Observation of the Halperin-Lubensky-Ma effect in a liquid crystal

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Experiments reveal a nonlinear behavior of the heat of the nematic-smectic A phase transition because of a screening of transverse fluctuations of the nematic director in the *A* phase.

According to Halperin, Lubensky, and Ma (HLM), a phase transition which is accompanied by a screening of a massless field must be a first-order transition.[1] For the case of the nematic-smectic A transition (the role of the massless field in this transition is played by transverse fluctuations of the nematic director), however, this assertation has not yet been rigorously proved.

In the present study we have shown experimentally that the nematic-smectic A (NA) transition is indeed a first-order phase transition in the case of a narrow nematic phase and that the change in the nature of the NA transition, which is continuous in the Landau approximation, results from a screening effect (the HLM effect).

Basic positions of the HLM theory for a NA transition with a narrow nematic phase.[1,2] The NA transition consists of the appearance of a density wave along the direction of the unperturbed director, $\mathbf{n}_0$:

$$\delta\rho = \mathrm{Re}[\psi e^{iq_0 \mathbf{n}_0 \mathbf{r}}] \tag{1}$$

(ψ is an amplitude that varies slowly in space, and q_0 is the wave number of the lattice). The corresponding free-energy functional is

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$$F[\psi, \delta\mathbf{n}] = \frac{k_B T}{v_0} \int dV [\alpha_{eff}[\tau|\psi|^2 + \xi_{0\parallel}^2 |\nabla_\parallel \psi|^2 + \xi_{0\perp}^2 |(\vec{\nabla}_\perp - iq_0 \delta\mathbf{n})\psi|^2]$$

$$+ \lambda_{eff}|\psi|^4 + \mu|\psi|^6 + \frac{1}{2}K[(\vec{\nabla}\cdot\delta\mathbf{n})^2 + (\vec{\nabla}\times\delta\mathbf{n})^2]], \quad (2)$$

where τ is the dimensionless deviation from the critical temperature of the NA transition, $\xi_{0\parallel}$ and $\xi_{0\perp}$ are the direct correlation lengths which are respectively longitudinal and transverse with respect to $\mathbf{n}_0$, K is the Frank constant (the fact that there are three Frank constants in a real situation is not important for a qualitative description of the HLM effect), and v_0 is the volume per liquid-crystal molecule.

The phenomenological constants α_{eff} and λ_{eff} are determined by the "singular" points on the phase diagram of the liquid crystal.[3] In a typical situation (far from singular points) we would have $\alpha_{\text{eff}} \sim 1$ and $\lambda_{\text{eff}} \sim 1$. As the width of the nematic phase is reduced, however, the fourth constant, λ_{eff}, decreases and changes sign, while the constant α_{eff} increases by at least an order of magnitude. This behavior of the phenomenological constants is explained in terms of their strong dependence on the distance from the isotropic-nematic transition.[3] The point with $\lambda_{\text{eff}} = 0$ is a tricritical point in the Landau approximation. We will call this point the "de Gennes point."[4] An increase in α_{eff} in the case of a narrow nematic phase is manifested in an experimentally observable decrease in the intensity of x-ray scattering and in a decrease in the direct correlation lengths.[5]

Assuming $|\psi|$ to be constant, and ignoring phonons in the A phase [if there is a single Frank constant, this simplification is legitimate since the ratio of correlation lengths is small $(\xi_\perp^2/\xi_\parallel^2) \lesssim 10^{-2}$], we find

$$F[\psi, \delta\mathbf{n}] = \frac{k_B TV}{v_0}[\alpha_{eff}\tau|\psi|^2 + \lambda_{eff}|\psi|^4 + \mu|\psi|^6]$$

$$+ \frac{1}{2}\frac{k_B T}{v_0}\int dV[D(\delta\mathbf{n})^2 + K[(\vec{\nabla}\cdot\delta\mathbf{n})^2 + (\vec{\nabla}\times\delta\mathbf{n})^2]], \quad (3)$$

where $D = 2\alpha_{\text{eff}} q_0^2 \xi_{0\perp}^2 |\psi|^2$ plays the role of a gap in the spectrum of transverse fluctuations of the nematic director. In the case $D \neq 0$ (the A phase), the fluctuations $\delta\mathbf{n}$ are screened over a characteristic length $\lambda_S = (K/D)^{1/2}$.

