# Electric field induced tricritical point in chiral polarized liquid crystals

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# ELECTRIC FIELD INDUCED TRICRITICAL POINT IN CHIRAL POLARIZED LIQUID CRYSTALS

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**Résumé.** — On présente une théorie de la transition entre un smectique C polarisé uniformément et un smectique C* hélicoïdal en présence d'un champ électrique parallèle aux couches, en utilisant la théorie de Landau. Le diagramme de phase (champ électrique-température) a un point tricritique ($E_t$, $T_t$). Les valeurs de $E_t$ et $T_t$ sont exprimées en fonction des propriétés macroscopiques du matériau.

**Abstract.** — We present a Landau theory of the transition between a uniformly polarized smectic C phase and a distorted smectic C* phase in the presence of an electric field parallel to the layers. The field-temperature (*E-T*) phase diagram is shown to exhibit a tricritical point ($E_t$, $T_t$). The values of $E_t$, $T_t$ are expressed in terms of observable macroscopic properties of the material.

We have been attempting recently [1] to explain some macroscopic properties of recently discovered [2-5] polarized liquid crystals composed of chiral molecules (DOBAMBC and related materials). These materials present a helicoidal smectic C phase (named the C* phase) with spontaneously polarized layers. On the basis of the suggested [2] linear coupling between the layer polarization and the quadrupolar order parameter characterizing the tilt in the C* phase, we found qualitative agreement with experiments on the structure of the C* phase and on the linear response to an external electric field $E$ parallel to the layers. For $E = 0$, experiments [2] and theory [1, 6] agree in showing a second-order phase transition from the smectic A to the C* phase. For an infinitesimal $E \neq 0$, the theory [1] predicts a monotonically decreasing line of critical temperatures $T_c(E)$ separating a uniformly polarized smectic C phase (at $T > T_c$) and a distorted smectic C* phase (at $T < T_c$). The distortion induced by the field in the C* phase is essentially a tilt of the axis of the helix with respect to the layer normal, which makes the C* phase biaxial.

In this paper, we go a step further in studying the line $T_c(E)$ and show that it terminates at a tricritical point ($E_t$, $T_t$), so that at $E > E_t$ the phase transition becomes first order. As in the previous works [1, 7], we use a formalism based on the Landau theory of second-order phase transitions.

Because of the linear coupling between the layer polarization and the tilt angle, these two are proportional below the transition [1, 2]. It can be shown [1] that only one complex parameter is independent, and one can choose $P = P_x + iP_y$ as such a parameter ($P_x$, $P_y$ are the cartesian components of the layer polarization ; the $z$-axis is chosen to be normal to the layers). In the smectic C* phase, $P$ varies helicoidally in the $z$-direction, with a pitch much larger than the interlayer distance. Therefore we will consider $P$ as a slowly varying function of $z$ and expand the free energy $F$ in both $P$ and $\partial P/\partial z$. The expansion of $F$ (per unit volume) has the form [7]

$$F = V^{-1} \int \frac{1}{2} [K_1 \mid P \mid^2 + iK_2(P\, \partial P^*/\partial z - P^*\, \partial P/\partial z) + K_3 \mid \partial P/\partial z \mid^2 + K_4 \mid P \mid^4 - E(P + P^*)]\, \mathrm{d}^3 r\,. \quad (1)$$

The integration is performed over the sample volume $V$, and the main assumption is that only $K_1$ is temperature dependent among the coefficients $K_1, \ldots, K_4$. The ordinary dielectric coupling, $-\frac{1}{2}\chi E^2$, is omitted from (1), since it is small [2] compared with the ferroelectric coupling, $-PE$. Expanding $P$ in a Fourier series $P(z) = \sum_k P_k\, \mathrm{e}^{ikz}$ and substituting into (1), we obtain

$$F = \frac{1}{2}[K_1 \mid P_0 \mid^2 + K_4 \mid P_0 \mid^4 - E(P_0 + P_0^*)] + \\ + \frac{1}{2}\sum_k{}' [(A_k + 4 K_4 \mid P_0 \mid^2) \mid P_k \mid^2 \\ + K_4(P_0^{*2} P_k P_{-k} + \text{c.c.})] \\ + \frac{1}{2} K_4 \sum_{kk'k''}{}' P_k P_{k'} P_{k''}^* P_{k+k'-k''}^* , \quad (2)$$

