EFFECT OF PERIODIC PERTURBATIONS ON THE CHOLESTERIC MESOPHASE

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The effect of inhomogeneous fields on cholesteric liquid crystals is considered. Various types of solutions that minimize the free energy arise, depending on the geometry of distribution of directions of the inhomogeneity and cholesteric helical axis. The effects should be taken into account in interpreting the experimental data on the appearance of a periodic structure in thin layers of cholesteric liquid crystals [3]. A phenomenon similar to critical opalescence is noted on transition from the cholesteric phase to the nematic phase in an external field.

1. The influence of homogeneous fields on cholesteric liquid crystals was first investigated by de Gennes[1]. (An analogous problem for helicoidal antiferromagnets was considered earlier by Dzyaloshinskiĭ [2]). The conclusions of these studies depend on the direction of the field relative to the axis of the helix and on the ratio of the elastic moduli K_{ii}

$$F=\frac{1}{2}\int dV\{K_{11}(\operatorname{div}\mathbf{n})^2+K_{22}(\mathbf{n}\operatorname{rot}\mathbf{n}+\alpha)^2+K_{33}(\mathbf{n}\operatorname{rot}\mathbf{n})^2-\chi(\mathbf{Hn})^2\}, \quad (1)$$

n is the director vector, χ is the anisotropic part of the dielectric or diamagnetic susceptibility, H is the external field, and α is the pitch of the helix. For real cholesteric substances $\chi > 0$.

In the absence of an external field, the ground state of the cholesteric mesophase is given by the following relations for the director components that minimize (1):

$$n_x=\cos\alpha z,\qquad n_y=\sin\alpha z,\qquad n_z=0, \quad (2)$$

where the z axis is directed parallel to the helix. The direction of the helix axis is determined, for example, by the boundary conditions to the functional (1), and the actual analysis pertains therefore to sufficiently thin films.

When a field is applied perpendicular to the z axis (e.g., parallel to y), the period along the z axis increases smoothly with the field and becomes infinite at $H_c = \frac{1}{2}\pi\alpha(K_{22}/\chi)^{1/2}$, i.e., a transition into the nematic phase takes place. If the field is directed along the z axis and $K_{22} = K_{33}$, the period does not change at all up to fields $2\pi^{-1}H_c$, where it becomes infinite suddenly. On the other hand, if $K_{22} \neq K_{33}$, then there exists a region of smooth variation of the period $2\pi^{-1}H_c(K_{22}/K_{33})^{1/2}$, $2\pi^{-1}H_c(K_{33}/K_{22})^{1/2}$. For simplicity, we shall henceforth neglect this region, and consider only the isotropic case $K_{11} = K_{22} = K_{33}$.

Everything stated above pertains to a homogeneous external field. In real devices that employ cholesteric liquid crystals, however, one uses inhomogeneous fields (usually periodic in space)[3]. This is therefore the situation considered in the present paper. In the case of inhomogeneous fields, the investigation is much more complicated and new possible solutions appear. Although it is difficult to analyze them in analytic form (nonlinear differential equations with variable coefficients), it is possible to understand the character of the solutions corresponding to the minimum value of the free energy. In addition, we consider in the present paper a question connected with the continuous transition from the cholesteric to the nematic phase in a magnetic field. Since a viscous mode that vanishes in the long-wave limit ($g \to 0$) exists in such a stransition, a phenomenon similar to the critical opalescence in ordinary phase transitions should be observed.

2. We consider first a field directed along the z axis and periodically dependent only on y (we have in mind only such types of inhomogeneities). In this case, a conical molecule configuration is possible, i.e.,

$$n_x=\cos\theta\cos\varphi,\qquad n_y=\cos\theta\sin\varphi,\qquad n_z=\sin\theta. \quad (3)$$

The functional for the free energy (1) is transformed with (3) in the following manner:

$$F=\frac{1}{2}\int dV\Big\{K\Big[\Big(\frac{\partial\theta}{\partial y}\Big)^2+\Big(\cos^2\theta\frac{\partial\varphi}{\partial z}-\alpha\Big)^2+\cos^2\theta\sin^2\theta\Big(\frac{\partial\varphi}{\partial z}\Big)^2\Big]-\chi H^2(y)\sin^2\theta\Big\}. \quad (4)$$

