is

$$U_{\text{int}} = \frac{2\Delta\varepsilon\, p^2}{135\varepsilon^2 R^3} Q_{\alpha\beta}^{\text{LC}} Q_{\alpha\beta}^{n} \,. \tag{5}$$

It is reasonable to assume the same alignment for both the tensors. So Eq. (5) takes the form

$$U_{\text{int}} = \frac{\Delta\varepsilon\, p^2}{45\varepsilon^2 R^3} S_{\text{LC}} S_n \,, \tag{6}$$

where S_{LC} and S_n are the liquid crystal and nanoparticles order parameters respectively. To study the thermodynamics of the system as a whole it is convenient to use the interaction free energy of all the nanoparticles and LC. To do that we shall avail of the standard relation between the free energy and interaction potential energy. Using the additive property for free energy we obtain

$$F_{\text{int}} = -\frac{\Delta\varepsilon\, p^2 \rho_n}{45\varepsilon^2 R^3} S_{\text{LC}} S_n \,, \tag{7}$$

where ρ_n is concentration of nanoparticles (the number in the unite volume).

Free Energy of System and Lagrange's Method of Multipliers. As was mentioned in the introduction, the most complete theory for thermodynamics of nematic liquid crystals is the Onsager classical theory. Where the system free energy is constructed classically, calculating interaction potentials. Onsager considered only the configurational interactions of LC molecules, but he showed that for charged particles the effect of electrical interactions will be the same if the effective diameter of molecules is increased. So, Onsager has written the NLC free energy per unit volume as [3]

$$F_{\text{LC}} = F_0 + \frac{k_B T}{V_m}\left[\int f_{\vec{a}}\ln(4\pi f_{\vec{a}})\,d\Omega + \frac{1}{2}c\iint f_{\vec{a}}f_{\vec{a}'}\beta_1(\vec{a},\vec{a}')\,d\Omega d\Omega' + O(c^2)\right].$$

Here F_0 is the free energy of isotropic part and V_m is the molecule's volume. The second term describes the reduction in entropy due to the molecules order, in other words, due to the presence of non-constant orientational distribution function. The third term shows the excluded volume presence (orientational interaction), β_1 is the excluded volume by molecule with great axis $\vec{a}$ for the molecule, whith $\vec{a}'$ axis. And c is the LC molecules concentration, $f_{\vec{a}}$ is the LC molecules orientational distribution function related to direction $\vec{a}$. The directions $\vec{a}$, $\vec{a}'$… for each molecule are defined with corresponding solid angles $d\Omega$, $d\Omega'$… If the space is split into these solid angles, the restriction for orientational distribution function is obtained to specify the so-called normalization condition:

$$\int f(\vec{a})\,d\Omega(\vec{a}) = 1. \tag{9}$$

Thus, the free energy of the whole system will be written as

$$F = F_{\text{LC}} + F_{\text{int}} \,. \tag{10}$$

We use the NLC order parameter definition and its connection with nanoparticles order parameter [15]:

$$S_{\text{LC}} = \frac{1}{2}\int f_{\vec{a}}\left(3\cos^2\theta - 1\right)d\Omega, \qquad S_n = \frac{\Delta\varepsilon\, p^2}{225\varepsilon^2 R^3 k_B T} S_{\text{LC}}, \tag{11}$$

where θ is the angle between **a** and the nematic axis. The free energy of system is rewritten as follows:

$$F_{LC} = F_0 + \frac{k_B T}{V_m}\left[\int f_{\bar{a}}\ln(4\pi f_{\bar{a}})d\Omega + \frac{1}{2}c\iint f_{\bar{a}}f_{\bar{a}'}\beta_1(\bar{a},\bar{a}')d\Omega d\Omega' - 2WS_{LC}^2\right]. \quad (12)$$

For *W* constant we denote

$$W = 0.1\rho_n V_m(\Delta\varepsilon p^2/45\varepsilon^2 R^3 k_B T)^2. \quad (13)$$

