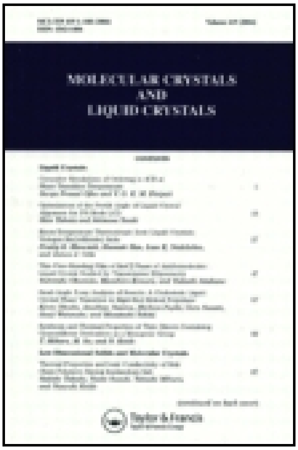

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CORRELATIONS OF THERMAL DIRECTOR FLUCTUATIONS IN FILLED LIQUID CRYSTALS

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CORRELATIONS OF THERMAL DIRECTOR FLUCTUATIONS IN FILLED LIQUID CRYSTALS

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The liquid crystal director-colloidal particle surface interaction in filled liquid crystals causes the thermally-induced director fluctuation correlations to be screened. This is consistent with the experimentally observed reduction in the thermal director fluctuation-induced Rayleigh light scattering in filled liquid crystals. The colloid-mesogen interaction also induces director non-uniformity in filled liquid crystals, thus further modifying the spatial dependence of the director fluctuation correlations, and shifts the critical temperature at which the isotropic phase loses its stability with respect to nematic fluctuations. The shift is specifically particle-size dependent, and this will enable the phenomenon to be recognized experimentally.

Keywords: filled liquid crystals; thermal director fluctuations

1. INTRODUCTION

Heterogeneous liquid crystal (LC) systems consisting of aerosil (small silica particles) suspensions in a nematic LC matrix possess extremely interesting electro-optical properties. These were first demonstrated by Eidenschink and de Jeu [1] and Kreuzer *et al.* [2], and have been the subject of numerous further studies [e.g. 3–7] These systems have become known as *Filled LCs*. Silica particles (diameter $\sim 100 - 1000$ Å) create multiple defects in the LC orientation structure, resulting in strong Rayleigh light scattering. The transformation and disappearance of some proportion of these defects in an external electric field causes the medium to become transparent.

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It seems likely that whether or not the filled LC state is transparent or scatters light strongly, the thermal director fluctuations responsible for Rayleigh light scattering in conventional LCs are strongly suppressed.

Filled LC is an example of the systems with quenched random disorder. It is of great importance to understand in which way the ordering of such systems varies as a function of the ordering and disordering field strengths. Yu *et al.* [8] performed Monte Carlo simulations to study the equilibrium ordering in a two-dimensional nematic system with quenched random disorder. When the disordering field is sufficiently strong it is found that the long-range correlations of the director orientation decay as $\exp(-\xi^{-1} r)$. Note that Imry and Ma [9] in the model of continuous random fields predict the decay of the long-range correlations of the order parameter as $\exp[(-\xi^{-1} r)^{4-d}]$ where d is the dimensionality of space. Fridrikh and Terentjev [10] theoretically studied order-disorder transition in an external field in random ferromagnets and nematic elastomers. In particular, they show that the external field exceeding some threshold value suppresses the thermal and the quenched disorder in these systems.

Below we show that LC director anchoring with the surface of the colloidal particles leads to thermal director fluctuation suppression which is similar to that obtained in [8,9]. We estimate the external field value that is required to obtain the same suppression of fluctuations as due to the director anchoring with colloidal particle surface.

This paper is organized as follows. In section 2 we study the nematic phase in the filled LC and show that director-colloidal particle surface interaction causes the screening of the director fluctuation correlations. In section 3 we show that the analogous interaction in the isotropic phase causes the effective critical temperature at which the isotropic phases loses its stability to be increased. Finally in section 4 we draw some brief conclusions.

