External-Field-Induced Tricritical Point in a Fluctuation-Driven Nematic–Smectic-A Transition

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We study theoretically the effect of an external field on the nematic–smectic-A transition close to the tricritical point, where fluctuation effects govern the qualitative behavior of the transition. An external field suppresses nematic-director fluctuations by making them massive. For a fluctuation-driven first-order transition, we show that an external field can drive the transition second order. In an appropriate liquid-crystal system, we predict the required magnetic field to be of order 10 T. The equivalent electric field is of order 1 V/μm.

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One of the seminal developments in the theory of phase transitions was the understanding of how thermal fluctuations can change the apparent analytic properties of the free energy and thereby render the predictions of mean-field theories invalid. The most widely appreciated consequence of thermal fluctuations is the shift in critical exponents from their mean-field values [1]. Another kind of consequence, less widely known, was predicted over two decades ago by Halperin, Lubensky, and Ma (HLM) [2]. They argued that the coupling between the fluctuations of a gauge field with the order parameter can convert a second-order transition to a first-order one (the "HLM effect"). Such fluctuation-induced first-order transitions are expected in two systems: the BCS transition in type-1 superconductors and the nematic–smectic-A (NA) transition of liquid crystals. In superconductors, the HLM effect is immeasurably weak; however, in liquid crystals, Anisimov, Cladis, and co-workers [3,4] have found experimental evidence that is consistent with it. But, as we discuss below, that evidence is indirect. In this paper, we show that applying a modest external field along the preferred orientation of the nematic leads to effects that may be unambiguously attributed to the coupling proposed by HLM, providing a direct test of the HLM scenario.

In liquid crystals, the HLM effect is sensitive to the ratio $T_{\mathrm{NA}}/T_{\mathrm{NI}}$ [T_{NA} and T_{NI} being the nematic–smectic-A (NA) and nematic-isotropic (NI) transition temperatures, respectively]. When the nematic range is large, i.e., when the NI transition is sufficiently far from the NA transition ($T_{\mathrm{NA}}/T_{\mathrm{NI}} \ll 1$), the transition is expected to be second order. Indeed, experiments on such systems yield critical exponents consistent with the 3D XY model [5,6] and show no detectable discontinuities.

For small nematic range ($T_{\mathrm{NA}}/T_{\mathrm{NI}} \to 1$), the nematic order parameter, which increases sharply on cooling below T_{NI}, has not yet saturated when the NA transition is reached. The nematic phase is thus only partially ordered at the NA transition, and the emerging smectic order parameter ψ is intrinsically coupled to both the nematic order parameter magnitude S (δS-ψ coupling) and the fluctuations in the director $\hat{\mathbf{n}}$ ($\delta\mathbf{n}$-ψ coupling).

There is some evidence for a crossover from a first-order transition driven by δS-ψ coupling to one driven by $\delta\mathbf{n}$-ψ coupling, as predicted by the HLM theory. Experimentally, $T_{\mathrm{NA}}/T_{\mathrm{NI}}$ can be tuned by mixing liquid crystals with slightly different aliphatic chain lengths. Based on the δS-ψ coupling, one expects that, in a mixture with mole-fraction x, the latent heat L at the NA transition goes as $L \propto x - x^{\star}$, where $x^{\star}$ is the mole fraction for a mixture at the Landau tricritical point (LTP). In one such mixture (of two cyanobiphenyls, 8CB and 10CB), Marynissen and co-workers [7] have found such a linear dependence. The extrapolation of this linear behavior gives the position of the LTP to be at 40% mole fraction of 10CB in 8CB. However, the latent heat does not go to 0 at the LTP. Instead, there is a quadratic crossover to a smaller value for $x < x^{\star}$. Anisimov and co-workers interpreted this result [3] as evidence supporting the HLM theory [2]. Independent work measuring the capillary length of 8CB-10CB mixtures by Tamblyn *et al.* [8] shows a similar crossover. Moreover, even for pure 8CB ($x = 0$), Cladis *et al.* [4] have deduced from front propagation experiments that the transition is first order. This has been confirmed by Yethiraj and Bechhoefer [9], who measured nematic fluctuations directly in real space.

