Phase transitions in cholesteric liquid crystals

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Phase transitions in cholesteric liquid crystals are investigated. It is shown that three nonuniform phases with different symmetry can exist in a narrow region near the transition line. Improved formulas describing the optical phenomena in the critical region are obtained.

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1. INTRODUCTION

As is well-known, as the temperature is lowered cholesteric liquid crystals (CLC) undergo a transition from the uniform isotropic phase to a spiral phase (SP) characterized by a spatially nonuniform distribution of the orientations of the molecules. This is the only example of a phase transition in liquid crystals in which the symmetry-breaking is the same as in the crystallization of ordinary liquids. However, the difference from ordinary crystallization are very important. The most important of these is the smallness of the heat of transition and of the discontinuity in the order parameter, and also the extremely large magnitude of the period L of the structure compared with the intermolecular distances a. The small magnitude of the ratio a/L leads to the result that the SP of a CLC far from the transition point has, at distances $r \ll L$ and with accuracy $(a/L)^2$, the structure of the uniform ordered phase of a nematic liquid crystal (NLC). In particular, the SP of a CLC is described, as in a NLC, by one director n, which undergoes a slow rotation, with period L, about the axis of the spiral.

It is clear that this picture is also preserved near the transition point, if the discontinuity of the order parameter is large. We shall call such a transition an orientational transition. In addition, as will be shown in Sec. 2, there exists a broad region of values of the CLC parameters in which the discontinuity of the order parameter is small. In this case, in the vicinity of the transition point the structure of the SP of the CLC will differ substantially, even at short distances, from that of a NLC. In particular, the structure of the SP can no longer be described by one director.

We shall call this type of transition a structural transition. If in the uniform phase of the CLC we introduce the correlation length ξ of the orientations of the molecules, which characterizes the NLC-related short-range order, it turns out that $\xi \ll L$ in a transition of the orientational type whereas $\xi \gg L$ in the immediate vicinity of the transition point of a structural transition. In the second case the order-parameter correlation function displays a sharply pronounced maximum with wave-vector $q_0 = 4\pi/L$, analogous to the maximum in the structure factor of ordinary liquids.

In the present paper the different types of phase transitions in a CLC are investigated. The role of the critical fluctuations in the vicinity of a structural-transition point is considered. A simple method of calculating the critical light scattering and the rotation of the plane of polarization is presented. Experimental data indicating the existence of phase transitions of both types are discussed.

Some of the results presented below in the framework of a general approach have been obtained earlier[1-3].

2. QUANTITATIVE DESCRIPTION OF THE PHASE TRANSITIONS IN A CLC

1. We shall assume, as is usually done, that the phase transitions in a CLC can be described with the aid of a symmetric traceless tensor $Q_{\alpha\beta} = Q_{\alpha\beta}(\mathbf{r})$, separated out from the local dielectric-permittivity tensor:

$$Q_{\alpha\beta} = \varepsilon_{\alpha\beta} - {}^1/_3 \varepsilon_{\nu\nu} \delta_{\alpha\beta}.$$

The expansion of the free-energy functional $F\{\hat{Q}\}$ in powers of the perturbation $\hat{Q}(\mathbf{r})$ has the form

$$\begin{aligned} F\{\hat{Q}\} &= F_0 + T[\mathscr{H}_2\{\hat{Q}\} + \mathscr{H}_3\{\hat{Q}\} + \mathscr{H}_4\{\hat{Q}\}], \\ \mathscr{H}_2\{\hat{Q}\} &= \frac{1}{2!}\int dr [aQ_{\alpha\beta}^2 + b(\partial_\alpha Q_{\gamma\delta})^2 + c\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma} + 2de_{\alpha\beta\gamma}Q_{\alpha\delta}\partial_\gamma Q_{\beta\delta}], \\ \mathscr{H}_3\{\hat{Q}\} &= \frac{\mu}{3!}\int dr\, Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta}, \\ \mathscr{H}_4\{\hat{Q}\} &= \frac{\lambda}{4!}\int dr (Q_{\alpha\beta}^2)^2, \end{aligned} \tag{1}$$

where $\partial_\alpha \equiv \partial/\partial r_\alpha$. The presence in $\mathscr{H}_2$ of the last term, linear in the gradients, is associated with the absence of inversion symmetry of the CLC molecules.

We shall study the structure of the Hamiltonian $\mathscr{H}_2$. In the momentum representation,

$$\mathscr{H}_2\{\hat{Q}\} = \frac{1}{2}\sum_{\mathbf{q}} t_\alpha^\gamma(\mathbf{q}) \delta_{\beta\delta} Q_{\alpha\beta,\mathbf{q}} Q_{\gamma\delta,-\mathbf{q}}, \tag{2}$$

where

$$\begin{aligned} \hat{Q}_{\mathbf{q}} &= V^{-1/2}\int \hat{Q}(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}}\, dr, \\ t_\alpha^\gamma(\mathbf{q}) &= (a + bq^2)\delta_{\alpha\gamma} + cq_\alpha q_\gamma + 2dqL_{\alpha\gamma}(\mathbf{q}), \\ L_{\alpha\gamma}(\mathbf{q}) &= ie_{\alpha\gamma\nu}q_\nu/q, \quad q = |\mathbf{q}|. \end{aligned} \tag{3}$$

It is clear that in the expression (2) we can symmetrize and subtract the trace over each pair of indices α, β and γ, δ, i.e., replace $t_\alpha^\gamma \delta_{\beta\delta}$ by $R_{\alpha\beta}^{\gamma\delta}$, where

$$\begin{aligned} 4R_{\alpha\beta}^{\gamma\delta} &= t_\alpha^\gamma \delta_{\beta\delta} + t_\beta^\gamma \delta_{\alpha\delta} + t_\alpha^\delta \delta_{\beta\gamma} + t_\beta^\delta \delta_{\alpha\gamma} \\ &- {}^2/_3(t_\alpha^\delta + t_\beta^\alpha)\delta_{\gamma\delta} - {}^2/_3(t_\gamma^\delta + t_\delta^\gamma)\delta_{\alpha\beta} + {}^4/_9 t_\nu^\nu \delta_{\alpha\beta}\delta_{\gamma\delta}. \end{aligned}$$