where

$$A_k = K_1 + 2 K_2 k + K_3 k^2 , \quad (3)$$

and the primes exclude $k = 0$ from the summation on $k$. The quantity $P_0$, corresponding to a uniform polarization, obviously vanishes for $E = 0$. In this case the helicoidal phase is characterized by a pitch $l = 2\pi/|k_0|$, where $k_0$, the wave number of the soft mode of the smectic A to C* phase transition, is determined from the minimization of $A_k : \partial A_k/\partial k = 0$. This yields

$$k_0 = - K_2/K_3 . \quad (4)$$

The critical temperature $T_{c0}$ at $E = 0$ is determined from the equation $A_{k_0}(T_c) = 0$, where

$$A_{k_0}(T) = K_1(T) - K_2^2/K_3 . \quad (5)$$

Assuming linear dependence of $A_{k_0}$ on $T$ near $T_{c0} : A_{k_0}(T) = C^{-1}(T - T_{c0})$, we obtain from (5) :

$$K_1(T) = C^{-1}(T - T_{c0}) + K_2^2/K_3 . \quad (6)$$

The zero-field dielectric susceptibility at $T > T_{c0}$ is $\chi = K_1^{-1}$ ; it tends to the finite value

$$\chi_c = K_3/K_2^2 \quad (7)$$

at $T \to T_{c0} + 0$, and behaves according to the Curie-Weiss law

$$\chi \cong C(T - T_{c0})^{-1} \quad (8)$$

at

$$T - T_{c0} \gg C\chi_c^{-1} .$$

For $E \neq 0$, the higher-temperature phase is a uniformly polarized smectic C, characterized by a real $P_0 \neq 0$ and $P_k = 0$ for all $k \neq 0$; $P_0$ is determined, as a function of $T$ and $E$, from the equation

$$K_1(T) P_0 + 2 K_4 P_0^3 = E \quad (9)$$

following from the minimization of $F$ with respect to $P_0$. As $T$ goes below $T_c = T_c(E)$, the free energy (2) becomes unstable with respect to the appearance of a non-zero $P_k$, in addition to $P_0$, so that a second-order transition occurs to a distorted (distorted because of $P_0 \neq 0$) smectic C* phase. To determine the soft mode of this transition, one has to diagonalize the *harmonic* part of $F$, quadratic in $P_k$ ($k \neq 0$), and find the lowest eigenvalue $A'_{k_0}$ of the quadratic expression. One thereby determines the wave number $k_0$ of the soft mode $\psi$ which is a certain linear combination of $P_{k_0}$ and $P^*_{-k_0} : \psi = \alpha P_{k_0} + \beta P^*_{-k_0}$. $T_c = T_c(E)$ is found from the equation $A'_{k_0} = 0$ together with eq. (9). It is then possible to present $F$ in the effective form

$$F = F_0 + \frac{1}{2}(A'_{k_0} \mid \psi \mid^2 + B \mid \psi \mid^4 + \cdots) . \quad (10)$$

Then it can be shown that, on increasing $E$, the coefficient $B$ decreases along the line $T_c(E)$, until it vanishes at the tricritical point $(E_t, T_t)$. The procedure described, which is simple but rather tedious, makes it possible to find the exact (within the Landau theory) parametric equations of the critical line $T_c(E)$ and the values of $E_t$, $T_t$ (expressed in terms of $\chi_c$, $C$, and $K_4$). It turns out, however, that a much simpler, although approximate, calculation based on neglecting the off-diagonal terms $P_k P_{-k}$ in (2) leads to the same results with small differences (e.g., a difference of 4 % in the value of $E_t$). For the sake of brevity and simplicity, we will use the approximate method here.