The Euler-Lagrange equations corresponding to (4) take the form

$$\frac{d}{dz}\Big(\cos^2\theta\frac{\partial\varphi}{\partial z}-\alpha+\cos^2\theta\sin^2\theta\frac{\partial\varphi}{\partial z}\Big)=0,$$

$$-4K\Big(\cos^2\theta\frac{\partial\varphi}{\partial z}-\alpha\Big)\cos\theta\sin\theta\frac{\partial\varphi}{\partial z}+\sin2\theta\cos2\theta\Big(\frac{\partial\varphi}{\partial z}\Big)^2-2\chi H^2(y)\sin\theta\cos\theta-\frac{\partial^2\theta}{\partial y^2}=0. \quad (5)$$

The first of these equations requires

$$\partial\varphi/\partial z=(C_1+\alpha)/\cos^2\theta(1+\sin^2\theta). \quad (6)$$

The integration constant C_1 should be chosen to minimize (4):

$$F=\frac{1}{2}\int dV\Big\{K\Big[\Big(\frac{\partial\theta}{\partial y}\Big)^2+\Big(\frac{C_1-\alpha\sin^2\theta}{1+\sin^2\theta}\Big)^2+\frac{\operatorname{tg}^2\theta(C_1+\alpha)^2}{(1+\sin^2\theta)^2}\Big]-\chi H^2(y)\sin^2\theta\Big\}. \quad (7)$$

From the condition that (7) be minimal it follows that θ = const. From the second equation of (5) we see that θ can assume only the values 0 and $\pi/2$. If $H^2 > 4\pi^{-2}H_c^2$, then $\theta = \pi/2$ ($C_1 = -\alpha$, and if $H^2 < 4\pi^{-2}H_c^2$, then $\theta = 0$ ($C_1 = 0$). In this case we obtain from (6) $\partial\varphi/\partial z = \alpha$. Thus, in fields weaker than critical, we

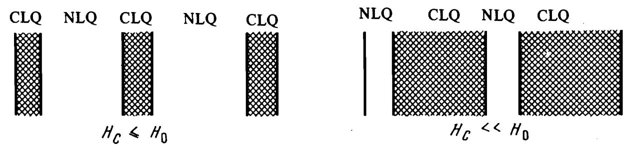

FIG. 1

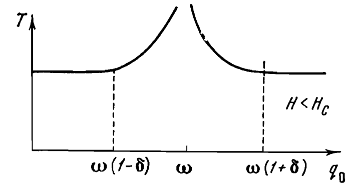

FIG. 2

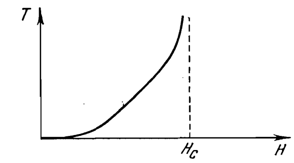

FIG. 3

have the usual cholesteric structure, and at $H > 2\pi^{-1}H_c$ we obtain the nematic structure $n(0, 0, 1)$. In the case of a periodic dependence $H = H_0 \cos(q_0 y)$, where $H_0 > 2\pi^{-1}H_c$, we obtain alternating layers of cholesteric and nematic phases (Fig. 1). The layer thickness is obviously determined by the value of q_0 and by the ratio H_c/H_0. At $H_c/H_0 \ll 1$, thick nematic layers alternate with thin cholesteric ones; the situation is reversed at $H_c/H_0 \sim 1$. We note here that structures of this type can find important applications in all types of liquid-crystal indicators and pickups [3].

We consider now another case, in which the field is directed along the y axis and depends periodically on x. We are then left with the cholesteric configuration

$$n_x = \cos\varphi, \quad n_y = \sin\varphi, \quad n_z = 0. \tag{2a}$$

But now φ can depend on x and z, so that the free energy takes the following form:

$$F = \frac{1}{2}\int dV\left\{K\left[\left(\frac{\partial\varphi}{\partial x}\right)^2 + \left(\frac{\partial\varphi}{\partial z} - \alpha\right)^2\right] - \chi H^2 \sin^2\varphi\right\}. \tag{8}$$

For the time being we consider fields H weaker than critical. Then [1]

$$z = \frac{4}{\pi\alpha}K(k,\varphi)E(k,\varphi), \tag{9}$$

where K and E are elliptic integrals of the first and second kind with modulus

$$k = E\left(k, \frac{\pi}{2}\right)\frac{H}{H_c}. \tag{9a}$$

We therefore have at $H \ll H_c$

$$\partial\varphi / \partial z = \alpha. \tag{10}$$

If $H = H_0 \cos(q_0 x)$, then we can rewrite (8), taking (10) into account, in the form

$$F = \frac{1}{2}\int dV\left\{K\left(\frac{\partial\theta}{\partial x} - q_0\right)^2 - \frac{\chi H_0^2}{4}\left[\sin(\theta - 2q_0 x) + \sin\theta\right]^2\right\}, \tag{11}$$

where $\theta = \varphi + q_0 x$.