It is not difficult to see that the tensor $R_{\alpha\beta}^{\gamma\delta}(\mathbf{q})$ and the correlation function

$$G_{\alpha\beta}^{\gamma\delta}(\mathbf{q}) = \langle Q_{\alpha\beta,\mathbf{q}} Q_{\gamma\delta,-\mathbf{q}} \rangle,$$

calculated in the Gaussian approximation, are mutually inverse tensors:

$$R_{\alpha\beta}^{\mu\nu}(\mathbf{q}) G_{\mu\nu}^{\gamma\delta}(\mathbf{q}) = I_{\alpha\beta}^{\gamma\delta},$$

where the unit tensor $I_{\alpha\beta}^{\gamma\delta}$ has the form

$$I_{\alpha\beta}^{\gamma\delta} = {}^1/_2\delta_{\alpha\gamma}\delta_{\beta\delta} + {}^1/_2\delta_{\alpha\delta}\delta_{\beta\gamma} - {}^1/_3\delta_{\alpha\beta}\delta_{\gamma\delta}.$$

The tensor $R^{\gamma\delta}_{\alpha\beta}(\mathbf{q})$ is a Hermitian operator acting in the five-dimensional space of the symmetric traceless tensors $Q_{\alpha\beta}$. We shall find its "eigenvectors" $\sigma^{s}_{\alpha\beta}(\mathbf{q})$ and eigenvalues $\tau^{s}(\mathbf{q})$ (s = 0, ...,4):

$$R_{\alpha\beta}{}^{\gamma\delta}(\mathbf{q})\,\sigma_{\alpha\beta}{}^{s}(\mathbf{q})=\tau^{s}(q)\,\sigma_{\gamma\delta}{}^{s}(\mathbf{q})$$

or

$$^{1}/_{2}t_{\alpha}{}^{\gamma}\sigma_{\gamma\beta}{}^{s}+{}^{1}/_{2}t_{\beta}{}^{\gamma}\sigma_{\gamma\alpha}{}^{s}-{}^{1}/_{3}t_{\delta}{}^{\gamma}\sigma_{\gamma\delta}{}^{s}\delta_{\alpha\beta}=\tau^{s}(q)\,\sigma_{\alpha\beta}{}^{s}. \tag{4}$$

The matrix $t^{\gamma}_{\alpha}(\mathbf{q})$ is the sum of the unit matrix and the matrices of projection on to the direction of $\mathbf{q}$ and of rotation in the plane perpendicular to $\mathbf{q}$. Consequently, the solutions of Eq. (4) should have the following form:

$$\begin{gathered}\sigma_{\alpha\beta}{}^{1}=l_{\alpha}l_{\beta},\quad \sigma_{\alpha\beta}{}^{2}=l_{\alpha}{}^{*}l_{\beta}{}^{*},\\ \sigma_{\alpha\beta}{}^{3}=i\cdot 2^{-1/2}(l_{\alpha}n_{\beta}+l_{\beta}n_{\alpha}),\quad \sigma_{\alpha\beta}{}^{4}=i\cdot 2^{-1/2}(l_{\alpha}{}^{*}n_{\beta}+l_{\beta}{}^{*}n_{\alpha}),\\ \sigma_{\alpha\beta}{}^{0}=6^{-1/2}(3n_{\alpha}n_{\beta}-\delta_{\alpha\beta}),\end{gathered} \tag{5}$$

where $\mathbf{n} = \mathbf{q}/q$, $\mathbf{l} = \mathbf{l}(\mathbf{q}) = (\mathbf{m} + i\mathbf{m}')/\sqrt{2}$ and the real unit vectors $\mathbf{m}$, $\mathbf{m}'$ and $\mathbf{n}$ form a right-handed set. The vectors $\mathbf{l}$ and $\mathbf{l}^{*}$ are the basis vectors of the circular polarization and satisfy the conditions

$$L_{\alpha\beta}l_{\beta}=l_{\alpha},\quad L_{\alpha\beta}l_{\beta}{}^{*}=-l_{\alpha},\quad \mathbf{l}^{2}=\mathbf{l}^{*2}=0,\quad \mathbf{l}\mathbf{l}^{*}=1.$$

The eigenvalues $\tau^{s}(\mathbf{q})$ are determined by substituting the expressions (5) into Eq. (4). We obtain

$$\begin{gathered}\tau^{1,2}(\mathbf{q})=a+bq^{2}\mp 2dq,\quad \tau^{3,4}(\mathbf{q})=a+(b+c)\,q^{2}\mp 2dq,\\ \tau^{0}(\mathbf{q})=a+(b+{}^{4}/_{3}c)\,q^{2}.\end{gathered} \tag{6}$$

The tensors $\sigma^{s}_{\alpha\beta}(\mathbf{q})$ for any $\mathbf{q}$ are a complete orthonormal basis in the space of the symmetric traceless tensors, i.e., they satisfy the conditions

$$\sigma_{\alpha\beta}{}^{s}(\mathbf{q})\,\sigma_{\alpha\beta}{}^{s'*}(\mathbf{q})=\delta_{ss'},\quad \sum_{s}\sigma_{\alpha\beta}{}^{s}(\mathbf{q})\,\sigma_{\gamma\delta}{}^{s*}(\mathbf{q})=I^{\gamma\delta}_{\alpha\beta}.$$

We shall assume in the following that the vectors $\mathbf{m}(\mathbf{q})$ and $\mathbf{m}'(\mathbf{q})$ are chosen such that $\mathbf{m}(-\mathbf{q}) = \mathbf{m}(\mathbf{q})$ and $\mathbf{m}'(-\mathbf{q}) = -\mathbf{m}'(\mathbf{q})$. Then $\mathbf{l}(-\mathbf{q}) = \mathbf{l}^{*}(\mathbf{q})$ and $\sigma^{s}_{\alpha\beta}(-\mathbf{q}) = \sigma^{s*}_{\alpha\beta}(\mathbf{q})$.

