# Field-Induced First-Order Phase Transition and Spinodal Point in Nematic Liquid Crystals

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We report the discovery of a novel, magnetic-field-driven first-order phase transition in nematic liquid crystals. The transition is between a spatially periodic distortion, stable at intermediate-field strengths, and a uniform distortion which is the ground state at high fields. From studies of dynamics we show that the transition is first order. We also find a spinodal point, below which the transition from the uniform to the periodic state occurs continuously. We discuss the utility of thickness gradient samples and determine the equilibrium wavelength of the periodic phase as a function of magnetic-field strength.

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The field-induced distortion of a thin nematic liquid-crystalline film, known as the Frederiks transition, is one of the most studied phenomenon in the physics of liquid crystals [1]. In its conventional form, it is a second-order phase transition in which the system, initially undistorted and uniformly aligned in one direction, evolves to a homogeneously distorted ground state when the applied magnetic field exceeds a well-defined critical strength $H_c$. Recently, it has been discovered that in nematic liquid crystals composed of very long particles, a second-order transition to a periodic, rather than homogeneous, ground state supercedes the usual Frederiks transition [2]. Theory and experiments on the critical-field strength for this transition and the wavelength of the periodic phase at the transition are in good agreement [3], and much theory has been developed on related phenomena and other sample geometries [4]. However, until now no studies of this new periodic phase above its critical field have been reported.

In this Letter, we report such studies, including the discovery of a first-order transition at higher fields to the homogeneously distorted state. In the course of our studies of this unusual system, we discovered a spinodal point, and developed new techniques important for achieving equilibrium. We have been able to make both detailed equilibrium measurements, resulting in an accurate determination of the wavelength of the periodic structure as a function of field strength, and time-resolved observations of transition dynamics, including nucleation and growth phenomena and completely novel observations of a spinodal transition in a continuous one-component system transforming from a homogeneous to a periodic phase.

A nematic liquid crystal is a fluid phase composed of elongated molecules which are oriented, on the average, along a common axis called the director $\hat{\mathbf{n}}$, which can vary in orientation continuously throughout the sample in response to applied torques. In our samples, the nematic is contained between parallel glass plates separated by distance $d$. The director is initially aligned uniformly in the $\hat{\mathbf{x}}$ direction, parallel to the sample surfaces, by interaction with the surfaces, which are specially treated. Sample geometry is indicated in Fig. 1.

Any deviation from this uniform ground state of the sample is opposed by elastic restoring torques, propagating from the surfaces, at which the director is strongly anchored. In general, there are three geometrically distinct forms of distortion of the director field, splay, twist, and bend, associated with three curvature elastic constants, $K_1$, $K_2$, and $K_3$, respectively. In the material we studied, a solution of the polymer poly-$\gamma$-benzyl gluta-

