New Ground State for the Splay-Fréedericksz Transition in a Polymer Nematic Liquid Crystal

Franklin Lonberg and Robert B. Meyer
The Martin Fisher School of Physics, Brandeis University, Waltham, Massachusetts 02254
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We have discovered a new form of Fréedericksz transition in which uniform splay distortion is replaced by a complex periodic twist-splay pattern having a lower critical field than that for uniform splay. Experimental evidence is presented along with an exact calculation of both the critical field and the initial form of the distortion as a function of the ratio of the splay and twist elastic constants.

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One of the most useful and well-studied phenomena in the physics of liquid crystals is the field-induced distortion of a thin liquid-crystal film called the Fréedericksz transition.[1] This Letter describes a new type of Fréedericksz transition which occurs in the important class of liquid crystals composed of very long particles. A Fréedericksz transition in a polymer liquid crystal will be described in which the equilibrium structure of the sample is spatially periodic in the plane of the sample. This periodic state is seen in Fig. 1, which shows a polarized-light photomicrograph of a polymer-liquid-crystal sample, well aligned parallel to the glass, which has been in a magnetic field about 1.3 times the critical field and has slowly, over a period of several hours, developed stripes which appear to remain static thereafter. These static equilibrium stripes are parallel to the original alignment direction of the liquid crystal, while stripes which are the result of dynamic effects[2] are oblique. We propose that the periodic distortion shown in Fig. 1 occurs because, in liquid crystals composed of very long particles, the elastic constant associated with splay is much larger than that associated with twist.

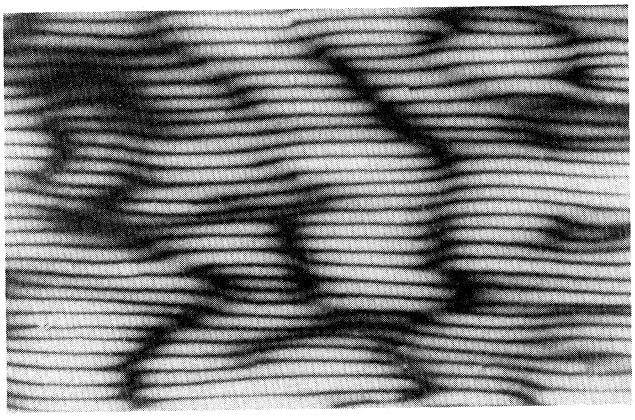

FIG. 1. Polarized-light photomicrograph of the periodic splay-twist distortion in PBG. The distance between two dark bands is 32.5 μm. The field is perpendicular to the plane of the sample, and the unperturbed director is parallel to the stripes.

A nematic liquid crystal is a fluid phase composed of elongated particles oriented more or less parallel to each other in their ground state. The average local orientation of the particles can be described by a unit-vector field $\hat{\mathbf{n}}$ called the director field. The director can be aligned by interaction with a surface; in our case the surface is treated so that the director will be parallel to the surface and oriented in a well-defined azimuthal direction, $\hat{\mathbf{n}}_0$. If a thin film of liquid crystal is placed between two so-treated parallel plates, the lowest-energy state of the system will be one in which, as a result of the elasticity of the liquid crystal, the director is constant throughout the bulk of the sample.

The director can also be aligned by an applied magnetic field, $\mathbf{H}$, through the anisotropy of the susceptibility, $\Delta\chi$. In our case, $\Delta\chi$ is positive, so that the director aligns parallel to $\mathbf{H}$. Thus, when we orient the field perpendicular to the plane of the sample a competition results. The director in the interior of the sample is subjected to the field torque trying to rotate it, but at the same time, it experiences an elastic restoring torque due to the strongly anchored surface layers. For an applied field below a critical strength, H_c, no distortion occurs. For fields larger than H_c, the ground state of the system is one in which the director in the interior is distorted by some angle from its undisturbed alignment direction. This is known as the splay-Fréedericksz transition because, in the limit of small amplitude, a resulting distortion which is uniform in the plane of the sample involves only splay deformation.