The expansions of the fields and correlation functions of interest to us have the following form:

$$Q_{\alpha\beta,q}=\sum_{s}\varphi_{q}{}^{s}\sigma_{\alpha\beta}{}^{s}(\mathbf{q}), \tag{7a}$$

$$R^{\gamma\delta}_{\alpha\beta}(\mathbf{q})=\sum_{s}\tau^{s}(q)\,\sigma_{\alpha\beta}{}^{s}(\mathbf{q})\,\sigma_{\gamma\delta}{}^{s}(-\mathbf{q}), \tag{7b}$$

$$G^{\gamma\delta}_{\alpha\beta}(\mathbf{q})=\sum_{s}[\tau^{s}(q)]^{-1}\,\sigma_{\alpha\beta}{}^{s}(\mathbf{q})\,\sigma_{\gamma\delta}{}^{s}(-\mathbf{q}). \tag{7c}$$

It is obvious that $\varphi^{s}_{-\mathbf{q}} = \varphi^{s*}_{\mathbf{q}}$, i.e., the fields $\varphi^{s}(\mathbf{r})$ are real. The tensors $\sigma^{s}_{\alpha\beta}(\mathbf{q})$ depend only through a common phase factor on the way of choosing the vectors $\mathbf{m}(\mathbf{q})$ and $\mathbf{m}'(\mathbf{q})$, i.e., the products $\sigma^{s}_{\alpha\beta}(\mathbf{q})\sigma^{s}_{\gamma\delta}(-\mathbf{q})$, in terms of which all observable quantities are expressed, do not depend on this choice. These products can be represented in invariant form by means of the relation

$$l_{\alpha}l_{\beta}{}^{*}={}^{1}/_{2}(L_{\alpha\beta}+\delta_{\alpha\beta}-n_{\alpha}n_{\beta}). \tag{7d}$$

However, in calculating scalar quantities it is more convenient to make use of the method described below.

2. We now turn to the investigation of the phase diagram of a CLC. In the vicinity of transitions of the orientational type we shall confine ourselves to the framework of the Landau theory. The applicability of this theory up to the first-order transition point is confirmed by the experimental data of the paper[2], and also by the fact that, as a rule, anomalous critical behavior of a NLC is not observed. In the neighborhood of transitions of the structural type the influence of specific fluctuations of the short-range order will be discussed in subsection 5.

The ordered phase of a CLC is characterized by the existence of the mean value $\bar{Q}_{\alpha\beta}(\mathbf{r})$. The symmetry of this tensor depends on which of the modes (6) has the lowest energy. It can be seen from the formulas (6) that the conditions for stability against the appearance of large gradients should always be fulfilled: b > 0, b + c > 0, b + 4c/3 > 0. These inequalities permit an arbitrary sign of the coefficient c. For c > 0 the purely transverse mode with s = 1 will possess the lowest energy:

$$\tau^{1}(q)=a+bq^{2}-2dq=\tau_{1}+\Delta_{1}(q/q_{1}-1)^{2},$$

where

$$\Delta_{1}=d^{2}/b,\quad \tau_{1}=a-\Delta_{1},\quad q_{1}=d/b.$$

For c < 0 the lowest will be the longitudinal-transverse mode with s = 3:

$$\begin{gathered}\tau^{3}(q)=a+(b+c)\,q^{2}-2dq=\tau_{3}+\Delta_{3}(q/q_{3}-1)^{2},\\ \Delta_{3}=d^{2}/(b+c),\quad \tau_{3}=a-\Delta_{3},\quad q_{3}=d/(b+c).\end{gathered}$$

(We assume that d > 0. For d < 0 we must replace s = 1 by s = 2 and s = 3 by s = 4.) In the first case the ground state of the one-dimensionally ordered phase should be a simple spiral (the dielectric-permittivity ellipsoid $\epsilon_{\alpha\beta} = \epsilon_{0}\delta_{\alpha\beta} + \bar{Q}_{\alpha\beta}$ rotates about the mean axis) and in the second case should be conical (the mean axis of the ellipsoid is perpendicular to the axis of the spiral and the other two axes have an angle of precession of 45°).

Assuming that the expansion (1) also describes well the properties of a CLC substantially below the transition point, where the CLC is described by the Frank energy, we obtain the well-known expressions for the Frank constants: $K_{11} = K_{22} = b + c$, $K_{22} = b$. Inasmuch as the condition $K_{22} < K_{11} \approx K_{33}$ is always fulfilled in the known liquid crystals, we may expect that c > 0 always. As will be shown below, the experimental data of Yang[4] also indicate a positive sign of c. Bearing these facts in mind, we shall carry out certain calculations for the case c > 0 only.