Although these experiments suggest the existence of the nonanalytic cubic term in the smectic free energy, they do not show unambiguously that this effect arises from the HLM mechanism. One can directly probe the effect of director fluctuations on the nature of the transition by expanding the parameter space of the free energy to include an external magnetic (or electric) field. As we shall see below, the HLM theory, thus modified, gives rise to a peculiar form for the external-field dependence of measured quantities. An experimental observation of this specific form would be hard to attribute to any other mechanism.

In addition, applying an external field affords an experimentalist two other opportunities: first, direct suppression

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of fluctuation effects provides a continuously variable parameter with which to study the approach to the tricritical point in a single material. In contrast, each data point in mixtures corresponds to a different concentration and is therefore a different experiment. More important, mixtures may differ in properties other than simply the ratio of $T_{\rm NA}/T_{\rm NI}$, which complicates the comparison of different experiments. Second, the external field provides a way of suppressing the anisotropic coupling that gives the correlation-length exponents at the NA transition their weak anisotropy. In what follows, we will show that the subtle fluctuation effects at play at the NA transition can be tuned by modest magnetic (or electric) fields, making concrete predictions that can be checked experimentally.

We start with the free energy proposed by de Gennes. Because the nematic phase from which the smectic condenses is only partially ordered, the free-energy expansion must consider the effects of both nematic and smectic ordering. As the density modulation in smectic liquid crystals is nearly harmonic, one may write $\rho(\mathbf{r}) \simeq \rho_0(\mathbf{r})[1 + \rho_1(\mathbf{r})\sin(\mathbf{q}_0 \cdot \mathbf{r} - \phi)]$ and define the smectic order parameter by $\Psi(\mathbf{r}) \equiv \rho_1(\mathbf{r})e^{i\phi(\mathbf{r})}$. Assuming that $\hat{\mathbf{n}}$ fluctuates about the z axis, one can write the free energy as [10]

$$F_{\rm NA} = \int d^3x\, f_{\rm NA}(\Psi, \delta\mathbf{n}) = \frac{1}{2}\int d^3x \Big\{ \bar{r}|\Psi|^2 + \frac{u}{2}|\Psi|^4 + C_\parallel \Big| \frac{\partial \Psi}{\partial z} \Big|^2 + C_\perp |(\nabla_\perp - iq_0 \delta\mathbf{n}_\perp)\Psi|^2 + K_1(\nabla \cdot \delta\mathbf{n}_\perp)^2 + K_2(\hat{z} \cdot \nabla \times \delta\mathbf{n}_\perp)^2 + K_3\Big(\frac{\partial}{\partial z}\,\delta\mathbf{n}_\perp\Big)^2 \Big\}, \quad (1)$$

where $\delta\mathbf{n}_\perp = (\delta n_x, \delta n_y, 0)$. We rescale lengths in the $\hat{z}$ direction relative to other directions so that $C_\perp = C_\parallel = C$ and thus the three Frank constants $K_{1,2,3}$ are also rescaled. Close to the NA transition, $\bar{r}$ has the usual form $\alpha[(T - T_0)/T_0]$. The last three terms in the free energy correspond to the splay, twist, and bend contributions to the Frank elastic energy for nematics. Note that we have not explicitly included the coupling between the smectic order parameter Ψ and nematic order parameter S, as its main effect is to shift $\bar{r}$ and u. We thus use effective values of $\bar{r}$ and u. In the absence of $\delta\mathbf{n}$ fluctuations, $u = 0$ corresponds to the tricritical point, and $u > 0$ implies a second-order transition. However, when $\delta\mathbf{n}$ fluctuations are taken into account, nothing special happens at $u = 0$: we merely cross over from a mean-field first-order transition to a fluctuation-driven first-order transition. Here, we assume $u \geq 0$.

Next, we consider the effect of an external field along the director $\hat{\mathbf{n}}$ (assumed to lie along the z axis). We assume that the field reinforces the nematic ordering and neglect its much smaller effects on smectic ordering. For concreteness, we consider a magnetic field H. Then the Landau free energy becomes

$$F^H_{\rm NA} = F_{\rm NA} - \int d^3x\, \frac{1}{2}\chi_a(\mathbf{H} \cdot \hat{\mathbf{n}})^2 \simeq F_{\rm NA} - \frac{1}{2}V\chi_a H^2 + \int d^3x\, \frac{1}{2}\chi_a H^2 \delta n^2, \quad (2)$$

using $n_z^2 = (1 - \delta\mathbf{n}^2)$, and expanding in δn^2. Here, V is the sample volume. Thus, the magnetic field makes the nematic director fluctuations "massive." Because the field also couples to the nematic order parameter S, the free-energy-expansion coefficients also have a magnetic-field dependence [11,12]; however, one would need a field of several hundred tesla to change u appreciably, which is a much weaker effect than the one we shall be considering here.

