Phase transition of a cholesteric liquid crystal to a smectic

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The transition from the cholesteric phase of a liquid crystal to the smectic phase is studied using the analogy between a smectic-*A* and a superconductor. It is shown that in the experimentally controllable region of temperature the fluctuations are small and the pre-transitional phenomena cannot be described, as they have been by Pindak, Huang and Ho, by universal power functions. The result obtained in the experiment of Pindak, Huang and Ho for the dependence of the "indices" on the impurity concentration is explained from this standpoint. The nonuniversal dependences obtained coincide, with good accuracy, with the experimental dependences.

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Experimental studies of the critical phenomena in a phase transition of a cholesteric liquid crystal to a smectic-A phase have recently appeared[1]. Like the transition from a nematic to a smectic phase[2], this transition is a very weak first-order transition and has a broad pre-transitional region. A study of the pre-transitional growth of the Frank constants in the nematic → smectic-A transition, carried out using de Gennes' suggested analogy between a superconductor and a smectic-A phase[3], gives satisfactory agreement with experiment. Using this analogy, it is possible to investigate the pre-transitional phenomena in a cholesteric → smectic-A transition (the increase in the pitch of the spiral as the transition point is approached).

In the experiment of Pindak, Huang and Ho[1], a strong pre-transitional increase of the spiral pitch p was observed in a broad temperature region ($\delta p/p_0 \sim 1$, $0.2 < T - T_c < 6$ K). The results of the experiment were interpreted by the authors from the standpoint of the universal scale-invariant behavior $p - p_0 = D(T - T_c)^{-\nu}$. It was observed that the index ν here depends essentially on the concentration of added impurity.

It is shown in the present paper that in almost the entire experimentally controllable region of temperature the fluctuations are small and can be taken into account using perturbation theory. In the framework of this approximation the pre-transitional growth of the spiral pitch is described by a complicated function that is by no means a power function. Nevertheless, this function approximates the experimental results with good accuracy and explains their dependence on the concentration of impurities.

In the phase transition to a smectic-A phase the order parameter is the Fourier component ψ of the density ρ with wave vector $2\pi n_0/d$, where d is the interplanar distance and n_0 is the average director, which is always perpendicular to the equally-spaced layers: $\rho = \mathrm{Re}[\psi \exp(2i\pi n_0 \cdot r/d)]$. The invariance of the free energy under spatial rotations leads to the result that the interaction between fluctuations of the order parameter ψ and of the director (δn) should be determined by the gauge-invariant derivative $|(\nabla - i2\pi\delta n/d)\psi|^2$. Thus, the fluctuations δn play the role of the vector potential of the electromagnetic field, and $2\pi/d = e$ plays the role of the electric charge. The energy of director fluctuations not associated with a variation of density is given by the Frank formula[3].

Continuing this analogy, the cholesteric-smectic phase transition corresponds to the transition of a normal metal to the superconducting state in an external magnetic field. The corresponding Hamiltonian has the form

$$H=\tau|\psi|^2+\frac{1}{2}b|\psi|^4+\frac{1}{2m_\parallel}|(\nabla_x-ie(1-n_x))\psi|^2+\frac{1}{2m_\perp}|(\nabla_y-ien_y)\psi|^2 \quad (1)$$

$$+\frac{1}{2m_\perp}|(\nabla_z-ien_z)\psi|^2+\frac{1}{2}[K_1(\nabla\mathbf{n})^2+K_2(\mathbf{n}\,\mathrm{rot}\,\mathbf{n}+d_0)^2+K_3[\mathbf{n}\times\mathrm{rot}\,\mathbf{n}]^2],$$

where the x-axis is the direction perpendicular to the layers. In the cholesteric phase the density is uniform; therefore, $\psi = 0$ and the average director has the form $\mathbf{n}_0 = (\cos\alpha_0 z, \sin\alpha_0 z, 0)$, $\alpha_0 = 2\pi/p_0$. The smectic phase arising below the transition point can, as in superconductors, be of type I or type II, and is described by a uniform or nonuniform order parameter ψ. In the known crystals the long optical axis of the molecules is perpendicular to the layers, and these are type-I smectics (ψ = const). According to the Landau theory, a first-order transition to such a smectic occurs at the point $\tau_c = -\alpha_0(bK_2)^{1/2}$.

