

Critical opalescence in thin films of cholesteric liquid crystals

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It is shown that critical opalescence can arise near a nematic–cholesteric structural transition in a thin layer of a cholesteric liquid crystal, even when the orientation is strongly oriented at the boundaries of the sample. The geometric variational approach, previously developed by the authors (V. L. Golo and E. I. Kats, *Pis'ma Zh. Eksp. Teor. Fiz.* **55**, 275 (1992) [*JETP Lett.* **55**, 275 (1992)]), is used to calculate the corresponding cross section for light scattering, taking into account fluctuations which are nonuniform in the plane of the layer.

1. In sufficiently thin layers of cholesteric liquid crystals a very distinctive nematic–cholesteric structural phase transition occurs on the boundary of the sample when the orientation is strongly anchored. There is an extensive literature on the theoretical and experimental investigation of this transition (see, for example, Ref. 2 and the works cited there). Thus far, however, all investigations concerning this subject have been limited to polarization—optical determination of the structure of the liquid crystal.

In the present paper we wish to call attention to the fact that the scattering of light in a thin layer of a cholesteric liquid crystal also exhibits a number of features, and near this structural phase transition it increases critically, which leads to the critical opalescence phenomenon.

It should be noted that anomalous enhancement of scattering (or fluctuations) in thin layers is associated not with fluctuations of the director, which usually occur in liquid crystals and which, when there is strong anchoring at the boundaries, are themselves significantly suppressed. Critical opalescence in this case is caused by the softness of the system near the structural phase transition. This softness is manifested as a quite wide “plateau” in the curve of the effective energy versus the structural characteristic in the degeneracy space, i.e., versus some angle β , which plays the role of the order parameter (see our work in Ref. 1; we use the same notation here).

In the present paper we employ the geometric variational method, developed in Ref. 1, for calculating the intensity of light scattering. The crux of this method is that specially chosen contours in the space S^2 of the order parameter, which correspond to the symmetry of the system, are employed as the trial functions. In the case of a cholesteric liquid crystal these contours are circles on the sphere S^2 . Of course, a contour must pass through a point (on the sphere) corresponding to strong-anchoring conditions:

$$\mathbf{n}(z=0) = \mathbf{n}(z=L) = \mathbf{n}_0, \quad (1)$$

where \mathbf{n} is the director, z is the coordinate along the normal to the boundaries of the sample, and L is the thickness of the film of liquid crystal. Without loss of generality, we can set $\mathbf{n}_0 \equiv (\sin \alpha, 0, \cos \alpha)$.

The second structural parameter characterizing our variational contour is determined by the unit vector \mathbf{m} drawn from the center of the sphere S^2 to the center of the

circle (contour). This unit vector can also be parameterized with the help of a single angular variable β (see Ref. 1):

$$\mathbf{m} \equiv (\sin \beta, 0, \cos \beta).$$

In Ref. 1 we studied a one-dimensional problem, i.e., we assumed that all quantities are functions of the coordinate z only. In this case the Frank energy, calculated on the variational contours described above, prescribes some effective energy $V(\beta)$, which determines all structural transformations occurring in the film. We present the expression obtained in this manner for $V(\beta)$, assuming for simplicity that $K_1 = K_3$ and $K_2 = \kappa K_1$ (where $K_{1,2,3}$ are the Frank constants and κ is a dimensionless parameter) and measuring $V(\beta)$ in units of $K_1 L$:

$$V(\beta) = \frac{1}{2} \sin^2(\alpha - \beta) \sin^2 \beta + \frac{1}{2} \sin^4(\alpha - \beta) \sin^2 \beta + \cos^2(\alpha - \beta) \sin^2(\alpha - \beta) \cos^2 \beta + \kappa \{ [q_0 + \sin^2(\alpha - \beta) \cos \beta]^2 + \frac{1}{2} \cos^2(\alpha - \beta) \sin^2(\alpha - \beta) \sin^2 \beta \}, \quad (2)$$

where q_0 is the inverse pitch of the cholesteric helix.

2. As usual,³ in order to study scattering of light in one or another structure we must determine (under a prescribed boundary condition) the minimum of the effective potential $V(\beta)$ and expand the energy of the nonuniformity E_g up to terms of second order in the gradients. The latter energy, like $V(\beta)$, is obtained from the Frank energy by integrating along the variational contours given by the parameter β , but taking into account the coordinate dependence of the parameter β .