Recall that we are working in the regime where massless nematic director fluctuations, by coupling to the smectic order parameter, induce a first-order transition. Adding an external field adds mass to these director fluctuations, thus suppressing their effect. When the magnetic field is sufficiently strong, director fluctuations can be ignored, resulting in a 3D XY, second-order transition. To estimate the required critical field, we recall that nematic twist and bend distortions are expelled by the smectic phase over a length scale λ (defined to be the penetration depth). At a mean-field level, and in the one-constant approximation $K_1 = K_2 = K_3 = K$, the penetration length is given by

$$\lambda = \Big(\frac{K}{C}\Big)^{1/2} \frac{1}{q_0|\Psi_0|}. \quad (3)$$

When a field is added, we introduce a new length, the magnetic coherence length $\xi(H)$, which measures the distance over which elastic deformations decay in the nematic phase. One finds [10]

$$\xi(H) = \Big(\frac{K}{\chi_a}\Big)^{1/2} \frac{1}{H}. \quad (4)$$

At zero field, if the transition is first order, we can imagine smectic droplets in the nematic phase at the coexistence temperature. Bulk twist and bend excitations penetrate a distance λ into the smectic droplets. When H is turned on, as long as $\xi(H)$ is much larger than λ, the nematic-smectic interface is not much affected. But when $\xi(H)$ is much smaller than λ, nematic fluctuations are suppressed in both the nematic and smectic phases. They then play no role at the transition, which becomes second-order XY. Thus, a rough estimate of magnetic field H_c needed to reach the tricritical point can be obtained by setting $\xi(H_c) = \lambda$. In reality, the different values of K_1, K_2, and K_3 lead to different penetration depths and magnetic coherence lengths for the twist and bend modes, somewhat complicating the above arguments.

We can study the effect of a magnetic field within the Halperin, Lubensky, and Ma formalism, where fluctuations in $|\Psi|$ are ignored (the strongly "type-1" limit). In order to decouple fluctuations in the phase of the order parameter, Ψ, from director fluctuations, we carry out the gauge transformation [13], $\delta\mathbf{n}_\perp = \mathbf{A} + \nabla L$, and $\psi = \Psi e^{-iq_0 L}$, where $\nabla \cdot \mathbf{A} = 0$. Under this transformation, $|(\nabla - iq_0\delta\mathbf{n}_\perp)\Psi|^2$ goes to $(\nabla - iq_0\mathbf{A})\psi|^2$. Details will be given in a longer paper [14]. Following HLM, we write

$$e^{-F(\psi)/k_BT} = \int \mathcal{D}\{\mathbf{A}\} e^{[-F_{\rm NA}(\psi,\mathbf{A})]/k_BT}. \tag{5}$$

Differentiating with respect to $|\psi|$ gives

$$\frac{df}{d|\psi|} = \bar{r}|\psi| + u|\psi|^3 + Cq_0^2|\psi|\langle\mathbf{A}^2\rangle. \tag{6}$$

For simplicity, we will assume that we are in the limit $K_1 \ll K_2, K_3$, and, hence, set K_1 to zero; however, the results would not change much for finite K_1. Treating $|\psi|$ as a constant, we obtain

$$\frac{df}{d|\psi|} = r|\psi| + u|\psi|^3 - w_1|\psi|\sqrt{(|\psi|^2 + a_H^2H^2)} + w_2 a_H|\psi||H|\ln\left[\frac{\sqrt{|\psi|^2 + a_H^2H^2} + a_H|H|}{2a_H|H|}\right], \tag{7}$$

where $w_1 = (k_BT/\pi)(C^{3/2}q_0^3/2K_3^{1/2})(1/K_3 + 1/K_2)$, $w_2 = (k_BT/\pi)(C^{3/2}q_0^3/2K_3^{3/2})$, $a_H = \sqrt{\chi_a/C_\perp q_0^2}$, and r corresponds to a shift of $\bar{r}$. At this point, it is convenient to introduce the scaled (dimensionless) variables $|\psi'| = \frac{u}{w}|\psi|$, $r' = (u/w^2)r$, $H' = (ua_H/w)H$, $f'_{\rm NA} = (u^3/w^4)f_{\rm NA}$. In terms of these variables, the scaled effective free-energy density takes the form