2. FILLED LC: NEMATIC PHASE

The nematic phase, which exists in the absence of colloidal impurities, remains in the filled LC. However, the director field is in general now inhomogeneous. This inhomogeneity is caused by the interaction between the LC and the surfaces of the colloidal particles. We suppose the colloidal concentration to be sufficiently small that any consequent change in the LC elastic constants can be neglected. The free energy of filled LC can then be written in the form

$$F = \frac{K}{2}\int\left[(\nabla.\mathbf{n})^2 + (\nabla\times\mathbf{n})^2\right]dV - \frac{W}{2}\int_\Sigma (\mathbf{n}.\mathbf{e})^2 dS,\ W > 0 \qquad (1)$$

In Eq. (1) first integral is the usual Frank-Oseen-Zocher elastic energy in the one constant approximation [11]. The second integral is taken over the surface of all particles, and gives the free energy contribution from the so-called anchoring interaction between the director and the colloidal particle surfaces [12]. Here $\mathbf{n} = \mathbf{n(r)}$ is the LC director, K is an elastic constant, W is a director anchoring energy with particle surface, and $\mathbf{e}$ is a unit vector along the easy orientation axis on the particle surface.

To obtain the director equilibrium distribution in the filled LC it is necessary to minimize the free energy (1) to obtain a differential equation for $\mathbf{n}(\mathbf{r})$ subject to specific boundary conditions. The corresponding solutions $\mathbf{n}_0(\mathbf{r})$ have been obtained in papers [3–7] in the case of small concentration of spherical and cylindrical particles. Taking into account the thermal director fluctuations $\delta\mathbf{n}(\mathbf{r})$ one must replace $\mathbf{n}(\mathbf{r})$ by $\mathbf{n}_0(\mathbf{r}) + \delta\mathbf{n}(\mathbf{r})$ in formula (1). We suppose that there is no correlation between an equilibrium director $\mathbf{n}_0(\mathbf{r})$ and $\delta\mathbf{n}(\mathbf{r})$. In this case we can omit in (1) terms containing $\nabla.\mathbf{n}_0(\mathbf{r})$, $\nabla.\delta\mathbf{n}(\mathbf{r})$, $\nabla \times \mathbf{n}_0(\mathbf{r})$, $\nabla \times \delta\mathbf{n}(\mathbf{r})$, $\mathbf{n}_0(\mathbf{r})$, $\delta\mathbf{n}(\mathbf{r})$; these terms give zero after thermal averaging. As a result we can write the free energy of filled LC as $F = F_0 + \delta F$, where F_0 is a free energy equilibrium value and δF is a free energy fluctuation contribution, which takes the form

$$\delta F = \frac{K}{2}\int \left[(\nabla.\delta\mathbf{n}(\mathbf{r}))^2 + (\nabla \times \delta\mathbf{n}(\mathbf{r}))^{\mathbf{2}}\right] dV + \frac{W}{2}\int_{\Sigma} (\delta\mathbf{n}(\mathbf{r}))^2 \cos^2 \alpha \, dS, \quad (2)$$

where α is the angle between the director and the easy orientation axis on the particle surface.

It is convenient to take the Fourier transform

$$\delta\mathbf{n}(\mathbf{r}) = \frac{1}{\mathrm{V}}\sum_{\eta} \delta\mathbf{n}(\mathbf{q}) \exp(\mathbf{iq}.\mathbf{r}), \quad (3)$$

where V is the volume of the system.

Assuming the particles to be distributed homogeneously, one can write

$$\sum_{\mathrm{m}} \exp(\mathbf{iq}.\mathbf{r}_{\mathrm{m}}) = \mathrm{N}\delta_{\mathrm{q},0}, \quad (4)$$

where $\mathbf{r}_m$ is the position of particle m, N is the total number of colloidal particles, and we sum over all particles.

Performing the Fourier transform in (2) and taking into account (4) we obtain for δF the following expression

$$\delta F = \frac{K}{2V}\sum_{q} (q^2 + \xi_W^{-2}) |\delta\mathbf{n}(q)|^2 , \quad (5)$$

where the screening length ξ_W is defined by:

$$\xi_W = \left(\eta \frac{WS}{Kv_0} \overline{\cos^2 \alpha} \right)^{-1/2} \quad (6)$$

In Eq. (5) and (6), $\eta = Nv_0/V$ is the so-called colloidal *packing fraction* (i.e the proportion of the volume occupied by colloidal particles), S and v_0 are respectively the surface area and volume of a particle, and $\overline{\cos^2\alpha} = \frac{1}{S}\int \cos^2\alpha dS$, where the integral is taken over the surface of a particle.