A general calculation of this type would lead to complicated expressions. We shall simplify the problem. Specifically, since we are interested only in long-wavelength fluctuations (i.e., scattering of light with small transferred wave vectors in the plane), we can separate the longitudinal (in the plane of the layer) and transverse (i.e., along the z -axis) degrees of freedom. On the basis of the geometry of the system (thin films), the transverse degrees of freedom can be eliminated from the analysis; i.e., we assume that the structure is an equilibrium one along the z -axis. As concerns the longitudinal degrees of freedom, they must be included in the harmonic approximation in the energy of nonuniformity.

Thus our problem consists of finding the effective stiffness coefficients of the structure, i.e., the coefficients of the matrix $C_{\mu\nu}$ in the expansion of the energy of nonuniformity

$$E_g = c_{\mu\nu} (\nabla_\mu \beta) (\nabla_\nu \beta),$$

where μ and ν are longitudinal coordinates (x or y). We note that elimination of the transverse degrees of freedom in this manner is conceptually analogous to the approach employed in hydrodynamics for describing so-called shallow water.⁴ In both cases the geometry of the problem makes it possible to take into account approximately the transverse degrees of freedom and to obtain the effective energy only for longitudinal degrees of freedom.

Even in the shallow-water approximation the two-dimensional problem is still too complicated to be solved analytically. In order formally to simplify the problem, we examine the dependence only on one coordinate (x) in the plane of the layer. We emphasize that this assumption is not fundamental and we employ it exclusively in order to obtain easily interpretable expressions.

Direct calculation of the gradient energy in the approximations described above reduces to averaging the Frank energy over the transverse coordinate (z). As trial functions we employ, as done in Ref. 1, the following parametrization of the director \mathbf{n} . This parametrization corresponds to choosing circular contours on S^2 :

$$\mathbf{n} = \cos(\alpha - \beta) (1 - \cos z) \hat{m} + \sin z \sin(\alpha - \beta) \hat{y} + \cos z \hat{n}_0, \quad (3)$$

where \hat{y} is the unit vector along the y -axis, and the other parameters were explained above. In contrast to Ref. 1, however, we now take into account the x -dependence of the parameter β and include in the expansion of the energy terms quadratic in $\nabla_x \beta$. The corresponding calculation gives

$$E_g = (\nabla_x \beta)^2 \left\{ \frac{1}{2} \cos^2(\alpha - 2\beta) + \frac{15}{8} \cos^2(\alpha - \beta) \sin^2 \beta + \frac{7}{8} \sin^2 \alpha - \frac{15}{4} \cos(\alpha - \beta) \sin \beta \sin \alpha + \frac{5}{8} \cos^4(\alpha - \beta) \sin^2 \beta + \frac{1}{2} \cos^2(\alpha - \beta) \sin^2 \alpha - \frac{1}{4} \cos^3(\alpha - \beta) \sin \beta \sin \alpha + \frac{1}{2} \kappa [(\cos^2(\alpha - \beta) \cos \beta + \sin(\alpha - 2\beta) \sin(\alpha - \beta))^2 + \frac{1}{4} (\cos^2(\alpha - \beta) \cos \beta + \sin(\alpha - 2\beta) \sin(\alpha - \beta) - \cos \alpha \cos(\alpha - \beta))^2] \right\}. \quad (4)$$

Thus in the present case only the stiffness coefficient c_{11} is different from zero, and its value is determined by the expression in brackets in Eq. (4). Generally speaking, $c_{11} \sim K$. As an illustration, the function $c_{11}(\beta)$ with $\alpha = 0.47$ and $\kappa = 1.6$ is shown in Fig. 1.

3. The formulas (2) and (4) determine the total energy of the nonuniformly deformed structure of a thin cholesteric layer:

$$E = V(\beta) + c_{11} (\nabla_x \beta)^2. \quad (5)$$

For fixed values of the parameter β (and the material coefficients of the liquid crystal) controlling the structural transition, one or another equilibrium state of the system, determined by the minimum of $V(\beta)$, is established. The energy corresponding to the fluctuation deviation $\tilde{\beta} = \beta - \beta_m$ of β from the minimum value β_m is determined from Eq. (5) as

$$E_f = a \tilde{\beta}^2 + c_{11} (\nabla_x \tilde{\beta})^2, \quad (6)$$

where $a \equiv (\partial^2 V / \partial \beta^2)_{\beta_m}$.