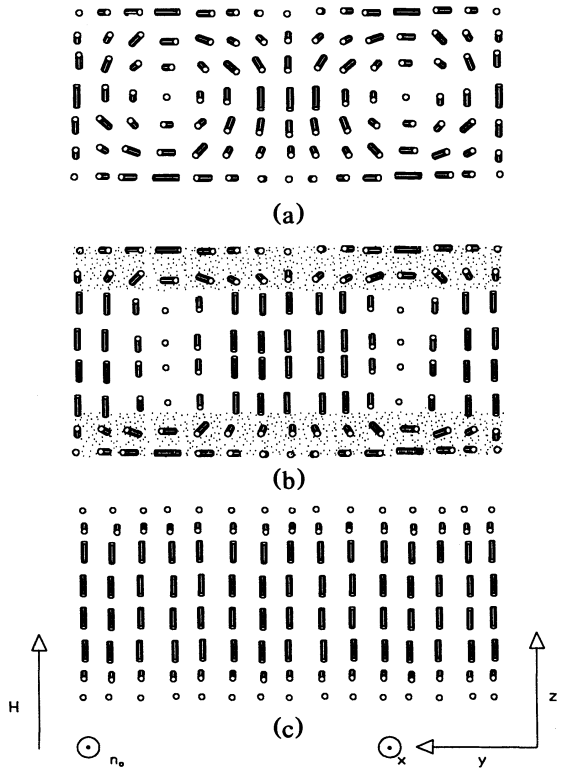


FIG. 1. (a) The director field of the periodic ground state just above the critical field. For simplicity, thin layers very near the rigid sample boundaries are not shown. (b) Similar to (a) but at higher fields. The shading near the sample surfaces indicates where splay cancellation still occurs. (c) The homogeneously distorted state at high fields.

mate in a mixture of the solvents dioxane, methylene chloride, and dimethyl formamide, the elastic constants had been determined by light-scattering and Frederiks transition experiments to be $K_1 = 1.2 \times 10^{-6}$ dyn, $K_2 = 8.1 \times 10^{-8}$ dyn, and $K_3 = 2.4 \times 10^{-6}$ dyn. Note that $K_1/K_2 \simeq 15$, a crucial property for our experiments.

An external magnetic field, **H**, interacting with the nematic through the anisotropy of its diamagnetic susceptibility, $\Delta\chi$, applies a torque to the director, tending to align it parallel to the field. In our experiments, **H** is applied perpendicular to the initial orientation of $\hat{\mathbf{n}}$, and to the sample surfaces, $\mathbf{H} = H\hat{\mathbf{z}}$. There is a distinct threshold field $H_c$ below which the elastic restoring torques overcome the destabilizing magnetic torque, and no reorientation of the director occurs. In the classic splay Frederiks transition, for $H > H_{c1} = (\pi/d)(K_1/\Delta\chi)^{1/2}$, the director takes on a homogeneously distorted structure dominated by splay, with an initially sinusoidal form, $n_z = \theta \sin(\pi z/d)$, with $\theta \sim (H - H_{c1})^{1/2}$, as its new equilibrium state. However, for a nematic in which $K_1/K_2 > 3.3$, a different ground state appears, again as a second-order transition, at a critical field $H_c < H_{c1}$. This is the periodic ground state sketched in Fig. 1(a), in which to a large extent splay is replaced by twist distortion, resulting in the lower critical field.

The replacement of splay by twist is accomplished by "splay cancellation" in the nearly sinusoidal two-dimensional undulating director structure that occurs just above $H_c$. Cuts through this structure in the $(x,y)$ and $(x,z)$ planes reveal apparent splay components $\partial n_y/\partial y$ and $\partial n_z/\partial z$ which enter the total splay, $\nabla \cdot \hat{\mathbf{n}}$, with opposite signs. The characteristic wavelength of the undulations is of the order of the magnetic coherence length, $\xi_H \simeq (1/H)(K/\Delta\chi)^{1/2}$, in which $K$ is an appropriate curvature elastic constant. Near $H_c$, $\xi_H$ is of order $d$. This picture of the periodic ground state of the Frederiks transition near $H_c$ has been firmly established in theory and experiments.

What happens as $H$ is raised above $H_c$? As $\xi_H$ becomes significantly smaller than $d$, the regions in which energetically favorable splay cancellation occurs are squeezed into thin layers near the sample boundaries, as indicated in Fig. 1(b), with the remaining vertical twist wall-like structures connecting these layers being energetically unfavorable defects, when compared to the homogeneous structure one would have without the periodic structure and walls, i.e., the structure that evolves at high fields from the classic splay Frederiks transition, sketched in Fig. 1(c). Therefore, at high enough fields a transition from the periodically distorted state (PD state) back to the homogeneously distorted state (HD state) should occur.