We now recall that the components of vector $\boldsymbol{\delta}\mathbf{n}(\mathbf{q})$ are in general not independent due to the condition

$$\mathbf{n}_0(\mathbf{r}).\delta\mathbf{n}(\mathbf{r}) = 0\,, \tag{7}$$

which follows from the condition that $\mathbf{n}$ is a unit vector. However, it is possible to use the local coordinate frame with the z'-axis directed along $\mathbf{n}_0(\mathbf{r})$. The condition (7) now determines two independent components $\delta \mathrm{n}_1{}'(\mathbf{r})$ and $\delta \mathrm{n}_2{}'(\mathbf{r})$ of the vector $\boldsymbol{\delta}\mathbf{n}(\mathbf{r})$, where indices 1,2 denote two coordinate axes in the plane perpendicular to the z' -axis. Thus in the local coordinate frame one may write:

$$|\delta\mathbf{n}(\mathbf{q})|^2 = |\delta\mathbf{n}_1'(\mathbf{q})|^2 + |\delta\mathbf{n}_2'(\mathbf{q})|^2\,, \tag{8}$$

where the Fourier components $\boldsymbol{\delta}\mathbf{n}_1'(\mathbf{q})$ and $\boldsymbol{\delta}\mathbf{n}_2'(\mathbf{q})$ are independent.

Using Eq. (8), the expression (5) now takes the form:

$$\delta F = \frac{K}{2V}\sum_q (q^2 + \xi_W^{-2})\left(|\delta\mathbf{n}_1'(\mathbf{q})|^2 + |\delta\mathbf{n}_2'(\mathbf{q})|^2\right) \tag{9}$$

Performing thermal averaging in (9) and using the equipartition theorem we obtain:

$$\left\langle |\delta\mathbf{n}_i(\mathbf{q})|^2 \right\rangle = \frac{k_B T V}{K(q^2 + \xi_W^{-2})}\,, \tag{10}$$

where $i = 1{,}2$.

The thermal director fluctuation correlation function can be written in Fourier transformed form as:

$$\left\langle \delta\mathbf{n}_i'(\mathbf{r}_1).\delta\mathbf{n}_i'(\mathbf{r}_2) \right\rangle = \frac{1}{V^2}\sum_{\mathbf{q}} \left\langle |\delta\mathbf{n}_i'(\mathbf{q})|^2 \right\rangle \exp(-\boldsymbol{i}\mathbf{q}.(\mathbf{r}_2 - \mathbf{r}_1)) \tag{11}$$

Substituting the expression (10) in (11) and taking the integration over $\mathbf{q}$ now yields the result:

$$\left\langle \delta\mathbf{n}_i'(\mathbf{r}_1).\delta\mathbf{n}_i'(\mathbf{r}_2) \right\rangle = \frac{k_B T}{4\pi K|\mathbf{r}_2 - \mathbf{r}_1|}\exp(-\xi_W^{-1}|\mathbf{r}_2 - \mathbf{r}_1|) \tag{12}$$

Let us denote the transition matrix between the local coordinate frame and that of the laboratory by $\hat{A}$. The director fluctuation in the laboratory coordinate frame now can be written as:

$$\delta\mathbf{n}_i'(\mathbf{r}) = \sum_{j=1}^{3} A_{ij}(\mathbf{r})\delta\mathbf{n}_j'(\mathbf{r}) \tag{13}$$

Likewise, the thermal director fluctuation correlation function in the laboratory coordinate frame takes the form:

$$\left\langle \delta n_i(\mathbf{r}_1).\delta n_j(\mathbf{r}_2)\right\rangle = \sum_{k,l=1}^{3} A_{ik}(r_1)A_{jl}(r_2)\left\langle \delta n_k'(r_1)\delta n_1'(r_2)\right\rangle \tag{14}$$