$$f' = \left(\frac{r'}{2} - \frac{b}{4}|H'|\right)|\psi'|^2 + \frac{1}{4}|\psi'|^4 - \frac{1}{3}\sqrt{(|\psi'|^2 + H'^2)^3} + \frac{b}{2}H'^2\sqrt{(|\psi'|^2 + H'^2)} + \frac{b}{2}|H'|\,|\psi'|^2\ln\left[\frac{\sqrt{|\psi'|^2 + H'^2} + |H'|}{2|H'|}\right], \tag{8}$$

where $b = K_2/(K_2 + K_3)$, and $0 < b < 1$. Qualitatively, one sees that as $H \to 0$ there is a negative $|\psi|^3$ term, indicating a first-order transition; for large $|H|$ the last three terms in Eq. (8) give only corrections to $|\psi|^2$ and $|\psi|^4$, implying a second-order transition. Thus, we expect a tricritical point at $H_c \simeq \psi_0/a_H \simeq (1/a_H)\frac{w}{u}$.

At the coexistence point, using $f(|\psi_0|) = f(0)$ and $[\frac{df}{d|\psi|}]_{\psi=\psi_0} = 0$, we obtain

$$|\psi_0'|^2 = \begin{cases} \frac{(2-9b|H'|)+\sqrt{\Delta}}{9} & \text{for } 0 < H' < \frac{1}{3} \\ \frac{(2-9b|H'|)-\sqrt{\Delta}}{9} & \text{for } \frac{1}{3} < H' < H_c', \end{cases} \tag{9}$$

where

$$\Delta = (9b|H'| - 2)^2 - 108(1 - 3b/2) \times H'^2[(1 - b/2) - 2|H'|]. \tag{10}$$

Here $H_c' = \frac{1}{2}(1 - b/2)$ is the critical field; at $H = H_c$ we have $\psi_0 = 0$ at the coexistence point. Thus, the tricritical point corresponds to $H = H_c$; for larger magnetic fields the NA transition is second-order. Our earlier informal argument giving $\lambda_{H=0} = \xi_{H_c}$ corresponds to $H_c' = \frac{2}{3}$. Note that, despite appearances, $\psi_0(H)$ is analytic at $H' = 1/3$. (See Fig. 1 inset.) The coexistence temperature $r_{\rm NA}$ satisfies

$$r'_{\rm NA} = -|\psi_0'|^2 + \sqrt{|\psi_0'|^2 + H'^2} - b|H'|\ln\left[\frac{\sqrt{|\psi_0'|^2 + H'^2} + |H'|}{2|H'|}\right]. \tag{11}$$

Because the spinodal temperature T^* changes linearly in $|H|$, there is a cusp at $H = 0$ in the function $t_0(H)$. (See Fig. 1.) The behavior of $t_0(H)$ near zero field is the nonanalytic "signature" of the field-driven HLM effect in the same way that a $|\psi|^3$ term is the signature of the zero-field HLM effect. Recall that only H^2 figures in the original free energy. It should also be noted that t_0 as a function of H/H_c does not depend significantly on b.

To estimate the magnitude of magnetic field required to drive the transition second order, we consider the material 8CB, where the NA transition appears to be in the HLM fluctuation-driven first-order regime. It is useful to express H_c in terms of the measured value of t_0 at zero field. In the HLM formalism, $t_0 = 2w^2/9\alpha u$, and we have

$$H_c = \left[\frac{9}{8}\frac{\alpha}{u}\frac{C_\perp q_0^2}{\chi_a}\right]^{1/2}(1 - b/2)\sqrt{t_0} \equiv H_0\sqrt{t_0}. \tag{12}$$

Using $C_\perp = 2 \times 10^{-7}$ dyn, $q_0 = 2 \times 10^7$ cm^{-1}, $\chi_a = 10^{-7}$ cgs, $\alpha/u = 1$, we estimate $H_0 \approx 3500(1 - b/2)$ T, which is the field required to quench fluctuations at molecular scales. Using $t_0 = 6 \times 10^{-6}$ [9], we obtain the critical field $H_c \approx 5$–10 T. For an electric field, the critical electric field is roughly 0.5–1 V/μm.