To test this argument, a sample with $d = 80$ $\mu$m in the HD state (prepared by initially applying the field obliquely, to produce a single domain) was placed in a field $H = 10$ kG. The fact that the sample remained HD after several days in this field suggested that this is indeed the stable phase at high fields. The next step was to study the nature of the HD to PD transition. When the field was decreased from 10 to 7.5 kG in the HD sample, the following observations were made: First, stripes, signifying the emergence of the PD phase, nucleated from sites in the sample where the director was locally perturbed, such as a curved spacer or a dust particle, as shown in Fig. 2(a). Second, when the magnetic field was subsequently raised to 10 kG, the stripes, instead of uniformly fading, as might be seen in a second-order transition, first formed acute ends and then started to retract, causing the length of the stripes to decrease. The higher the field, the faster the stripes retracted. The whole sample eventually became stripe free. Third, despite repeating the procedure several times, most of the sample stayed uniformly distorted at 7.5 kG, and only a few stripes (one to six) appeared randomly. If the field strength was further decreased, a few more stripes appeared, but the number of stripes appearing for the same field varied, so it was meaningless to assign a wavelength to these pieces of PD

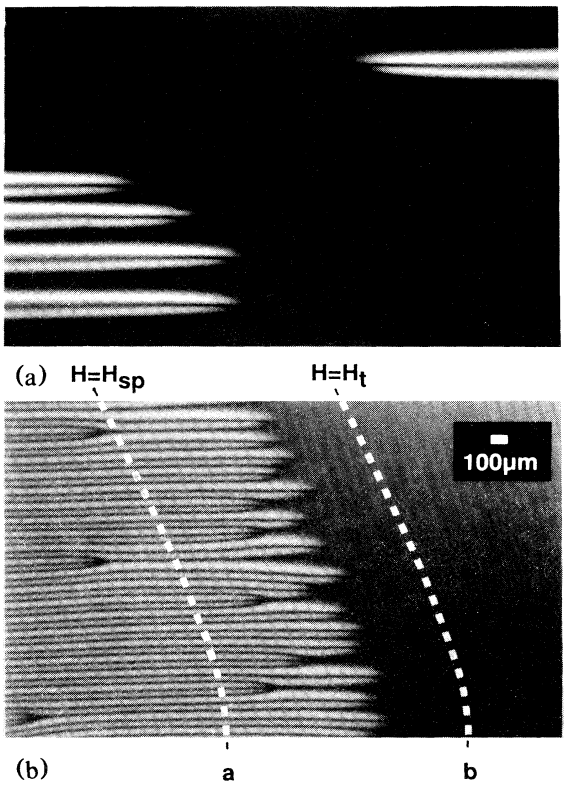


FIG. 2. Polarized-light photomicrographs of the periodically distorted and homogeneously distorted states. (a) Fragments of periodic state structure that nucleated and grew in a sample of uniform thickness upon quenching the field into the range for which the homogeneous state is metastable. (b) Periodic state in a thickness gradient sample. The structure appeared by a spinodal transition to the left of line *a*, and grew as shown, approaching an eventual stable configuration when the front reached line *b*.

phase. The most important conclusion from these experiments was that for lower fields the PD state had a lower energy than the HD state but there was a finite energy barrier separating the states.

The transition from the HD to the PD state followed a different scenario when the field was lowered from 10 to 4.5 kG in a single step. In this case, the stripes gradually appeared uniformly throughout the sample, first as a faint pattern, then steadily increasing in contrast, but not changing in other ways, and never forming a sharp boundary between the two phases. The absence of large localized director distortions or nucleation events (associated with the tips of the stripes) mediating the transition suggested that in this case there was no energy barrier involved in going from the HD to the PD state.

These observations are consistent with a first-order transition between HD and PD states at some high field, $H_t$, near which one of the states is metastable with respect to the other. They also suggest that below some field, the spinodal field $H_{sp}$, the HD state becomes unstable with respect to the PD state. To make this picture quantitative offered an experimental challenge, due to the problems of obtaining equilibrium. The nucleation process involved in going from HD to PD states did not produce structures with uniform properties. Once a PD structure was formed, it was difficult for the wavelength to change as field was varied. To further complicate the problem, in attempting to enter the PD state from low fields, for sudden large increases in $H$, there are transient dynamic processes that produce complex oblique stripe patterns quite different from the ones studied here, that again made attainment of equilibrium difficult.