Incorporating the screening of fluctuations of the director at the transition to the A phase causes the NA transition, which is continuous in the Landau approximation, to "collapse" to a first-order transition (in the case $\lambda_{\text{eff}} \geqslant 0$). The formal reason for this result is that a term $-k_B TV\lambda_S^{-3}$, which is cubic in $|\psi|$, appears in the free energy of the smectic phase after an integration over $\delta\mathbf{n}$. The free energy per mole of the material can be written

$$\frac{\tilde{F}}{RT} = \alpha_{eff}\tau|\psi|^2 - \gamma|\psi|^3 + \lambda_{eff}|\psi|^4 + \mu|\psi|^6, \quad (4)$$

where

$$\gamma \sim \left(\frac{\alpha_{eff} q_0^2 \xi_{0\perp}^2}{K} \right)^{3/2} v_0 . \qquad (5)$$

The appearance of the term $-\gamma|\psi|^3$ in (4) unavoidably leads to a first-order phase transition.

The physical reason for the change in the order of the transition is that when τ is small and positive the abrupt establishment of $|\psi| \neq 0$ is favorable from the energy standpoint since the benefit in the screening energy is greater than the penalty in the condensate energy.

Expressions (4) and (5) were derived disregarding the fluctuations in ψ and are thus of an especially qualitative nature. Unfortunately, we cannot rigorously find the conditions for their applicability, because we lack a theory of the NA transition. All that we can do is assert that the single-loop fluctuation corrections to the Frank constants (K_2 and K_3) and to the values of $\alpha_{\text{eff}}\tau$ and $\alpha_{\text{eff}}\xi_{0\perp}^2$ do not qualitatively change results (4) and (5) for a NA transition which occurs near the de Gennes point (this is an NA transition with a "narrow" nematic phase). To avoid any misunderstanding, we emphasize that the fluctuation corrections to the Frank constants must be taken at the wave numbers characteristic of the HLM effect, $k_{\text{char}} \sim \lambda_S^{-1}$; in the case of a narrow nematic phase, these wave numbers satisfy the condition $k_{\text{char}}\xi \gg 1$.

Estimates. Assuming $K^{-3/2} v_0 \sim 1$ and $\alpha_{\text{eff}} q_0^2 \xi_{0\perp}^2 \sim \xi_\perp^2/\xi_\parallel^2 \sim 10^{-2}$, we find $\gamma \sim 10^{-3}$. The reason for this small value is the relative "weakness" of the interaction of the fluctuations of the director with the smectic lattice (the quantity $\alpha_{\text{eff}} q_0^2 \xi_{0\perp}^2$ plays the role of the constant of this interaction). In turn, this "weakness" reflects the proximity of the actual NA transition to the triple NAC point.[3]

Let us evaluate the heat of the NA transition under the assumption that expressions (4) and (5) give a qualitatively correct description of the overall situation. For large widths of the nematic phase ($\alpha_{\text{eff}} \lesssim 1$, $\lambda_{\text{eff}} \sim 1$), the dimensionless heat of the NA transition is then $\Delta S_{\text{NA}}/R \sim \alpha_{\text{eff}}(\gamma^2/\lambda_{\text{eff}}^2) \lesssim 10^{-6}$, i.e., beyond present experimental capabilities (high-precision adiabatic calorimetry is capable of reliably measuring heats[6,7] $\Delta S_{\text{NA}}/R \gtrsim 5 \times 10^{-3}$). When we go to a narrow nematic phase, in contrast, the heat of the NA transitions should also increase near the de Gennes point ($\lambda_{\text{eff}} \sim 0$, $\alpha_{\text{eff}} \sim 10$), reaching characteristic values $\Delta S_{\text{NA}}/R \sim \alpha_{\text{eff}}(\gamma/\mu)^{2/3} \sim 10^{-1}$ ($\mu \sim 1$) which are completely accessible experimentally.