These figures are encouragingly low, but one should be cautious since smectic fluctuations, which we have ignored, are important for such weak first-order transitions. The calculation of the critical magnetic field is on firmer ground in the vicinity of the Landau tricritical point ($u = 0$), where the neglect of ψ fluctuations is more valid. Close to the tricritical point, we retain a $v(|\psi|^6/6)$ term in the Hamiltonian. Then the critical field for a second-order transition is $(1/a_H)(\frac{w}{v})^{1/3}$. The expression for H_c in this

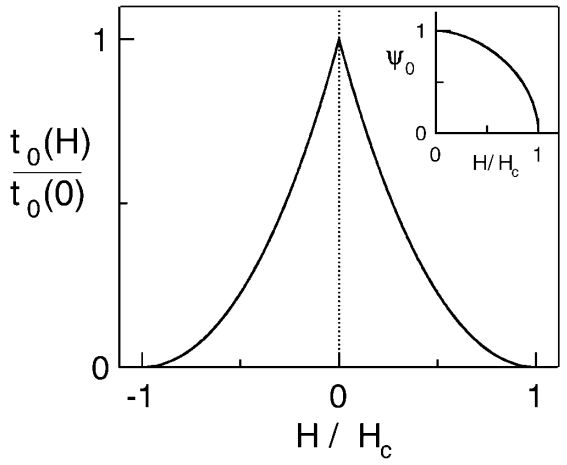

FIG. 1. Plot of the reduced temperature $t_0(H) = (T_{\mathrm{NA}} - T^*)/T_{\mathrm{NA}}$ as a function of the scaled magnetic field H, at $b = 0$. Note the cusp at $H = 0$. In the inset, we plot the (scaled) smectic order parameter at the transition as a function of H.

case is

$$H_c \approx \left[\left(\frac{\alpha}{\upsilon}\right)^{1/2} \frac{C_\perp q_0^2}{\chi_a}\right]^{1/2} t_0^{1/4}. \tag{13}$$

In the 8CB-10CB system studied by several groups [7,8], the LTP occurs at a mole fraction of roughly 40% 10CB in 8CB. In this system, one of us has measured t_0 to be roughly 10^{-4} [15]. Unfortunately, the $t_0^{1/4}$ dependence then results in a much higher critical field, on the order of 300 T (or roughly 30 V/μm).

Lelidis and Durand have extensively studied the effects of large electric fields on the NA transition [16,17]. In his Ph.D. thesis, Lelidis looked for evidence of an electric field-induced tricritical point at the NA transition of 8CB. The experiments, which measure S, give some evidence for a tricritical point at an external electric field somewhere between 5 and 20 V/μm. Unfortunately, the temperature resolution was 25 mK. Since the zero-field discontinuity is only 2 mK, this does not rule out a much smaller critical field for 8CB, and better temperature resolution will be needed to confirm these results.

External fields may have other interesting, observable effects. In the type-2 limit, where the NA transition should be second order, applying a field should be a relevant perturbation that changes the universality class of the transition to second-order XY. In the superconductor analogy, adding a field in the liquid-crystal system corresponds to adding mass to the gauge fluctuations in superconductors. For massless fluctuations, in type-2 superconductors, magnetic vortices are screened by current loops. The interaction between the current loops (and not the vortices) is long range, giving rise to the inverted XY transition. However, when the gauge fluctuations become massive, the interaction between current loops decays exponentially while that between vortices becomes long range, leading to the usual XY transition. It would be very interesting to probe the experimental consequences of this crossover to the XY fixed point.

One such consequence would be the suppression of spatial anisotropy in the critical region. It has been proposed that experiments probe the crossover region between an isotropic, high-temperature region and the true critical region governed by a renormalization group fixed point [18]. The nature of the fixed point is still under debate. Since with a magnetic field we could tune the strength of nematic fluctuations, it would give us a better understanding of the role of these fluctuations in the crossover region, and the observed weak anisotropy. This is currently under investigation.

In conclusion, we have shown that the HLM effect for the NA transition leads to an unusual, nonanalytic form for the effective smectic free energy in the presence of an external field. Measurements by Lelidis and Durand seem consistent with the predicted effects. More precise experiments on the field dependence would be an extremely promising way to probe these unusual effects of thermal fluctuations.

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