In Eq. (12) the last term corresponds to the nanoparticles interaction with LC order parameter. To obtain molecules orientational distribution function, we are going to solve variation problem using the Lagrange's multiplier method. The physical purport of the problem is that the free energy has minimum for any variation of orientational distribution function that satisfies the normalization condition. Mathematically this statement can be written as $\delta F = \lambda\int\delta f_a d\Omega$, λ is the Lagrange multiplier. For variation of free energy we get

$$\delta F = \frac{kT}{V_m}\int\delta f_{\bar{a}}\left[\ln(4\pi f_{\bar{a}}) + 1 + c\int f_{\bar{a}'}\beta_1(\bar{a},\bar{a}')d\Omega' - 2WS_{LC}(3\cos^2\theta - 1)\right]d\Omega. \quad (15)$$

Solution of Non-Linear Integral Equation. So, by solving variation problem by means of Lagrange method we obtain an equation for the orientational distribution function. It is a nonlinear integral equation

$$\ln(4\pi f_{\bar{a}}) + 1 + c\int f_{\bar{a}'}\beta_1(\bar{a},\bar{a}')d\Omega' - 2W(3\cos^2\theta - 1)\int f_{\bar{a}'}(3\cos\theta' - 1)d\Omega' - \lambda = 0. \quad (16)$$

The excluded volume β_1 for LC cylindrical molecules is $\beta_1 = 2L^2 D|\sin(\theta' - \theta)|$. By denoting $C = cL^2 D$, we get the dimensionless equation

$$\ln(4\pi f_{\bar{a}}) + C\int 4\pi f_{\bar{a}'}|\sin(\theta' - \theta)|\sin\theta' d\theta' - W(3\cos^2\theta - 1)\times$$
$$\times\int 4\pi f_{\bar{a}'}(3\cos\theta' - 1)\sin\theta' d\theta' = \lambda - 1. \quad (17)$$

Eq. (17) always has an "isotropic" solution ($f_a = 1/4\pi$, independent of **a**), but if *C* is large enough, it may also have anisotropic solutions describing a nematic phase. It is difficult to solve the non-linear integral Eq. (17) exactly. For this reason following Onsager, we will use variational method, based on a trial function of the form

$$f_{\bar{a}} = \Phi\,\mathrm{ch}(\alpha\cos\theta), \quad (18)$$

where α is a variational parameter, and the constant Φ factor is chosen to normalize *f* according to Eq. (9). In the region of interest, α turns out to be large (~20), and the function *f* is strongly peaked around $\theta = 0$ and $\theta = \pi$. Minimizing the energy F_{LC} (Eq. (12)) with respect to α, one obtains a function $F_{LC}(c)$. For solution (18) the condition (9) will be fulfilled, when $\Phi = (\alpha/4\pi)\,\mathrm{sh}^{-1}\alpha$. It is more convenient to solve the equation for $4\pi f_a = f$:

$$\ln f + C\int f|\sin(\theta' - \theta)|\sin\theta' d\theta' - W(3\cos^2\theta - 1)\times$$
$$\times\int f(3\cos\theta' - 1)\sin\theta' d\theta' = \lambda - 1. \quad (19)$$

In the absence of nanoparticles (*W*=0)

$$g(\theta) = \ln f + C\int f|\sin(\theta' - \theta)|\sin\theta' d\theta' = \lambda - 1.$$

When *C*<<1 the solution is isotropic $\alpha = 0$ and $f = 1$. At higher *C* the solution shows a first-order phase-transition from isotropic ($\alpha = 0$) to nematic ($\alpha = 18.6$).