3. First we shall consider the one-dimensional spiral structures. We shall determine the equilibrium value $\bar{Q}_{\alpha\beta}(\mathbf{r})$ by substituting the expansions (7a) and (7b) into the functional (1) and varying with respect to the amplitudes $\varphi^{s}_{\mathbf{q}}$. It is clear, in the first place, that terms with $\mathbf{q} = \pm\mathbf{q}_{s}\cdot\mathbf{n}$ should exist, where $\mathbf{n}$ is the direction of the spiral axis, and s = 1 or s = 3, depending on the sign of c. In addition, generally speaking, the zeroth harmonic $\varphi^{0}_{0}\sigma^{0}_{\alpha\beta}(\mathbf{n})$ should exist. Generation of higher harmonics with $q/q_{s} = 2, 3, \ldots$ does not occur, because of the relation $\sigma^{s}_{\alpha\beta}(\mathbf{n})\sigma^{s'}_{\beta\delta}(\mathbf{n}) = 0$ for $s + s' \neq 0$. Denoting $\varphi^{0}_{0} \equiv \varphi_{0}$, $\varphi^{s}_{q_{s}\mathbf{n}} \equiv \varphi_{s}$, we obtain

$$\frac{F-F_{0}}{T}=\frac{1}{2}\tau_{0}\varphi_{0}{}^{2}+\tau_{s}\varphi_{s}{}^{2}+C_{s}\mu\varphi_{s}{}^{2}\varphi_{0}+\frac{C_{0}}{6}\mu\varphi_{0}{}^{3}+\frac{\lambda}{24}(\varphi_{0}{}^{2}+2\varphi_{s}{}^{2})^{2}, \tag{8}$$

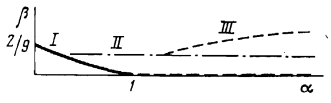
where

$$\tau_{0}=\tau^{0}(0)=a,\quad C_{0}=\mathrm{Sp}(\sigma_{\alpha\beta}{}^{0})^{3},\quad C_{s}=\sigma_{\alpha\gamma}{}^{0}\sigma_{\gamma\delta}{}^{s}\sigma_{\delta\alpha}{}^{0},$$

i.e., from (5), $C_{0} = 1/\sqrt{6}$, $C_{1} = -1/\sqrt{6}$ and $C_{3} = -5/2\sqrt{6}$.

Studying the expression (8) at the minimum, we find that the line of phase transitions with $\varphi_{0}, \varphi_{s} \neq 0$ is determined for s = 1 by the equation

$$\begin{gathered}9\beta^{2}+2(9\alpha-1)\beta-3\alpha(1-\alpha^{2})=0,\\ \alpha=2\lambda\Delta_{1}/\mu^{2},\quad \beta=4\lambda\tau_{1}/\mu^{2}.\end{gathered} \tag{9}$$



In this case,

$$\varphi_0=\frac{9}{2\sqrt{6}}\frac{\alpha-\alpha^2+\beta}{1+3\alpha}\frac{\mu}{\lambda},\quad \varphi_1^2=\frac{3}{2}\varphi_0^2\left(1+\frac{2}{3}\sqrt{6}\frac{\Delta_1}{\mu\varphi_0}\right). \qquad (10)$$

The quantity α characterizes the part of the energy associated with the nonuniformity. The quantity β determines the relative transition temperature, reckoned from the point of absolute instability of the uniform phase, $\tau_1 = 0$. The relation (10) is fulfilled everywhere below the transition point. For $\Delta_1 = 0$ we obtain from (10) $\varphi_1 = \pm(3/2)^{1/2}\varphi_0$, which, as is easily verified, corresponds to exact local uniaxiality of the tensor $\bar{Q}_{\alpha\beta}(\mathbf{r})$:

$$\bar{Q}_{\alpha\beta}\sim(\varkappa_\alpha\varkappa_\beta-{}^1/_3\delta_{\alpha\beta}),$$

where the director $\varkappa$ rotates with period $L = 4\pi/q_1$. Consequently, the quantity $\Delta_1/\mu\varphi_0$ is a measure of the non-uniaxiality of the CLC. This quantity increases along the transition line with increase of α, but decreases in the ordered phase with increase of φ_0, i.e., with decrease of the temperature.

The line of transitions of the orientational type, determined by Eq. (9), is shown in the figure by the solid line. For $\alpha = 0$ we obtain obvious agreement with the transition point in a NLC: $\beta_0 = 2/9$. For $\alpha \ll 1$ we have $\beta \approx 2/9 - \alpha/2$. At $\alpha = 1$ we reach the line $\beta = 0$ of absolute instability. For $\alpha > 1$ the boundary between the isotropic and the one-dimensional spiral phase lies along the second-order transition line $\beta = 0$. Near this line,

$$\varphi_*\approx(|\tau_1|/\lambda)^{1/2},\quad \varphi_0\approx\varphi_*^2\mu/\Delta_*,$$

i.e., the zeroth harmonic appears only as a perturbation. As a result, in the expansion (1) the cubic part $\mathcal{F}_3$, which, according to (8), generates terms that are odd in φ_0, is found to be even in φ_1. Consequently, the cause of the discontinuous nature of the phase transition for $\alpha < 1$ disappears. The line ($\beta = 0$, $\alpha \geq 1$) of transitions of the structural type is shown in the Figure by a thick dashed line.

For $c < 0$ the phase diagram has an analogous form.

4. By the Landau theory[5] the line $\tau_S = 0$ is not reached, because of the competition of non-one-dimensional structures with hexagonal symmetry. The energy of such structures is easily calculated in the region $\tau_S \ll \Delta_S$, i.e., $\beta \ll \alpha$, since in this case it is sufficient to take into account harmonics with wave vectors equal in modulus to q_S. It is not difficult to convince oneself that the most favorable structure near the transition point is the planar structure with reciprocal-lattice vectors $\pm\mathbf{k}_1, \pm\mathbf{k}_2, \pm\mathbf{k}_3$, where $|\mathbf{k}_i| = q_S$ and $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$. The temperature at which this phase becomes more favorable is determined from the condition $\tau_1 = a_1\mu^2/18\lambda$, where $a_1 \approx 0.8$. The line $\beta = 0.8\beta_0$, shown by the dashed-dotted line in the Figure, corresponds to this transition.