Taking into account that $\delta n_3'(r) = 0, \langle \delta n_1(r)\delta n_2(r)\rangle = 0$ and substituting the expression (12) in (14) we now obtain:

$$\left\langle \delta n_i(\mathbf{r}_1).\delta n_j(\mathbf{r}_2)\right\rangle = \frac{k_B T \exp\left(-\xi_W^{-1}|\mathbf{r}_2 - \mathbf{r}_1|\right)}{4\pi K|\mathbf{r}_2 - \mathbf{r}_1|} \sum_{k,l=1}^{2} A_{ik}(\mathbf{r}_1)A_{jk}(\mathbf{r}_2) \tag{15}$$

If, for example, the laboratory coordinate frame is chosen so that $\mathbf{r}_1 = 0$ and the matrix $A_{ij}(0) = \delta_{ij}$, then

$$\left\langle \delta n_i(0)\delta n_j(\mathbf{r})\right\rangle = \frac{k_B T}{4\pi K} \cdot \frac{A_{ij}(\mathbf{r})}{r}(1 - \delta_{i3})\exp(-\xi_W^{-1} r) \tag{16}$$

In the case of a homogeneous director distribution in the filled **LC** (i.e. there is no orientational interaction between the **LC** and the colloidal particle surfaces) the matrix $A_{ij}(r) = \delta_{ij}$ and the nonzero components of correlation function are equal:

$$\langle \delta n_x(0)\delta n_x(r)\rangle = \left\langle \delta n_y(0)\delta n_y(r)\right\rangle = \frac{k_B T}{4\pi K} \cdot \frac{\exp(-\xi_W^{-1} r)}{r} \tag{17}$$

Equations (15)–(17) show that director fluctuation correlations are screened and this screening is the result of the director-colloidal particle surface interaction. Furthermore, these correlations are also influenced by the static disturbance of the director field caused by the director-surface interaction. We note that elements of the transition matrix $\hat{A}$ can be expressed in terms of the Euler angles of director orientation around the particle, but that the corresponding expressions obtained for spherical and cylindrical particles in papers [3–7] are too cumbersome to consider here.

A similar screening effect can also be obtained by imposing an external electric field in a pure nematic. It is useful to estimate the value of the equivalent field E required to obtain the same screening effect as found in the filled LC. The screening parameter in the electric field case is $\xi_E^{-2} = \frac{\varepsilon_a E^2}{4\pi K}$ [11]. Thus, putting $\xi_E = \xi_W$, we obtain:

$$E = \left(\frac{4\pi}{\varepsilon_a} \cdot \eta \frac{WS}{v_0} \overline{\cos^2 \alpha} \right)^{\frac{1}{2}} \tag{18}$$

For spherical particles of radius R

$$E = \left(\frac{12\pi}{\varepsilon_a} \cdot \eta \frac{W}{R} \overline{\cos^2 \alpha} \right)^{\frac{1}{2}} \tag{19}$$

Substituting typical values $\eta = 0.03$, $R = 10^{-7}\, m$, $\varepsilon_a = 0.5$, $W = 0{,}1\, J/m^2$ [13], and putting $\overline{\cos^2 \alpha} = 1$ we obtain $E = 10^8\, V/m$. This means that for typical LC cell with thickness $L = 10^{-4}\, m$, the stabilizing effect of the colloidal particles is equivalent to an external voltage $U = 10^4\, V$. This is more than two orders of magnitude greater than that usually applied to optically clear filled LC in cells of this thickness. As a result, one can assume the LC director-colloidal particle interaction is the principal factor stabilizing thermal director fluctuations in filled LCs.