By neglecting the coupling terms $P_k P_{-k}$ in (2), the soft mode is again $\psi = P_{k_0}$ with $k_0$ from (4). However, $T_c$ is now determined from the equation

$$A'_{k_0} = A_{k_0} + 4 K_4 P_{00}^2 = 0 , \quad (11)$$

where $P_{00}$ is the equilibrium value of $P_0$ at the transition point. Since at this point $P_k = 0$ ($k \neq 0$), $P_{00}$ must satisfy eq. (9) with $K_1 = K_1(T_c)$. It then follows from (5)-(7), (9), (11) that

$$E = \chi_c^{-1} P_{00}(1 - 2 \chi_c K_4 P_{00}^2) , \quad (12)$$

$$T_c = T_{c0} - 4 C K_4 P_{00}^2 . \quad (13)$$

Eq. (12), (13) are parametric equations of the line $T_c(E)$. For

$$E \ll (\chi_c^3 K_4)^{-1/2} , \qquad P_{00} \cong \chi_c E ,$$

and we return to the quadratic dependence

$$T_{c0} - T_c(E) \propto E^2$$

found in our previous work [1].

Slightly below $T_c$, the system is characterized by two parameters, $\psi$ (complex) and $P_0$ (real). Putting in (2) $P_k = 0$ for $k \neq 0, k_0$ and $P_{k_0} = \psi$, we obtain

$$F = \frac{1}{2}(K_1 P_0^2 + K_4 P_0^4 - 2 E P_0 + \\ + A_{k_0} \mid \psi \mid^2 + 4 K_4 P_0^2 \mid \psi \mid^2 + K_4 \mid \psi \mid^4) . \quad (14)$$

Here $\psi$ is the order parameter of the phase transition, and $P_0$ is a non-critical parameter coupled to $\psi$ through the term $P_0^2 \mid \psi \mid^2$. To express $F$ as a function of $\psi$ only, we proceed as in a recent work of Benguigui [9]. Solving the equation $\partial F/\partial P_0 = 0$ with respect to $P_0$ infinitesimally below $T_c$ and expanding the solution in powers of $\mid \psi \mid^2$, we get

$$P_0 = P_{00} - \frac{4 K_4 P_{00} \mid \psi \mid^2}{K_1 + 6 K_4 P_{00}^2} + O(\mid \psi \mid^4) . \quad (15)$$

Substituting (15) into (14), we arrive at (10), with

$$B = K_4 \frac{K_1 - 10\,K_4\,P_{00}^2}{K_1 + 6\,K_4\,P_{00}^2}. \tag{16}$$

To find the tricritical point, we put $B = 0$ and, using eqs. (5) and (11), we obtain

$$P_{00}^2 = K_2^2/14\,K_3\,K_4 = 0.071/\chi_c\,K_4\,. \tag{17}$$

Substituting (17) into (12), (13), we get

$$E_t = 0.228\,\chi_c^{-3/2}\,K_4^{-1/2}\,, \tag{18}$$

$$T_t = T_{c0} - 0.284\,C\chi_c^{-1} \tag{19}$$

(the values obtained by the exact method are $E_t = 0.220\,\chi_c^{-3/2}\,K_4^{-1/2}$ and $T_{c0} - T_t = 0.238\,C\chi_c^{-1}$). According to the Landau theory [8], $K_4$ is related to the jump in specific heat $\Delta c$ occuring at the smectic A to C* phase transition (at $E = 0$) by the formula $\Delta c = C^2\,T_{c0}/4\,K_4$; hence (we use the exact value for $E_t$)

$$E_t = 0.44(\Delta c/C^2\,\chi_c^3\,T_{c0})^{1/2}\,. \tag{20}$$

Formula (20) expresses $E_t$ in terms of measurable quantities.

The simplified calculation presented in this paper results in $k_0$ independent of $E$ (eq. (4)). According to the more accurate calculation mentioned before, $k_0$ is a decreasing function of $P_{00}$, and thereby of $E$. However, for $E \leqslant E_t$, the decrease in $k_0$ is negligible, and therefore the above approximation is completely justified. For $E \gg E_t$, the growth of $E$ should lead to an appreciable decrease of $k_0$ until the helix is completely unwound [2, 3] ($k_0 = 0$). A theoretical description of this unwinding poses great difficulties, because the Landau theory is inapplicable for first-order transitions far from the tricritical point.

In conclusion, we have demonstrated on the basis of the Landau theory [8], that the line $T_c(E)$ of second-order phase transitions between the electrically induced uniform smectic C phase and the electrically distorted smectic C* phase terminates at a tricritical point. Having related the critical quantities $E_t$, $T_t$ to other measurable properties of the material, we hope to stimulate further experimental work on these interesting liquid crystal phases.

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