The coefficient a_1 is expressed in terms of the amplitudes of the interaction of three and four spiral waves. The products $l(\mathbf{k}_1)\cdot l(\mathbf{k}_2)$ arising in the calculation of these are determined in the following way: let $l(\mathbf{k}_j) = 2^{-1/2}(\mathbf{m}_j + i\mathbf{m}_j')$. We sweep the vectors $\mathbf{m}_2$ and $\mathbf{m}_2'$ about the direction of $\mathbf{k}_2$ until $\mathbf{m}_2'$ and $\mathbf{m}_1'$ coincide: $\mathbf{m}_2' \to \tilde{\mathbf{m}}_2' = \mathbf{m}_1'$, $\mathbf{m}_2 \to \tilde{\mathbf{m}}_2$. Then, as an eigenvector of the operator $\hat{L}$ of a rotation about $\mathbf{k}_2$, $l_2 \to \tilde{l}_2 = l_2 e^{i\varphi_2}$. It is obvious that $\mathbf{m}_1\cdot\tilde{\mathbf{m}}_2 = \cos\theta$, where θ is the angle between the vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. Consequently, $l_1\cdot l_2 = e^{-i\varphi_2}(-1 + \cos\theta)/\sqrt{2}$. The fourth-order terms do not depend on the angle φ_2, and in the third-order terms the angles $\varphi_{2,3}$ are determined from the energy-minimum condition. The phases of the three waves forming the structure turn out to be correlated.

5. It is interesting to investigate the limits, considered above, of the existence of the SP of a CLC by another method, enabling us to establish a connection with the low-temperature description of the CLC in terms of the Frank energy.

We write $\bar{Q}_{\alpha\beta}(\mathbf{r})$ in the form

$$\bar{Q}_{\alpha\beta}=\beta n_\alpha n_\beta-\delta m_\alpha m_\beta-\rho\delta_{\alpha\beta},$$

where the unit vectors $\mathbf{m}$, $\mathbf{n}$ and $\mathbf{m}\times\mathbf{n}$ are directed along the principal axes of the dielectric ellipsoid, and $\rho = {}^1/_3(\beta - \delta)$. We also introduce the parameters S and θ, related to the independent invariants:

$$\mathrm{Sp}\,\hat{Q}^2={}^3/_2S^2 \text{ and } \mathrm{Sp}\,\hat{Q}^3={}^3/_4S^3\cos 3\theta.$$

In this notation the expression (1) for the energy acquires the form

$$(F-F_0)/T=\int d\mathbf{r}(E_1+E_2),$$

where

$$\begin{aligned}E_1=&{}^1/_2 b\{[\nabla(\beta-\rho)]^2+[\nabla(\delta+\rho)]^2+[\nabla\rho]^2\}\\&+b\{\beta^2(\mathbf{n}[\nabla\times\mathbf{n}]-{}^1/_2q_1)^2+\delta^2(\mathbf{m}[\nabla\times\mathbf{m}]-{}^1/_2q_1)^2+2\beta\delta\\&\times(n_\beta\partial_\alpha m_\beta-{}^1/_2q_1[\mathbf{n}\times\mathbf{m}]_\alpha)^2+\beta^2(\nabla\mathbf{n})^2+\delta^2(\nabla\mathbf{m})^2\\&+\beta^2[\mathbf{n}\times[\nabla\times\mathbf{n}]]^2+\delta^2[\mathbf{m}\times[\nabla\times\mathbf{m}]]^2\}+c\{\beta\mathbf{n}(\nabla\mathbf{n})+\mathbf{n}(\mathbf{n}\nabla)\beta-\\&-\beta[\mathbf{n}\times[\nabla\times\mathbf{n}]]-\delta\mathbf{m}(\nabla\mathbf{m})-\mathbf{m}(\mathbf{m}\nabla)\delta+\delta[\mathbf{m}\times[\nabla\times\mathbf{m}]]-\nabla\rho\}^2,\end{aligned} \qquad (11)$$

$$\begin{aligned}E_2=&S^2\left[\frac{3}{32}\lambda\left(S+\frac{2}{3}\frac{\mu}{\lambda}\cos 3\theta\right)^2\right.\\&\left.+\frac{3}{4}\left(a-\Delta_1\cos^2\left(\theta-\frac{\pi}{6}\right)-\frac{1}{18}\frac{\mu^2}{\lambda}\cos^2 3\theta\right)\right].\end{aligned} \qquad (12)$$

Here, as before, it has been assumed that $c > 0$.

The energy E_1 is non-negative and vanishes only in the case of a simple spiral: β, δ and ρ are constants, and $\mathbf{m}$ and $\mathbf{n}$ rotate uniformly, with period $L = 4\pi/q_1$, in the plane perpendicular to the axis of the spiral. In the expression (12) we should put

$$S=-\frac{2}{3}\frac{\mu}{\lambda}\cos 3\theta.$$

The transition point a_c and the value of θ_c are determined from the condition

$$\Delta_1\cos^2\left(\theta_c-\frac{\pi}{6}\right)+\frac{\mu^2}{18\lambda}\cos^2 3\theta_c-a_c=0, \qquad (13)$$

where θ_c is the position of the minimum of the left-hand side of Eq. (13). This expression has two minima, symmetric about the point $\theta = \pi/6$, if $\alpha = 2\lambda\Delta_1/\mu^2 < 1$. The choice of one of the minima is determined, depending on the sign of μ, from the condition $S(\theta_c) > 0$. For $\alpha > 1$ the minimum moves to the point $\theta = \pi/6$. In this case $S_c = 0$, i.e., the phase transition becomes a second-order transition. As a result we obtain the phase boundaries shown in the Figure by thick lines (solid and dashed).