Allowance for fluctuations substantially alters the pattern of the transition. As the transition point is approached the spiral untwists and the quantity $\alpha(\tau) = 2\pi/p$ minimizing the free energy tends to zero. The condition for the minimum has the form

$$\alpha(\tau)-\alpha_0=\frac{M}{K_2V}, \qquad M=-\frac{\partial\Delta\mathcal{F}_\psi}{\partial\alpha}, \quad (2)$$

where $\Delta\mathcal{F}_\psi$ is that part of the free energy associated with the fluctuations of ψ, and V is the volume of the system. We shall take the fluctuations into account in the self-consistent field approximation. This means that the Ginzburg parameter (Gi), defined as the ratio of the singular part of the heat capacity of the cholesteric phase

$$\frac{\partial\mathcal{F}_{\mathrm{chol}}}{\partial\tau}=\int\langle|\psi|^2\rangle d^3r$$

to the heat capacity of the smectic phase calculated from the Landau theory, is small. As will be seen below, the Ginzburg-Landau region (Gi ≪ 1) in the experiment of[1] is sufficiently broad, and the pre-transitional phenomena can be studied while remaining in the framework of the self-consistent field approximation.

In this approximation we write the Hamiltonian (1) in the form

$$H=\left(\tau+\frac{e^2}{2m}\langle\delta n^2\rangle\right)|\psi|^2+\frac{1}{2m}[|\nabla_x-ie(1-\cos\alpha z))\psi|^2 \qquad (3)$$
$$+|(\nabla_y+ie\sin\alpha z)\psi|^2+|\nabla_z\psi|^2]+\frac{e^2}{2m}\langle|\psi|^2\rangle\delta n^2+H_F$$

where H_F is the Frank energy. (For brevity, we shall not distinguish $m_\perp$ and $m_\parallel$ in the intermediate calculations.)

The fluctuations δn make the following contribution to the free energy:

$$\Delta\mathcal{F}_n=-T\ln\int\exp\left\{-T^{-1}\left(\frac{e^2\langle|\psi|^2\rangle\delta n^2}{2m}+H_F\right)\right\}D\delta n \qquad (4)$$

and shift the transition point by an amount $\partial\Delta\mathcal{F}_n/\partial\langle|\psi|^2\rangle$. We note that the range of integration in (4) is bounded by the condition $n^2 = 1$, i.e., $n_0\cdot\delta n = 0$.

In addition to the additive corrections from the region of large momenta $k \sim 2\pi/d = e$ (e is the momentum cutoff) to the transition temperature and energy, shifting only their origins, there is a nonadditive contribution from the region of momenta of the order of α and $e(\langle|\psi|^2\rangle/K_2m)^{1/2}$. However, for not very large Gi (the Ginzburg-Landau parameter) and small α/e, these contributions are unimportant. The value of α/e is very small for all cholesteric liquid crystals ($\alpha/e \sim 10^{-2} - 10^{-3}$). The small size of this ratio simplifies the problem still further, making it possible to keep the terms of first order in α in the vector $(1-\cos\alpha z, \sin\alpha z, 0)$ in formula (3). In fact, along the z-direction it is sufficient to consider distances not exceeding the Larmore radius $\zeta = (2\alpha e)^{-1/2}$, i.e., $\alpha z < \alpha\zeta \sim (\alpha/e)^{1/2} \ll 1$. As a result, we have a form coinciding with the Ginzburg-Landau Hamiltonian for a superconductor in a uniform field $(0, \alpha_0, 0)$.