The solution to all these problems was the use of samples with a gradient in thickness, such that $d=d(x)$, an approximately linear increase in thickness roughly along the $x$ direction, with $d$ varying from 66 to 85 $\mu$m. This thickness function was measured very accurately by optical interference methods. The properties of the PD and HD states all scale with thickness in a simple way. The critical magnetic field $H_c$ at any point scales as $1/d$, and the wavelength $\lambda$ in the PD phase scales as $d$. Measurements at different points in the sample can be reduced to functions of $Hd$ and $\lambda/d$. Thus the gradient sample in a uniform magnetic field could have one end below the effective $H_c$ for that end's thickness, the other end above $H_t$ for that end's thickness, with the thickness corresponding to the spinodal field $H_{sp}$ occurring along a line in between. The equilibrium wavelength in the PD phase would vary continuously with $d$ across the sample, with the change in wavelength occurring in conjunction with an oriented array of edge dislocations in the periodic structure.

Such a wedge-shaped sample was prepared to be initially all in the HD state at a high field. Subsequently, the magnetic field was suddenly decreased to a fixed lower value, $H_{quench}$, so that the effective-field strength was above $H_{sp}$ in the thicker part, and below $H_{sp}$ in the thinner part of the sample. Thus in the thinner part the HD state was unstable and relaxed homogeneously into the PD phase via spinodal transformation. At a particular thickness, corresponding to $H_{sp}$, the PD stripes, which are parallel to the $x$ direction, terminated in a row of acute stripe ends [initially at line $a$ in Fig. 2(b)]. The spinodal thickness consistently shifted towards larger $d$ for smaller values of $H_{quench}$, and, conversely, towards smaller $d$ for larger $H_{quench}$. For instance, we obtained $H_{sp}=6.9$ kG at a thickness of $d=82$ $\mu$m.

After the field quench, the PD structure formed by the spinodal transformation process grew into the region in which the HD structure was metastable, i.e., the thicker part of the sample, by the steady movement of the acute stripe ends, as indicated in Fig. 2(b). During this growth, two things happened. First, some stripe tips were passed by their neighbors and stopped moving, leaving an array of edge dislocations in the pattern and increasing the average wavelength of the PD structure as thickness increased. Second, the growth velocity steadily decreased, and eventually stopped as the PD phase front reached the thickness corresponding to the transition field $H_t$ [line $b$ in Fig. 2(b)]. It was clear that the growth rate was governed by the energy difference between the two phases, and, indeed, the front came to a halt at the thickness for which the energies were equal. After the PD and HD phases had equilibrated at a given field, if the field was raised or lowered, the PD phase front would recede or advance as expected. Note that in this viscous polymer solution, front velocities are of order 1 mm/day, making transient events easy to follow, and changes in $H$ effectively instantaneous. In practice, $H_t(d)$ was determined by interpolating the front velocity to zero at the line across the sample where the thickness was $d$. We obtained $H_t=8.06$ kG at $d=82$ $\mu$m.

Finally, we discuss the use of the gradient sample to measure the equilibrium wavelength in the PD state. The array of edge dislocations in the PD state in the gradient sample served as an effective mechanism for wavelength equilibration. If the field was raised or lowered, the dislocations would move to locally add or subtract stripes to the structure, which would then elastically relax to accommodate the change. To measure the equilibrium wavelength as a function of field, we measured the wavelength along the lines of constant thickness in the sample at fixed field after equilibration. We plot $\lambda/d$ as a function of $Hd$ in Fig. 3. At $H_c$, $\lambda/d$ agrees well with the theoretically calculated value. For fields above but near $H_c$, $\lambda/d$ decreases slightly with increasing field until $Hd=40$ Gcm, and, beyond that point, $\lambda/d$ increases more and more rapidly with field up to $H_t$.