The correlation function $\langle \tilde{\beta}, \tilde{\beta} \rangle$ is found in the standard manner from Eq. (6). In terms of the Fourier components, the correlation function has the form

$$\langle \tilde{\beta}, \tilde{\beta} \rangle = T / (a + c_{11} q_x^2). \quad (7)$$

The formula (7) is structurally reminiscent of the expression for the correlation function³ of the orientation of a liquid crystal in an external field, though the physical meaning of the coefficients a is entirely different. The cross section for the scattering of light is proportional to the correlation function (7):

$$\sigma = v (\epsilon_a \omega^2 / 4\pi c^2)^2 \langle \tilde{\beta}, \tilde{\beta} \rangle (\mathbf{i}\mathbf{f})^2,$$

where v is the volume of the sample, ω is the frequency of light, c is the velocity of light, ϵ_a is the permittivity anisotropy, and \mathbf{i} and \mathbf{f} are unit polarization vectors of the incident

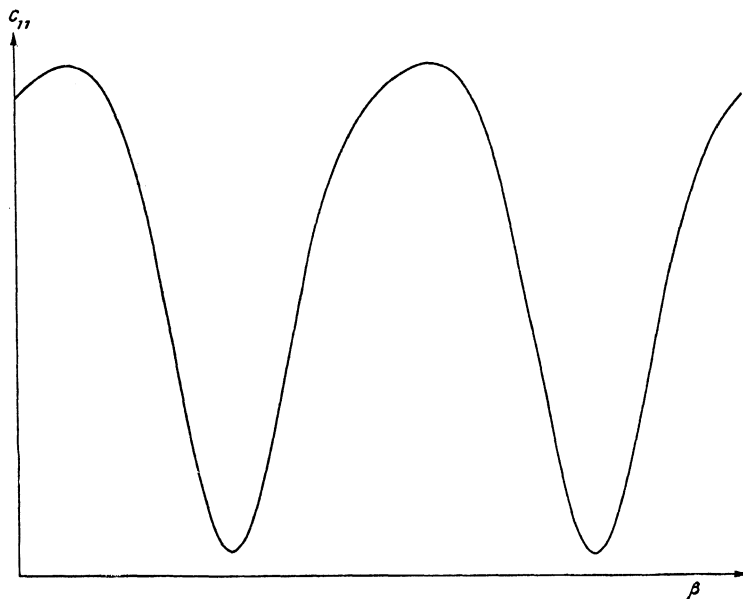


FIG. 1.

and scattered light, respectively. Important features, which in principle make it possible to distinguish experimentally the light-scattering mechanism under discussion here from other background mechanisms, are, first, the high permittivity ($\epsilon_a \sim 0.1$) and, second, the polarization factor. The first factor makes the scattering by fluctuations $\tilde{\beta}$ stronger than scattering by density fluctuations, while the second factor distinguishes the scattering of interest from the usual scattering by fluctuations of the director in liquid crystals.³

We now make some estimates. It should be expected that $c_{11} \sim K$ [see Eq. (4)], and the parameter a depends significantly on the structural state of the film. Far from phase-transition points we have $a \sim Kq_0^2$, and for this reason the long-wavelength scattering of light ($q_x \ll q_0$) is, to a large extent, suppressed.

A different situation arises near points of structural transformations. For example, as shown in Ref. 1, at a nematic-cholesteric transition the effective potential $V(\beta)$ is almost constant in a wide region ($\sim 30^\circ$). This corresponds to a very small parameter $a \ll Kq_0^2$. In the particular case $\alpha = 0$ the results of Ref. 5 lead to similar conclusions.

It is interesting to note that the smallness of the parameter a in a wide range of values of the parameter of β determining the structure of the cholesteric in the thin layer is, in a certain sense, a numerical fact and for this reason the phenomenon of critical opalescence, corresponding to this small

value of a , is not simply a softening of the fluctuations of the order parameter, as usually happens for all second-order transitions (incidentally, the nematic-cholesteric transition which we are studying can be a strong first-order transition). The smallness of a is determined by the presence of a plateau in the effective potential $V(\beta)$ and for this reason it is a consequence of the additional degeneracy of the cholesteric structure in the thin layer.

We believe that the phenomenon, which we have discovered, of anomalous degeneracy of a cholesteric near a structural transition could be associated with the diverse optical phenomena occurring in thin layers of liquid crystals. One aim of the present work was to bring these questions to the attention of experimentors.

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