The behavior of a cholesteric liquid crystal is determined by three characteristic lengths: the correlation length ($\xi^{-2} = 2m_\perp\tau + e\alpha$) in the xy-plane perpendicular to the direction z of the spiral, the depth of penetration of twist deformations ($\lambda^2 = bK_2m_\perp/e^2\tau$), and a length associated with the spatial nonuniformity in the z-direction ($\zeta^{-2} = 2e\alpha$). Depending on the relative sizes of these lengths, we can distinguish the following limiting cases: 1) $\zeta \ll \xi$, $\xi^2/\xi^2 = \gamma + 1/2 \ll 1$—"large fields"; 2) $\zeta \gg \xi$, $\gamma \gg 1$—"small fields". The case of small fields, which corresponds in the limit to a nematic ($\zeta^{-1} = 0$), is of interest only for superconductors. The case of large fields corresponds to cholesteric liquid crystals. This fact turns out to be important. The second quantity λ ($\lambda/\xi(0) = \kappa$, $\lambda/\zeta = \beta$), firstly, determines the character of the low-temperature phase, and, secondly, substantially affects the width of the Ginzburg-Landau region.

Allowance for the fluctuations of the order parameter leads to the well-known formula

$$\Delta\mathcal{F}_\psi=-\frac{Ve\alpha T}{4\pi}\int\frac{dp_z}{2\pi}\sum_{n=0}^{\infty}\ln\frac{\pi T}{E_n},\quad E_n=\tau+\frac{e\alpha}{m_\perp}\left(n+\frac{1}{2}\right)+\frac{p_z^2}{2m_\parallel}. \qquad (5)$$

The quantity $M = -\partial\Delta T_\psi/\partial\alpha$ has been calculated by Prange for any γ[4], and has the form

$$M=\alpha^{1/2}(2e)^{1/2}\left(\frac{m_\parallel}{m_\perp}\right)^{1/2}\frac{VT}{4\pi}f(\gamma), \qquad (6)$$

where $f(\gamma)$ is a function expressable in terms of generalized Riemann zeta-functions with second argument $\gamma + 1/2$:

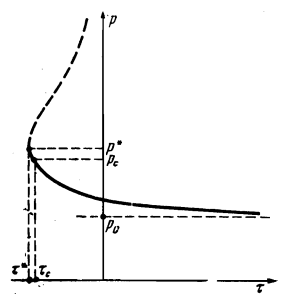
$$f(\gamma)=\frac{1}{8(\gamma+1/2)^{1/2}}-\frac{1}{32}\sum_{n=1}^{\infty}\left[\frac{1}{2}\left(n+\gamma+\left[(n+\gamma)^2-\frac{1}{4}\right]^{1/2}\right)\right]^{-3/2}$$
$$\times\left[1+\gamma\left[(n+\gamma)^2-\frac{1}{4}\right]^{-1/2}\right].$$

For large arguments, $f(\gamma) = \gamma^{-1/2}/24$, and for the moment M we obtain the usual result $M \propto \alpha$. In the other limiting case ($0 < \gamma + 1/2 \ll 1$) we have $f(\gamma) = 1/4(\gamma + 1/2)^{-1/2}$. We note that $f(\gamma)$ approaches its asymptotic form only at very small values of $\gamma + 1/2$. In the situation obtaining in the experiment of[1] we cannot use the asymptotic form. However, the asymptotic behavior of $f(\gamma)$ is sufficient for the elucidation of the qualitative picture.

Thus, we have an equation determining the dependence of the spiral pitch on the distance from the transition point:

$$\alpha_0-\alpha=T(2e)^{1/2}\left(\frac{m_\parallel}{m_\perp}\right)^{1/2}\frac{\alpha^{1/2}f(\gamma)}{4\pi K_2}. \qquad (7)$$

This dependence differs substantially from a power dependence and is presented qualitatively in the figure. At the point p^* the curve $p(\tau)$ has an infinite derivative. This point (p^*, τ^*), being the boundary of absolute instability of the cholesteric state, is never reached, since a first-order transition occurs earlier at a certain point (p_c, τ_c). The closeness of p_c to p^* makes it possible to explain the strong influence of impurities on the dependence $p(\tau, x)$ (x is the impurity concentration) obtained in the experiment of[1].