6. We now study the role of the fluctuations in the neighborhood of a phase-transition point of the structural type. In this case, depending on the sign of c in the expansions (7a)—(7c), it is sufficient to retain the term with $s = 1$ or $s = 3$. Neglecting the cubic term, we find that the field φ^S is described by the Hamiltonian

$$\mathcal{H}^s\{\varphi^s\}=\frac{1}{2}\sum_{\mathbf{q}}\tau^s(q)\varphi_{\mathbf{q}}^s\varphi_{-\mathbf{q}}^s+\frac{1}{24}\sum_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4=0}\lambda^s(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)\varphi_{\mathbf{q}_1}^s\varphi_{\mathbf{q}_2}^s\varphi_{\mathbf{q}_3}^s\varphi_{\mathbf{q}_4}^s, \tag{14}$$

where

$$\lambda^s(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)=\frac{\lambda}{3}[\sigma_{\alpha\beta}^s(\mathbf{q}_1)\sigma_{\alpha\beta}^s(\mathbf{q}_2)\sigma_{\gamma\delta}^s(\mathbf{q}_3)\sigma_{\gamma\delta}^s(\mathbf{q}_4)+\ldots+\ldots].$$

As was shown in[6] using the example of a field with the Hamiltonian (14) with λ = const, the system should experience a first-order transition to an ordered state with a nonzero average $\langle\varphi(\mathbf{r})\rangle$ forming a one-dimensional periodic distribution.

In[6] the reason for the discontinuous character of the transition was given a formal basis, starting from the change in sign of the renormalized coefficient λ. Here we present a more transparent explanation of this phenomenon. In zeroth order in λ the correlation function $g_S(q)=\langle\varphi_{\mathbf{q}}^S\varphi_{-\mathbf{q}}^S\rangle$ is equal to $[\tau_S+\Delta_S(q/q_S-1)^2]^{-1}$. Then,

$$\langle\varphi_s^2(\mathbf{r})\rangle=\int g_s(q)\frac{d\mathbf{q}}{(2\pi)^3}=\frac{q_s^3}{2\pi(\Delta_s\tau_s)^{1/2}}.$$

With decrease of τ_S there occurs an increase of $\langle\varphi_S^2(\mathbf{r})\rangle$ and, correspondingly, an increase of the interaction energy of the fluctuations, which, in first order in λ, is equal to

$$\langle\mathcal{H}_4\{\varphi_s\}\rangle=\frac{\lambda}{8}\langle\varphi_s^2(\mathbf{r})\rangle^2=\frac{\lambda q_s^6}{22\pi^2\Delta_s\tau_s}.$$

It is clear that, for sufficiently small τ_S, it is favorable to introduce a mean field $\langle\varphi_{\mathbf{q}}^S\rangle$ with $|\mathbf{q}|=q_S$, limiting the growth of $\langle\varphi^2(\mathbf{r})\rangle$. This occurs at a value $|\tau_S|=\tau_{SC}$ such that $\langle\mathcal{H}_2\{\varphi\}\rangle\approx\langle\mathcal{H}_4\{\varphi\}\rangle$, i.e., $\tau_{SC}\approx\lambda\langle\varphi_S^2(\mathbf{r})\rangle$, whence

$$(\tau_{sc})^{1/2}\approx q_s^3\Delta_s^{-1/2}. \tag{15}$$

In this region certain corrections to τ_S are important; however, the order of magnitude of the estimates is not changed.

The phenomena considered in this subsection occur when the following two inequalities are fulfilled. The first requires a strongly pronounced dip in the soft mode at $q=q_S$, i.e., $\tau_{SC}\ll\Delta_S$ with τ_{SC} from formula (15) and $\Delta_S\approx\tau_0$. The second inequality demands that the calculated quantity $\langle\varphi^2(\mathbf{r})\rangle$ does not exceed its limiting value φ_0^2, where φ_0 is of the order of the magnitude S of the order parameter far from the transition point, i.e., $\varphi_0\approx 0.1-1$. For the theory to be quantitatively correct, these inequalities must be regarded as strong. They can be written in the form

$$q_s^6/\Delta_s\ll\lambda\ll\Delta_s^2/q_s^3$$

or, eliminating λ, in terms of the relation (15):

$$q_s^6/\Delta_s\ll\tau_{sc}\ll\Delta_s.$$

The condition for compatibility of these inequalities ($q_S^3\ll\Delta_S$) is fulfilled with a margin of 10^{-11}, i.e., it is sufficient in practice to fulfil the right-hand inequality, and this was achieved in the experiments of Yang[4].

In the disordered phase in the immediate vicinity of the structural-transition point the correlation function $G_{\alpha\beta}^{\gamma\delta}$ is determined as before by the expansion (7c), in which, however, we must change the gap in the spectrum of the lowest mode, i.e., replace τ_S by r_S, which, according to the results of[6], satisfies the equation

$$r_s=\tau_s+\frac{q_s^3}{4\pi(\Delta_s r_s)^{1/2}}\int\lambda^s(\mathbf{n},-\mathbf{n},\mathbf{n}',-\mathbf{n}')\frac{d\mathbf{n}'}{4\pi}. \tag{16}$$

The functions $\lambda^S(\mathbf{n},-\mathbf{n},\mathbf{n}',-\mathbf{n}')=\lambda^S(\theta)$, where $\cos\theta=\mathbf{n}\cdot\mathbf{n}'$, are calculated by the method described in subsection 3. We obtain that, for s = 1,

$$\lambda^1(\theta)=\frac{\lambda}{3}\left(1+\sin^6\frac{\theta}{2}+\cos^6\frac{\theta}{2}\right),$$

and for s = 3,

$$\lambda^3(\theta)=\frac{\lambda}{3}\left(1+\sin^4\frac{\theta}{2}(1+2\cos\theta)^2+\cos^4\frac{\theta}{2}(1-2\cos\theta)^2\right).$$

Substituting these values into Eq. (16) we obtain in both cases:

$$r_s=\tau_s+\rho_s/r_s^{1/2};\quad \rho_s=3\lambda q_s^3/40\pi\Delta_s^{1/2}. \tag{17}$$

The variation of the quantity τ_S with temperature is determined by extrapolating the experimental data from the region $\tau_S\gg\rho_S^{2/3}$. At $\tau_S=0$, i.e., at the transition point obtained by the extrapolation, $r_S=\rho_S^{2/3}$ and $dr_S/d\tau_S=2/3$. This number can be checked experimentally. The true transition point $\tau_S=-\tau_{SC}$, according to the results of the previous paper[6] and in agreement with the experimental data of Yang[4], lies lower ($\tau_{SC}\approx\rho_S^{2/3}$). As was shown in[6], all corrections to the correlation function that are not taken into account by Eq. (16) are small. Consequently, in the neighborhood of the transition point changes of the critical indices do not occur. In the case when, numerically, $\tau_{SC}\gg\rho^{2/3}$, or when the experiments are performed in the supercooled phase, according to Eq. (17) a crossover from the dependence $r_S\approx\tau_S$ to the dependence $r_S\approx(\rho_S/\tau_S)^2$ can be observed.