Dependence of the heat of the NA transition on the width of the nematic phase. We denote by x a variable which is related linearly to the width of the nematic phase (e.g., the concentration of one of the components of the binary mixture of the liquid crystal). Setting $\lambda_{\text{eff}} = \lambda_0(x - x^*)$ in (4) (x^* is the value of x at the de Gennes point), we can easily derive an analytic expression for $\Delta S_{\text{NA}}(x)$. An important consideration from the experimental standpoint is that under the condition $\lambda_0(x - x^*) \ll -\gamma^{2/3}\mu^{1/3}$ (in which case we have $\gamma|\psi|^3 \ll -\lambda_{\text{eff}}|\psi|^4 \sim \mu|\psi|^6$) the heat $\Delta S_{\text{NA}}(x)$ is a linear function of the variable x: $\Delta S_{\text{NA}}(x) = a(x - x^*)$, where $a/R = -(\alpha_{\text{eff}}\lambda_0/2\mu)$. This circumstance means that the position of the de Gennes point (x^*) and the value of a could in principle be determined experimentally from the linear $\Delta S_{\text{NA}}(x)$ asymptote.

The functional dependence $\Delta S_{\mathrm{NA}}(x)$ which follows from the HLM theory can be expressed in general in terms of $x - x^*$, a, and ΔS^*_{NA}, where $(\Delta S^*{}_{\mathrm{NA}}/R) = \alpha_{\mathrm{eff}}(\gamma/4\mu)^{2/3}$ is the heat evolution at the de Gennes point. The heat of the NA transition divided by ΔS^*_{NA} is a "universal" function of the dimensionless variable $y = (a/\Delta S^*{}_{\mathrm{NA}})x$:

$$\frac{\Delta S_{NA}(y)}{\Delta S^*_{NA}} = 2^{-2/3}\left[\left[1+\left(1+\frac{4}{27}(y-y^*)^3\right)^{1/2}\right]^{1/3} + \left[1-\left(1+\frac{4}{27}(y-y^*)^3\right)^{1/2}\right]^{1/3}\right]^2 \qquad (6)$$

(y^* is the value of y at the de Gennes point). In a real situation, in comparing experimental data with (6) we should treat x^* and a as adjustable parameters, since the transition to the linear asymptote of $\Delta S_{\mathrm{NA}}(x)$ is extremely slow.

Heat of the NA transition in a $\bar{6}0\bar{1}\bar{0}$-$\bar{6}0\bar{1}\bar{2}$ mixture. We have carried out an experimental study of the dependence $\Delta S_{\mathrm{NA}}(x)$ in the liquid-crystal mixture