Below the transition point, on the other hand, the density fluctuations are unimportant; however, it is necessary to take the director fluctuations δn into account. Their contribution to the free energy is given by formula (4), in which it is necessary to replace the quantity $\langle|\psi|^2\rangle$ by $|\langle\psi\rangle|^2$ and limit the range of integration by the condition $\delta n_x = 0$. The characteristic momenta λ^{-1} and α_0, which determine the nonadditive part in the integral (4), appear in the ratio $\lambda^{-1}/\alpha_0 = \beta^{-1}(2e/\alpha_0)^{1/2}$, and thus, for not very large β, we have $\lambda^{-1} \gg \alpha_0$.

Neglecting the quantity α_0 in H_F, we obtain the free energy of the low-temperature phase, which coincides with the result of Halperin and Lubensky[5] for a nematic crystal. The free energy is determined by the parametric relations

$$V^{-1}\mathcal{F}=\tau|\psi|^2+\frac{b}{2}|\psi|^4-\frac{\varkappa_1^{-3}Tb^{3/2}m_\perp m_\parallel^{1/2}}{3\cdot2^{1/2}\pi}|\psi|^3,\quad\frac{\partial\mathcal{F}}{\partial|\psi|}=0. \qquad (8)$$

The term proportional to $|\psi|^3$ changes the pattern of the transition qualitatively in the case when the transi-

tion occurs in the region $\tau > 0$. In this case the form (8) has a nonzero minimum, which, starting from a certain τ, becomes favorable. For $\tau < 0$ there is only one minimum. For small $\kappa_1^{-3} bTm_\perp m_\parallel^{1/2}\tau^{-2}/16\pi$ this minimum is reached for

$$|\psi| = \left(\frac{|\tau|}{b}\right)^{1/2} \bar{\psi}(x) = \left(\frac{|\tau|}{b}\right)^{1/2} \left(1 + \frac{\varkappa_1^{-3}\,\mathrm{gi}}{8} + O\left(\left(\frac{\varkappa_1^{-3}\,\mathrm{gi}}{8}\right)^2\right)\right)$$

and is equal to

$$V^{-1}\mathcal{F} = -\frac{\tau^2}{2b}\mathcal{F}'(x) = -\frac{\tau^2}{2b}\left[1 + \frac{\varkappa_1^{-3}\,\mathrm{gi}}{3} + O\left(\left(\frac{\varkappa_1^{-3}\,\mathrm{gi}}{8}\right)^2\right)\right], \quad (9)$$

where gi denotes the Ginzburg parameter for $\alpha = 0$:

$$\mathrm{gi} \equiv \mathrm{Gi}(\alpha=0) = bTm_\perp m_\parallel^{1/2}\tau^{-1/2}/2\varkappa, \quad x = \varkappa_1^{-3}\,\mathrm{gi}/8.$$

In these formulas the quantity κ_1 differs from the κ defined above.

Below the transition point twist deformations are in no way distinguished from others. The quantity κ_1 depends on K_1, K_2, and K_3 and is given by Halperin and Lubensky[5]:

$$\varkappa_1^{-3} = \frac{8e^3 m_\perp^{3/2} m_\parallel^{1/2}}{b^{3/2}K_3^{3/2}}\left[\frac{K_3}{K_2} + \frac{K_3 m_\perp}{[(K_1 m_\perp)^{1/2} + (K_3 m_\parallel)^{1/2}]^2}\right]. \quad (10)$$

At the transition point the free energies of the high-temperature and low-temperature phases are equal:

$$\tfrac{1}{2}K_2(\alpha_c^2 - 2\alpha_0\alpha_c) = -\tau_c^2\mathcal{F}'(x)/2b. \quad (11)$$

All the formulas given are inapplicable near the point of absolute instability $\gamma = -\frac{1}{2}$ (in fact, instability already arises at the point (p^*, τ^*)). It follows from formula (5) that

$$V^{-1}\int \langle|\psi(r)|^2\rangle d^3r = V^{-1}\frac{\partial\mathcal{F}}{\partial\tau} = \frac{e\alpha T}{4\pi}\int\frac{dp_z}{2\pi}\sum_n \frac{1}{E_n}$$
$$= \frac{e\alpha T m_\parallel^{1/2}}{2^{1/2}\pi}\sum_n\left[\tau + \frac{e\alpha}{m_\perp}\left(n + \frac{1}{2}\right)\right]^{-1/2}. \quad (12)$$