3. FILLED LC: ISOTROPIC PHASE

The degree of orientational order in the nematic phase is determined by the order parameter, which for rod-like molecules equals $\langle (3/2)\cos^2\theta - (1/2) \rangle$. In the isotropic phase the order parameter equals zero but there are significant non-zero order parameter thermal fluctuations, which we denote by $\varphi(\mathbf{r})$. One can write the fluctuation part of the free energy of filled LC in the isotropic phase in the following way:

$$\delta F(\varphi) = \frac{1}{2} \int \left[a\varphi^2 + b(\nabla\varphi)^2 \right] dV - \frac{1}{2} W \int_\Sigma \varphi^2 dS, \; W > 0, \tag{20}$$

where the first term is the familiar Landau-de Gennes formula in the isotropic phase [14]. The second term involves integration takes over the surface of all particles and describes the anchoring interaction at the particles surfaces, as well as the contribution from volume terms of the type $\varphi(\mathbf{r}) \frac{d}{dr} \varphi(\mathbf{r})$ coming from the integral over the particle surfaces. We remind the reader that $a = a_0(T - T^*)$ and b are the parameters of the system, the temperature T^* is the limit of absolute stability of the isotropic phase on cooling.

We now rewrite Eq. (20) in terms of Fourier components of $\varphi(\mathbf{r})$:

$$\varphi(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{q}} \varphi_{\mathbf{q}} \exp(i\mathbf{q}.\mathbf{r}) \tag{21}$$

This yields

$$\begin{aligned}\delta F(\varphi) = \frac{1}{2V}\sum_{\mathbf{q}} (a + bq^2)|\varphi_{\mathbf{q}}|^2 - \\ \frac{W}{2V^2}\sum_{\mathbf{q},\mathbf{q}_1} \varphi_{\mathbf{q}}\varphi_{\mathbf{q}_1}\sum_m \int \exp(i(\mathbf{q}+\mathbf{q}_1)(\mathbf{r}+\mathbf{r}_m))dS\end{aligned} \tag{22}$$

Here the summation is over all particles, the integral is taken over the particle surfaces, and $\mathbf{r_m}$ is the position of particle m.

For a homogeneous distribution of particles in the bulk of filled LC the Fourier transform can be written:

$$\sum_m \exp(i(\mathbf{q}+\mathbf{q}_1).\mathbf{r}_m) = N\delta_{\mathbf{q}+\mathbf{q}_1,0} = \eta\frac{V}{v_0}\delta_{\mathbf{q}+\mathbf{q}_1,0} \tag{23}$$

Substituting Eq. (23) into Eq. (22) we obtain

$$\delta F(\varphi) = \frac{1}{2V}\sum_{\mathbf{q}}\left(a - \eta\frac{WS}{v_0} + bq^2\right)|\varphi_{\mathbf{q}}|^2 \tag{24}$$

After thermal averaging (24) using the equipartition theorem, this yields:

$$\left\langle|\varphi_{\mathbf{q}}|^2\right\rangle = \frac{k_B T V}{a_0(T - T^*) - \eta\frac{WS}{v_0} + bq^2} \tag{25}$$

This expression for the order parameter thermal fluctuation correlation function is exactly analogous to that of a pure LC, but with an altered critical temperature T^*. The new limit of stability is now

$$T^*(\eta) = T^* + \eta\frac{WS}{v_0 a_0} \tag{26}$$

The critical temperature shift is linear in colloidal concentration, and proportional to the particle surface area. In particular, in the case of spherical particles of radius R the shift $\Delta T^* \sim R^2$. This can be verified experimentally, and enables this contribution to ΔT^* to be distinguished from others.

4. CONCLUSIONS

The interaction between the surfaces of colloidal particles suspended in a nematic liquid crystal and the nematic director causes the correlations of the thermally-induced director fluctuations to be screened. The screening parameter ξ_W^{-1} is proportional to the colloidal concentration, to the director anchoring energy at the particle surfaces and to the particle surface area. Numerical estimates for experimental filled LCs show that this screening must be responsible for the experimentally observed reduction in the Rayleigh light scattering from the thermal director fluctuations.

The presence of the colloid particle-director interaction also means that the director in the filled LC is no longer uniform. This also modifies the spatial dependence of the thermal director fluctuation correlation function.

Finally, the colloid particle surface-order parameter interaction shifts the effective critical temperature T^* at which the isotropic state becomes unstable with respect to nematic fluctuations. This shift has a specific signature, which depends on particle size and concentration in such a way that it can be immediately identified experimentally.

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