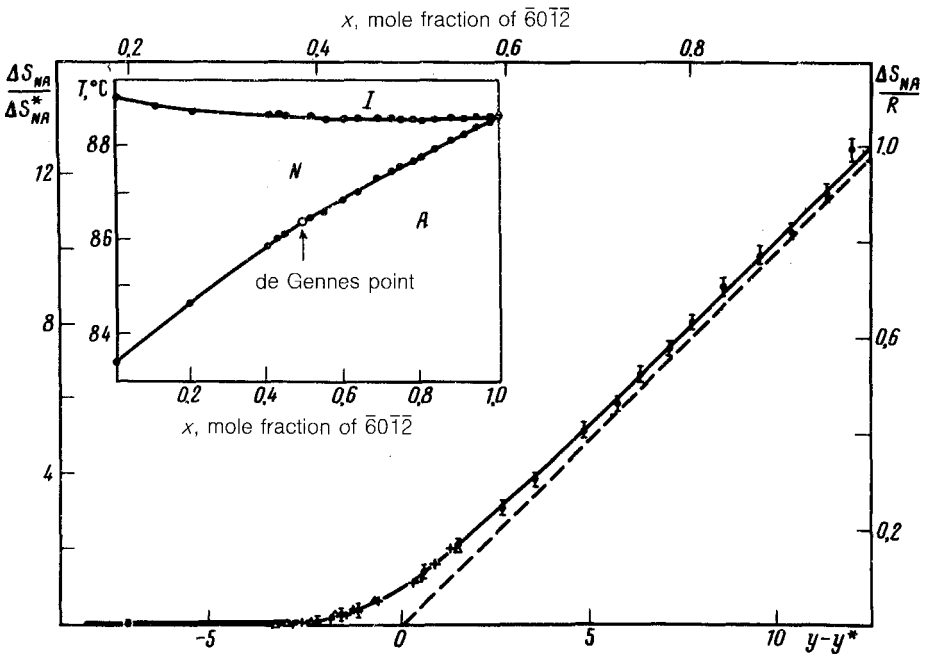

FIG. 1. Reduced heat of the NA transition ($\Delta S_{\mathrm{NA}}/\Delta S^*{}_{\mathrm{NA}}$) versus the dimensionless parameter (y–y^*), which is a measure of the proximity to the de Gennes point. Solid line: "Universal" dependence (6), which follows from the Halperin-Lubensky-Ma theory. Points: experimental. ●—$\bar{6}0\bar{1}\bar{0}$-$\bar{6}0\bar{1}\bar{2}$ mixture ($x^* = 0.49$, $a = 1.93R$); Δ—8CB-10CB ($x^* = 0.54$, $a = 1.83R$) (Ref. 8); +—the mixture 9CB-10CB ($x^* = 0.22$, $a = 0.91R$) (Ref. 8). The coordinates $\Delta S_{\mathrm{NA}}/R$ apply only to the $\bar{6}0\bar{1}\bar{0}$-$\bar{6}0\bar{1}\bar{2}$ mixture. The inset shows the phase diagram of the $\bar{6}0\bar{1}\bar{0}$-$\bar{6}0\bar{1}\bar{2}$ mixture.

$\bar{6}0\bar{1}\bar{0}_{1-x} - \bar{6}0\bar{1}\bar{2}_x$. The liquid-crystal samples were graciously furnished by D. Demus ($\bar{6}0\bar{1}\bar{0}$) and B. M. Bolotin ($\bar{6}0\bar{1}\bar{2}$). These measurements were carried out by a method of quasiequilibrium thermograms (the rate of change of the temperature was $\sim 1.4\times 10^{-5}$ K/s) on the adiabatic calorimeter described in Ref. 7.

Figure 1 shows a phase diagram of the mixture and the results of the measurements. The experimental data can be described satisfactorily by (6) with $a = 1.93\ R$ and $x^* = 0.49$. The heat of the NA transition at the de Gennes point is $\Delta S^*_{NA} \approx 0.08\ R$, in agreement with the estimate that follows from the HLM theory (see the "Estimates" section of this letter). We can thus assert that the nonlinear behavior of the heat of the NA transition which is observed upon a change in the width of the nematic phase is associated with the occurrence of a Halperin-Lubensky-Ma effect in the liquid crystal.

A nonlinear behavior of the heat of a NA transition similar to that observed by us here was observed previously by Gorodetskiĭ and Podnek.[3] Their experimental results, converted into the "universal" dimensionless variables, are also shown in Fig. 1. In summary, the NA transition with a narrow nematic zone is a first-order phase transition. The reason for the collapse of the NA transition, which is continuous in the Landau approximation, is the occurrence of a Halperin-Lubensky-Ma effect. As the width of the nematic phase is increased, the heat of the NA transition decreases and becomes experimentally unobservable. When the nematic phase has a large width, fluctuations in the amplitude of the smectic order parameter are definitely important, and the actual order of the NA transition is unclear both experimentally and theoretically.[9]

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