This is a formally divergent series, but the part depending on τ is finite. The regular part of the series (12) can be expressed in terms of the generalized Riemann ζ-function $\zeta(\frac{1}{2}, \gamma + \frac{1}{2})$, which is defined as the analytic continuation of $\zeta(s, a)$ from the cut $s > 1$ to the entire real axis. Making use of the asymptotic form of the ζ-function at small values of $\gamma + \frac{1}{2}$, we have

$$\mathrm{Gi} \approx \mathrm{gi}\left[\frac{1}{4}\left|\Gamma\left(\gamma + \frac{1}{2}\right)\right|^{-1/2} + \left(\left|\frac{\gamma + 1/2}{\gamma}\right|\right)^{1/2}\right] \approx \frac{bTm_\perp m_\parallel^{1/2}}{8\pi\tau^{1/2}}\left|\Gamma\left(\gamma + \frac{1}{2}\right)\right|^{-1/2}. \quad (13)$$

The term following the asymptotic one in (13) has been kept in order that the passage to the limit $\alpha \to 0$ $(\gamma \to \infty)$ be obvious.

The pre-transitional growth of the spiral pitch can be expressed in terms of the dimensionless quantities of the theory. For this we represent formula (2) in the form

$$\frac{\delta p}{p_0} = \frac{p - p_0}{p_0} = -\frac{1}{VK_2\alpha}\frac{\partial\Delta\mathcal{F}_*}{\partial\alpha} = \frac{1}{VK_2\alpha}\left\langle\int\psi\frac{\partial\hat{H}}{\partial\alpha}\psi^* d^3r\right\rangle,$$

where $\langle\ldots\rangle$ denotes statistical averaging and $\hat{H} = \tau + [\nabla_x^2 + \nabla_z^2 + (\nabla_y - ie\alpha z)^2]/2m$ is the Hamiltonian operator. Expansing the order parameter ψ in the eigenfunctions $\psi_{np_xp_y}$ of the operator $\hat{H}$, we obtain

$$\frac{\delta p}{p_0} = \frac{e^2}{K_2 m_\perp}\sum_n\int|\psi_{np_xp_y}|^2\left(z - \frac{p_y}{e\alpha}\right)^2\frac{1}{E_n}\frac{dp_x dp_y}{(2\pi)^2}dz = \frac{e^2}{K_2 m_\perp}\overline{\langle z^2\rangle}\langle|\psi|^2\rangle.$$

Bearing in mind that

$$\overline{z_n^2} = \int|\psi_{np_xp_y}|^2\left(z - \frac{p_y}{e\alpha}\right)^2 dz \geqslant \overline{z_0^2} = \frac{2}{e\alpha},$$

we obtain

$$\frac{\delta p}{p_0} = 2\overline{\langle z^2\rangle}\,\mathrm{Gi}\,\xi^{-2}\varkappa^{-2} > 8\,\mathrm{Gi}\frac{\gamma}{\varkappa^2} = 8\,\mathrm{Gi}\,\beta. \quad (14)$$

Thus, a small value of Gi, making it possible to regard the fluctuations of ψ as small, does not imply that pre-transitional effects are small. For a given variation of p the Ginzburg-Landau region depends essentially on the quantity β. The maximum change in the spatial pitch $(\delta p_c/p_0)$ can be determined from Eq. (11):

$$2\frac{\delta p_c}{p_0} = \frac{4\gamma_c^2}{\varkappa^2}\mathcal{F}'(x_c) - 1 < \frac{\mathcal{F}'(x_c)}{\varkappa^2} - 1. \quad (15)$$

The latter formula is only valid for not very large κ, up to the point when a smectic phase with a nonuniform smectic density becomes favorable.

We turn now to the experiment of[1]. In this work the dependence of the spiral pitch on the distance from the transition point was investigated for different concentrations x of an added cholesteric-liquid impurity with the opposite spiral direction. Significant pre-transitional phenomena were observed ($\delta p_c/p_0 \sim 1$) in a broad region of temperature ($T - T_c \sim 6°$).