The exact determination of the transition temperature requires the numerical solution of a system of transcendental equations. Moreover, the observed transition point may be too low because of the slow nucleation process. Therefore, we shall confine ourselves to the estimate obtained above (cf. (15)) $\tau_{SC}\approx\rho_S^{2/3}$, $r_{SC}\approx\rho_S^{2/3}$, which can be written as

$$r_{sc}\approx\Delta_s^{2/3}\lambda^{2/3}/b.$$

The corresponding line is shown in the Figure by the thin dashed line. Here it is assumed that the quantity r_S, related to τ_S by Eq. (17), is plotted along the ordinate axis. The form of the other lines is not changed by this relabeling. We see that the line of transitions to a triangular structure is bounded on two sides by the conditions

$$\mu^2/\lambda<\Delta_s<b^{1/2}\mu^3/\lambda^{5/2}.$$

Alternatively, these inequalities can be written as bounds on the magnitude of μ:

$$\lambda^{5/2}q_s^2/\Delta_s^{1/2}<\mu^2<\lambda\Delta_s.$$

3. LIGHT SCATTERING AND ROTATION OF THE PLANE OF POLARIZATION OF LIGHT

1. In this Section we shall calculate the scattering amplitude and rotation of the plane of polarization in the isotropic phase of a CLC near the phase-transition point. The problem of the critical light-scattering has been considered in the paper[1] by de Gennes; the result, however, was presented in a cumbersome form which excluded the possibility of treating the experimental data near a transition point of the structural type[4]. The fluctuational rotation of the plane of polarization

was investigated in[2,3]. In the paper[3] of Kats the vicinity of a transition of the structural type with s = 1 was considered and an answer was obtained to within a constant coefficient. In the work of Cheng and Meyer[2] the neighborhood of a transition of the orientational type was investigated theoretically and experimentally. However, the calculational method used contained microscopic model assumptions, so that the formulas obtained also have an indeterminate coefficient.

We shall start from the normal-mode expansions (7a) and (7c) and make use of the method proposed by Kats[3] for calculating corrections to the dielectric permittivity.

2. We shall consider the critical light-scattering. Let the incident and scattered light have wave vectors $\mathbf{k}$ and $\mathbf{k}'$, and $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. The integral scattering cross-section is determined by the formula

$$\frac{d\sigma}{d\Omega} = \frac{1}{32\pi^3} k_0^4 G_{\alpha\beta}^{\gamma\delta}(\mathbf{q}) e_\alpha e_\gamma e_\beta' e_\delta', \tag{18}$$

where $\mathbf{e}$ and $\mathbf{e}'$ are the polarization vectors of the incident and scattered light and $G_{\alpha\beta}^{\gamma\delta}(\mathbf{q})$ is determined by the expansion (7c). The differential scattering cross-section $d\sigma\omega/d\Omega d\omega$ for isotropic relaxation is determined by an expression analogous to (18), but with $\tau^S(\mathbf{q})$ replaced by $\frac{1}{2}T\eta[\tau_S^2(\mathbf{q})/T^2 + \omega^2/\eta^2]$, where η is the Landau-Khalatnikov relaxation constant.

Suppose, e.g., that $\mathbf{e} = \mathbf{e}' \parallel \mathbf{k} \times \mathbf{k}$, as in the experiments of[4]. Then from (7c), putting $\mathbf{m}(\mathbf{q}) \parallel \mathbf{e}$, we easily obtain

$$\frac{d\sigma}{d\Omega} = \frac{1}{32\pi^3} k_0^4 \left[\frac{1}{4\tau^1(q)} + \frac{1}{4\tau^2(q)} + \frac{1}{6\tau^0(q)}\right].$$

With this geometry, the longitudinal-transverse modes (s = 3, 4) make no contribution to the scattering.

In the vicinity of a transition point of the structural type and for $q \approx q_S$, it is sufficient to keep the term with s = 1 or with s = 3 in the expansion (7c). Let the incident light be polarized, as before, perpendicularly to the scattering plane. Then from formula (18) we obtain

$$\frac{d\sigma}{d\Omega} = \frac{1}{128\pi^3} k_0^4 (\tau_s(q))^{-1} f_s(\theta, \varphi),$$

where θ is the light-scattering angle and φ is the angle between the scattering plane and the plane of polarization of the light. By making use of formula (7d) in the calculation of the scalar products that arise, we find that, for s = 1,

$$f_1(\theta, \varphi) = \sin^2(\theta/2)\cos^2\varphi + \sin^2\varphi.$$

For s = 3 the scattered light is found to be polarized in the scattering plane and

$$f_3(\theta, 0) = 2\cos^2(\theta/2).$$

In Yang's experiments[4] the critical scattering, called "Bragg scattering," was observed through a polarizer set up perpendicularly to the scattering plane. Consequently, we can conclude that the case s = 1 occurred, i.e., c > 0.