The Euler-Lagrange equation corresponding to (11) cannot be solved in analytic form. The character of the solution can, however, be easily understood. There is a critical field

$$H_1 = \sqrt{K/\chi}\,q_0. \tag{12}$$

When $q_0 \ll \alpha$, this field satisfies the condition $H \ll H_c$ which is necessary for the derivation of (10). At fields $H < H_1$ there is a "homogeneous" distribution

$$\partial\varphi / \partial x = 0, \quad \partial\theta / \partial x = q_0. \tag{13}$$

It corresponds, according to (9), to a subdivision of the liquid crystal into layers (along the x axis) with different periods T of the cholesteric helix (along the z axis) (cf. Fig. 2). In visible light, these layers should be brightly colored. This is precisely what was observed in the experiments of [3]. On the other hand, when the field H_1 is reached, the inhomogeneous distribution

$$\partial\theta / \partial x = 0. \tag{14}$$

becomes more convenient, with

$$n_x = \cos(\alpha z - q_0 x), \quad n_y = \sin(\alpha z - q_0 x), \quad n_z = 0. \tag{15}$$

Such a doubly-periodic structure should have remarkable optical properties, and in particular selective reflection of circularly-polarized light with wavelength π/q_0 (when propagating along the x axis) and π/α (when propagating along the z axis).

In fields exceeding H ($\sim H_c$) our analysis no longer holds. It is clear, however, from the physical meaning of the problem that q_0 = const and $\alpha \to 0$ as $H \to H_c$, in accord with formula (9).

Other cases can be considered in similar fashion. We note also an interesting possibility that arises in the case of a field directed along the y axis and weakly modulated along the z axis. From (1) and (2a) we have in this case an equation for φ:

$$\frac{\partial^2\varphi}{\partial z^2} + \frac{\chi H_0^2}{2K}(1 + \delta\cos 2q_0 z)\sin 2\varphi = 0, \tag{16}$$

where it is assumed that

$$H = H_0(1 + {}^1\!/_2\,\delta\cos 2q_0 z), \quad \delta \ll 1. \tag{17}$$

The region of greatest interest is again $q_0 \sim \sqrt{\chi/K}H_0$, which corresponds to parametric resonance for a linear equation analogous to (16). Solving (16) by perturbation theory, we obtain for the period of the cholesteric helix the results shown in Fig. 3.

Leaving out the corresponding cumbersome derivations, we indicate only the possibility of obtaining a nematic structure, in the region of parametric resonance, also in fields weaker than the critical value H_c. This is due to the growth of φ in this region. The integral for the period T then diverges logarithmically

$$T = s\ln(\omega/\varepsilon).$$

Here s is the parametric growth exponent, $\omega = H_0\sqrt{\chi/K}$, $\epsilon = (q_0 - \omega)/2$, $s = {}^1\!/_2\sqrt{(\delta\omega/2)^2 - \epsilon^2}$.

3. We consider now the question mentioned in Sec. 1, the change over of the viscous modes in smooth transition from the cholesteric into the nematic phase in a magnetic field H_c. In cholesteric liquid crystal there are two types of oscillation [4]: twisting of the helical type, and viscous-shear modes. The first type of oscillation involves $n_x^{(1)}$ and $n_y^{(1)}$, and the second includes v_x, v_y, and $n_z^{(1)}$. Here $n_x^{(1)}$, $n_y^{(1)}$, and $n_z^{(1)}$ are the fluctuation corrections to the equilibrium values of the director (2a), and v_x and v_y are the velocity components of the liquid crystal. From the equations of hydrodynamics we can obtain (by linearizing these equations over the fluctuation increments) the dispersion equations

(q) for the modes. We put $n_x = \cos\varphi(z, t)$, $n_y = \sin\varphi(z, t)$, where $\varphi(z, t) = \varphi_0(z) + n_1(z, t)$; φ_0 is a function minimizing the functional (8) with H = const, and n_1 is the fluctuation increment. Since

$$\sin\varphi_0 = \mathrm{sn}(zH/kH_c),$$

(where sn is an elliptic function [5]), we obtain in the first type of oscillations

$$k^2\frac{H_c^2}{H^2}\frac{\partial^2 n_1}{\partial z^2} + k^2\left(\frac{i\omega\gamma_1 H^2}{K^2 H_c^2} + 1 - 2\,\mathrm{sn}^2\left(\frac{zH}{kH_c}\right)\right)n_1 = 0.$$