The authors approximated their results by the scale-invariant universal formula $p - p_0 = D(T - T_c)^{-\nu}$, using the least-squares method. In addition to the quantities D and ν, the transition temperature T_c was also a parameter of the approximation. Far from the transition, the presence of the impurity changed the spiral pitch in accordance with the law $dp_0/p_0 = -1.64dx$ (dx is the change in the impurity concentration) and shifted the transition point $T_c(x)$. It was found that the least-squares method approximated the curves, with different exponents $\nu(x)$ for different concentrations. On variation of x from 0 to 6%, ν changed from 0.5 to 0.8.

From our point of view, strong fluctuations begin to bring about appreciable changes in formulas (1)—(15) only at $T - T_c \sim 0.3 - 0.4°$. (We note that measurements were carried out only down to $T - T_c = 0.2°$). Evidently, the region of universal, pure-power behavior sets in still nearer to T_c.

In the region $T - T_c > 0.4°$, the experimental results can be approximated with high accuracy by formula (7). For the pure cholesteric crystal (x = 0) the best approximation is achieved with

$$dm_\perp = 0.41\ \text{Å}^{-1},\quad \tau_c = 2.7°,\quad K_2(m_\perp/m_\parallel)^{1/2}d^{3/2} = 2.15\cdot10^{-10}\ \text{erg-cm}^{1/3}$$

Taking, e.g., d = 36 Å and $m_\parallel/m_\perp = 0.1$, we obtain $K_2 \sim 3\times10^{-6}$ erg.cm^{-1}, $m_\perp \sim 0.01$ Å^{-2}. These values are perfectly reasonable and coincide in order of magnitude with the analogous values for nematic crystals (cf., e.g.,[2]). It follows directly from formulas (14) and (15) that $\kappa^2 = 0.5$, and, at the point $T - T_c = 0.4°$, the quantity Gi = 0.1. Direct measurements of the Frank constant, the specific-heat discontinuity and the quantities $m_\perp$, $m_\parallel$ and e appearing in the light-scattering amplitude for the nonanoate crystal would make it possible to check the validity of the theory based on the de Gennes Hamiltonian.

For low impurity concentrations it is possible, evidently, to assume that, of all the constants appearing in the theory, the only ones that depend on the concentration x are the spiral pitch p_0 far from the transition, the distance τ_c between the transition point and the absolute-instability point $\gamma = -\frac{1}{2}$, and the quantity b determining the specific-heat discontinuity. The in-

crease of the index ν on increase of the concentration x can be explained by the fact that the controlled region of temperatures in the experiment approaches the point (p^*, τ^*) at which $dp/d\tau = \infty$. This is achieved by increase of the quantity τ_c, which can be chosen so that the experimental curves for nonzero impurity concentrations are determined with sufficient accuracy by the dependence (7). On the other hand, an increase of τ_c and p_c with increasing concentration requires, according to (11), that b increase. Thus, when impurities are added there is a decrease in the liberation of latent heat, and, consequently the phase transition moves nearer to being a second-order transition. This decrease in the liberation of heat was indeed noted in[1]. In this case the quantity κ increases, which, for constant $\delta p_c/p_0$, narrows the Ginzburg-Landau region.

In conclusion we note that, with the estimate obtained above for κ, near the transition point surface "smecticality" (the analog of surface superconductivity) can arise. Surface superconductivity arises when $0.35 < \kappa^2 < 1$ and a magnetic field is parallel to the metal surface. For a liquid crystal this means that the director should be parallel, and the spiral axis perpendicular, to the surface of the sample. This geometry is realized in all experiments with liquid crystals, and is the only possible geometry, since the bounding plates orient the molecules in precisely this way. The effect consists in the appearance of a surface layer structure perpendicular to the surface and vanishing at distances of the order of $\xi = (2e\alpha)^{-1/2}$ from the boundary of the sample. The discovery of surface smecticality would be an important confirmation of the analogy between a superconductor and a smectic-A

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