3. We consider now the phenomenon of the rotation of the plane of polarization of light. This effect is associated with the appearance of a term that is noninvariant under the replacement $\mathbf{k} \to -\mathbf{k}$ in the dielectric-permittivity tensor $\epsilon_{\alpha\beta}(\mathbf{k})$. By the method of Kats[3] we obtain

$$\varepsilon_{\alpha\gamma}(\mathbf{k}) - \varepsilon_{\alpha\gamma}(-\mathbf{k}) = \frac{k_0^4}{12\pi\varepsilon_0} \int \frac{d\mathbf{q}}{(2\pi)^3} D_{\beta\delta}(\mathbf{q}+\mathbf{k}) [G_{\alpha\beta}^{\gamma\delta}(\mathbf{q}) - G_{\alpha\beta}^{\gamma\delta}(-\mathbf{q})], \tag{19}$$

where

$$D_{\beta\delta}(\mathbf{k}) = \frac{4\pi}{k_0^2 - k^2}\left(\delta_{\beta\delta} - \frac{k_\beta k_\delta}{k_0^2}\right),$$

$k_0 = \epsilon_0^{1/2}\omega/c$ and $|\mathbf{k}| = k_0$. We shall assume that $k_0 \approx q_S$, but $k_0 \neq 2q_S$.

First we shall consider the vicinity of a transition of the orientational type. In the integral in formula (19) momenta $q \approx q_S(\tau_S/\Delta_S)^{1/2} \gg q_S k_0$ are important. In this case the principal contribution to the integral is given by the longitudinal part (not interacting with the transverse modes (s = 1, 2)) of the photon Green function $D_{\beta\delta}$. Consequently, in the expression (7c) we should retain only the terms with s = 3, 4. (From the symmetry condition, the contribution of the term with s = 0 vanishes.) Expanding the integrand to first order in q_3 and $\mathbf{k}$, we obtain

$$\varepsilon_{\alpha\gamma}(\mathbf{k}) - \varepsilon_{\alpha\gamma}(-\mathbf{k}) = \frac{k_0 q_3}{18\pi\varepsilon_0} [(b+c)a]^{-1/2} L_{\alpha\gamma}. \tag{20}$$

In a transition of a structural type associated with a dip in a mode with s = 1, the region of momenta $|\mathbf{q}| \approx q_1$ is important in the integral in formula (19). Assuming that $k_0 \neq 2q_1$, we obtain

$$\varepsilon_{\alpha\gamma}(\mathbf{k}) - \varepsilon_{\alpha\gamma}(-\mathbf{k}) = \frac{k_0^3}{12\varepsilon_0} (\Delta_1\tau_1)^{-1/2} f(x) L_{\alpha\gamma}, \tag{21}$$

where $x = q_1/2k_0$ and

$$f(x) = \ln\left|\frac{x-1}{x+1}\right| + x\ln\left|\frac{1-x^2}{1+x^2}\right|.$$

The coefficients of $L_{\alpha\gamma}(\mathbf{k})$ in formulas (20) and (21) are the difference $\epsilon_+ - \epsilon_-$ of the squares of the refractive indices for right- and left-polarized waves.

4. CONCLUSION

As shown in Sec. 2, the line of transitions between the uniform and nonuniform phases in a CLC consists of three parts, shown in the Figure by a solid line, a dashed-dotted line and a thin dashed line, and labeled by the numbers I, II, and III. The line I corresponds to a CLC with a structure with large period L. Below this line the CLC is characterized by a tensor $Q_{\alpha\beta}(\mathbf{r})$ that is almost uniaxial, i.e., it can be described, as at low temperatures, by one director. For a CLC with a smaller period L the phase transition should occur on the line II and lead to a phase with hexagonal symmetry. In this case, on further lowering of the temperature a further transition to a one-dimensional spiral phase should occur. For still smaller values of L the phase transition occurs on the line III and again leads to a one-dimensional structure, describable, however, by a substantially nonuniaxial tensor $Q_{\alpha\beta}(\mathbf{r})$. The differences between the phases I and III, on the one hand, and the low-temperature phase of the CLC, on the other, can be manifested only in a narrow region near the corresponding lines. In this region, unfortunately, because of the nucleation the medium is strongly heterogeneous and inaccessible for optical observations[2,4].

Study of the optical effects in the isotropic phase makes it possible to distinguish the transition line I from II or III with confidence. In the vicinity of the line I the light scattering should be the same as in the vicinity of the transition point in a CLC (sic; NLC?). In the vicinity of the transition lines I and II, in light scattering with wave vector $q \approx q_S$ we should observe

"Bragg wings"[4], reflecting the existence of the dip in the mode $\tau_S(q)$ at $q \approx q_S$. The phenomenon of the rotation of the plane of polarization of light in the vicinity of the line I and in the outer neighborhood ($\tau_S \gtrsim \Delta_S$) of the lines II and III is described by formula (20), and in the immediate vicinity ($\tau_S \ll \Delta_S$) of the lines II and III is described by formula (21)[1)]. (The temperature dependences defined by these formulas are qualitatively equivalent.)

The data of Yang[4] on light scattering in CLC's of the type CEEEC, with typical value $L \approx 200$ μm, definitely indicate a phase transition of the structural type with $s = 1$ on line II or III. At the transition point, $\tau_1/\Delta_1 \approx -0.1$ (unfortunately, the possible errors were not indicated). The negative value of τ_1 would indicate a transition on line III. It would be possible to distinguish the lines II and III by the anomalies described in subsection 5 of Sec. 2. However, in Yang's work[4] a special study of the light scattering near the extremum $q = q_1$ was not carried out. The formulas given in Sec. 3 can make the treatment of experimental data easier, as compared with the formulas, derived by de Gennes in[1], which Yang[4] used.

In the work of Cheng and Meyer[2] the rotation of the plane of polarization of light was investigated in the vicinity of the phase transition in a CLC with an anomalously large $L \approx 700$ μm. In this case it is possible to obtain the stimate $\Delta_S/\tau_S \approx 0.2$, i.e., in accordance with the conclusions reached above, the transition occurs on the line I.

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[1)]We must distinguish the correction, calculated here, to the dielectric permittivity from the order parameter introduced earlier, which has a δ-function dependence on the wave-vector.

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