The existence of two distinct regimes is suggested by the following arguments. Initially, $\lambda\simeq\xi_H\sim 1/H$, so wavelength decreases with increasing field, as long as $\xi_H\simeq d$. This argument is correct as long as the undulation pattern is essentially sinusoidal, with its amplitude increasing with $H$. In that case, the splay cancellation

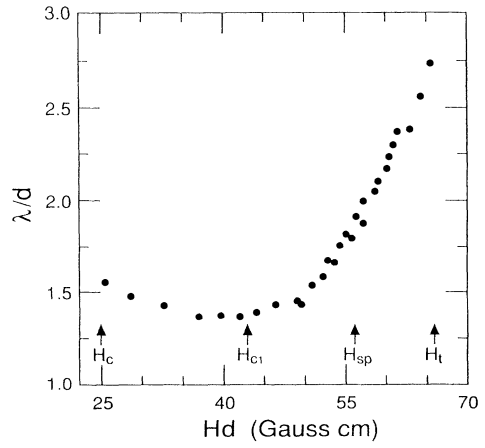


FIG. 3. The wavelength of the periodic state as a function of field, with indications of the significant field strengths discussed in the text.

mechanism is working throughout the sample, keeping the distortion energy mainly twist, with its low elastic modulus, while reorienting the director increasingly toward the field direction, on the average. However, as $\xi_H$ becomes much less than $d$, saturation effects appear, with regions near the midplane of the sample becoming almost uniformly oriented parallel to **H**. With these nonsinusoidal distortions, the splay cancellation mechanism also breaks down in increasingly large volumes around the midplane of the sample [Fig. 2(b)], which now contains an energetically costly array of twist walls. The remaining splay cancellation occurs only in boundary layers which get thinner as field increases. As this happens, the period begins to increase with field. One could imagine it diverging continuously, but that possibility is apparently cut off by the first-order transition back to the homogeneous state.

In conclusion, we have studied a novel field-induced first-order phase transition and spinodal point in a nematic liquid crystal, and made the first measurements of properties of the periodically distorted ground state above $H_c$. The phenomenology of this unique system can be studied with effectively microscopic spatial and temporal resolution, and we are pursuing further experimental and computational studies of the spinodal processes in particular. Our discovery of the great utility of gradient samples suggests their use in other mesoscopic systems in which nucleation and wavelength equilibration are nontrivial; they may soon be applied in studies of magnetic domain patterns [5].

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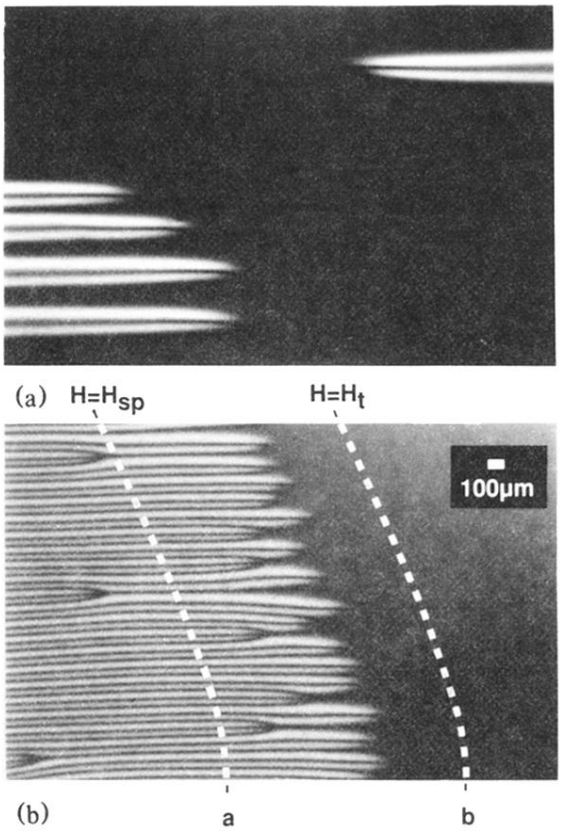


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