This is a generalized Lamé equation, the solutions of which are expressed in terms of the Jacobi Θ function. We write out only the oscillations of interest to us, which are separated by a gap in the cholesteric phase:

$$i\omega^{(1)} = \frac{K}{\gamma_1}\left\{\frac{1-k^2}{E(k,\pi/2)} - \frac{2k^2K(k,\pi/2)q^2}{[E(k,\pi/2)-(1-k^2)K(k,\pi/2)]^2}\right\}. \quad (18)$$

Here γ_1 is the characteristic viscosity, which remains unchanged with good approximations on going over to the nematic phase. The index 1 identifies the mode in which the cholesteric helix is twisted. As $H \to H_c$, according to (9a), the modulus $k \to 1$ and the gap vanishes like $(H - H_c)^2$.

In connection with the existence of such a mode, the effective cross section for small-angle scattering of light acquires the large factor $[\omega^{(1)}]^{-2}$,

$$\partial\sigma/\partial\Omega' \sim |(H-H_c)^2 + A(\theta/\lambda)^2|^{-2}, \quad (19)$$

where $d\Omega'$ is the solid angle element, λ is the wavelength of the incident light, and A is a constant quantity obtained from (18). Expression (19) for the intensity of the unshifted line is obtained by calculating the correlation function of the fluctuations of n at $\omega = 0$. Neglecting the angle factors, which play to role here, we have

$$\frac{d\sigma}{d\Omega'} = \frac{\langle n_q(0)n_{-q}(0)\rangle\,\omega^{(1)}}{\omega^2 + \omega^{(1)2}}.$$

On the other hand, the equal-time correlation function in the numerator takes the following form:

$$\langle n_q(0)n_{-q}(0)\rangle = T/\gamma_1\omega^{(1)}.$$

Therefore at $\omega = 0$ we have $d\sigma/d\Omega' \sim [\omega^{(1)}]^{-2}$. This indicates very intensive light scattering. The total cross section behaves near the transition like

$$(H-H_c)^{-2}. \quad (20)$$

This formula is not valid in the immediate vicinity of H_c, for we have neglected in it the logarithmic dependences on the field in the coefficient A. As to the shear modes, the dispersion equation for them cannot be expressed in analytic form. The equation that determines the dispersion of this mode is the general Hill equation

$$K\frac{\partial^2 n_z^{(1)}}{\partial z^2} - i\omega^{(2)}\gamma_2 n_z^{(1)} - \frac{KH^2}{k^2H_c^2}dn^2\left(\frac{zH}{kH_c}\right)n_z^{(1)} = 0, \quad (21)$$

where dn is the corresponding Jacobi elliptic function [5]. This function is doubly periodic with periods $2K(k, \pi/2)$ and $4iE(k, \pi/2)$, and has simple zeroes at all points comparable with $K(k, \pi/2) + iE(k, \pi/2)$. In weak fields, however, (21) goes over into the Mathieu equation

$$K\frac{\partial^2 n_z^{(1)}}{\partial z^2} - i\omega^{(2)}\gamma_2 n_z^{(1)} - \left[\frac{H^2}{k^2H_c^2}(1-k^2/2) + \frac{1}{2}\frac{H^2}{H_c^2}\cos\frac{2zH}{kH_c}\right]n_z^{(1)} = 0.$$

We can now obtain the dispersion law

$$i\omega^{(2)} = K(\alpha^2 + q^2)/\gamma_2. \quad (22)$$

The appearance of the gap $\sim\alpha^2$ in (22) is analogous to the appearance of the forbidden band in the periodic potential.

If it is assumed (as confirmed by direct substitution) that the dispersion equation retains its form when $H \to H_c$, but α is replaced by the corresponding period in the magnetic field (9)

$$\alpha \to {}^1\!/_4\pi\alpha / K(k, \pi/2)E(k, \pi/2),$$

then this mode also results in intensive scattering as $H \to H_c$

$$\sigma \sim \ln^2(H - H_c). \quad (23)$$

We note also that similar singularities should be observed in the scattering of slow neutrons. In this case the wave length of light λ should be replaced in (19) by 1/mv, where mv is the neutron momentum.

The questions considered in the present paper can be useful in the development of methods for determining the parameters of liquid crystals. On the other hand, intensive scattering of light on going over to the nematic phase can be used for indicator devices.

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