The nematic phase is obtained in case of concentration factor $C = 3.004$. This parameter may be expressed in terms of LC molecule volume V_m as $C = 4cV_mL/(\pi D)$. It follows from this formula that in order to have nematic phase for a fraction $cV_m \sim 0.3$ of LC volume it is necessary to have molecules with at least $L/D \sim 8$. The order parameter is

$$S = \frac{1}{4}\int f\left(3\cos\theta - 1\right)\sin\theta\,d\theta \approx 1 - 3/\alpha \qquad (\alpha \ll 1). \qquad (20)$$

Of particular interest is the value of order parameter S_c in the nematic phase in close vicinity of transition. This turns out to be ruther high ($S_c \approx 0.84$). In Fig. 1 the concentration factor dependence of the LC order parameter is shown.
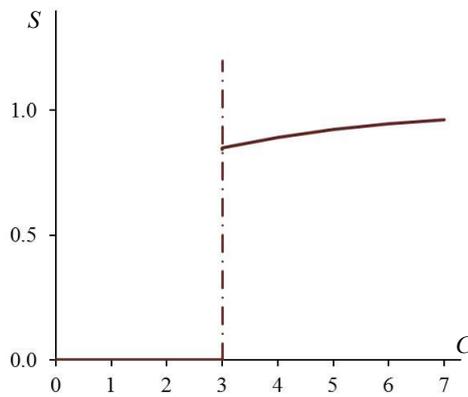
Fig. 1. Concentration factor dependence of the LC order parameter.
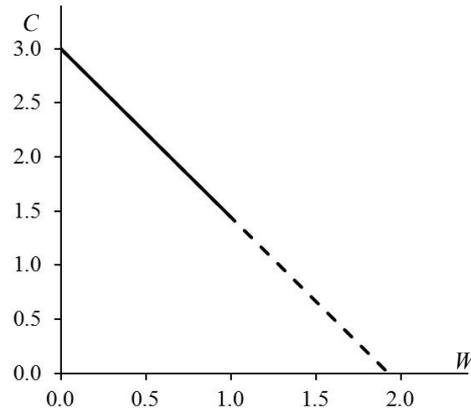
Fig. 2. Nanoparticle's factor dependence of NLC molecules concentration.

To consider the influence nanoparticles on phase transition let us make the following additional notations: $\varphi_n = \rho_n V_n$ is the volume fraction of nanoparticles, $P = p/V_n$ is the electrical moment per unit volume, and $V_n = 4\pi R^3/3$ is the nanoparticle volume. As a result we obtain for nanoparticle factor W:

$$W = 8.7 \cdot 10^{-4}\varphi_n\left(\Delta\varepsilon P^2 V_n / \varepsilon^2 k_B T\right)^2.$$

Taking for ferroelectric $Sn_2P_2S_6$ nanoparticles the following values of parameters: $P = 10^3$ CGSE $= 0.004\ cm^{-2}$, $V_n = 1.13 \cdot 10^{-16}cm^3$ ($R = 30\ nm$), $\varphi_n = 0.5\%$ and 5CB for NLC with $\Delta\varepsilon \sim \varepsilon \sim 10$, $k_B = 1.38 \cdot 10^{-16}\ ErgK^{-1}$, $T = 300\ K$, we obtain $W \approx 0.32$. It is possible to provide the values of 2 or 3 times as large as the obtained one, but it needs to keep in mind that when W is larger than unity, LC structure may be destroyed [9–14]. As it is shown in Fig. 2, with increasing nanoparticle's factor W decreases (approximately linearly $C \approx -1.556\ W + 3$) the concentration of LC necessary for nematic phase formation. This means that in the presence of nanoparticles nematic phase can be realized at very low concentration of LC molecules.

Conclusion. In the present work a complex system of nematic liquid crystals dispersed with ferroelectric nanoparticles has been considered. Within the framework of proposed theoretical model the nanoparticles interact with nematic liquid crystal or the tensor by means of their dipolar electric field. Expressions for the potential energy of interaction and free energy are obtained. For theoretical interpretation of

the thermodynamics of pure nematic liquid crystal we made use of the Onsager theory that was further developed for our system. Employing the Lagrange's method of multipliers for variation of the free energy of system as a whole, the orientation distribution functions of nematic liquid crystal molecules in the presence of nanoparticles was derived. The obtained non-linear equation is solved. Using the conditions proceeding from the physical properties of the system, orientational distribution function of the system is obtained. The proposed theoretical model may serve a solid base for more detailed studies of the thermodynamics of similar systems, particularly for prediction of new physical properties of the system and for theoretical substantiation of the existing properties.

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