In our case, however, the transition done in this geometry produces not a uniform distortion, but the stripes seen in the photograph of Fig. 1. The sample in this photograph had been in a field of about 6 kG, for several hours. During this time the stripes developed very slowly, becoming barely visible after 2 h. After 4 h the field was increased to 8 kG in order to cause the amplitude of the distortion to become large enough to photograph. The sample used is a 37-μm-thick film of a racemic mixture of the levo and dextro versions of the synthetic polypeptide polybenzylglutamate (PBG)

(obtained from Sigma Chemical Co.) dissolved in a mixture of dioxane and methylene chloride. The key material characteristic of this liquid crystal, in the present context, is that it is a solution of molecules which are of the order of 70 times as long as they are wide, while low-molecular-weight nematic molecules are of the order of 5 times as long as they are wide.

Figure 2(a) is a representation of the uniform Fréedericksz distortion, while Fig. 2(b) gives a schematic representation of the proposed periodic distortion. The periodic distortion shown in Fig. 2(b), while it appears to be composed of an orthogonal pair of spatially periodic splay patterns, is in fact a distortion that can be composed of twist alone. The fact that an apparent periodic splay pattern can actually be pure twist (in the small-amplitude limit) is the essential novelty of this structure.

In a given liquid crystal, the form of the Fréedericksz transition which actually occurs will be the one which has the lowest critical field. In a material with a splay elastic constant K_1 which is much larger than the twist elastic constant K_2, the periodic distortion will have a lower critical field than the uniform distortion since it avoids splay. On the other hand, because of its more complex structure, the periodic distortion requires more elastic energy to relax a given amount of field energy than does the uniform distortion. Therefore, it should be expected that in materials in which K_1 is not much bigger than K_2, the uniform distortion will have a lower critical field.

For quantitative analysis of this problem, a general method for computing the critical field for the Fréedericksz transition is required. Such a method is based on the variational calculation of the state of minimum free energy. Setting the variation of the free energy with respect to the director function equal to zero produces a set of differential equations. For an applied field which is smaller than the critical field, the lowest-energy solution to this set of differential equations will be a director function which describes the undistorted state, i.e., the trivial solution. For an applied field which is larger than the critical field, on the other hand, a state of finite-amplitude distortion will be the minimum energy state of the system. Consequently, we will adopt the definition of the critical field as the smallest field at which a nontrivial director function is the solution of these differential equations. Normally, this is a second-order transition so that the amplitude of the equilibrium distortion goes continuously to zero at the critical field.

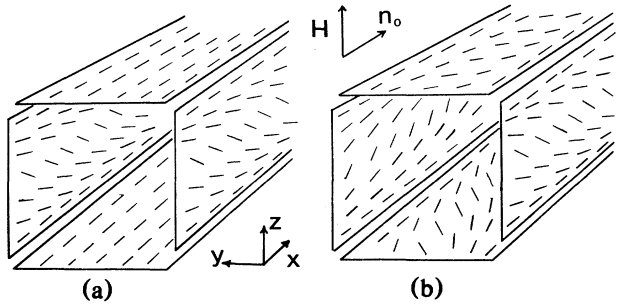

FIG. 2. Schematic representation of (a) the uniform splay-Fréedricksz distortion, and (b) the periodic splay-twist distortion.

Solving this problem exactly, as described above, involves dealing with nonlinear differential equations for which the possibility of obtaining analytic solutions is questionable. However, to study the critical field a simplifying limit can be taken. Because, close to the critical field, the distortion amplitude is arbitrarily small, linearized expressions can be used. In such a linearized picture a pattern of stripes parallel to the director is described by the functions

$$n_x = 1, \quad n_y = g(y,z), \quad n_z = f(y,z),$$

and the free energy is given by

$$F = \tfrac{1}{2} \int\int dy\, dz [K_1 (g_y + f_z)^2 + K_2 (g_z - f_y)^2 - \Delta\chi H^2 f^2].$$

(Subscripts on f and g in all following expressions indicate partial derivatives.)

The meaning of a variational calculation on a linearized free energy is somewhat special. It determines the form of the distortion for which the free energy is independent of the amplitude of the distortion, i.e., for which the negative field-energy change just cancels the positive elastic-energy change, since both of them are quadratic in the amplitude of the distortion. With boundary conditions which fix some parameters of the distortion, such as a wavelength corresponding to the sample thickness, this determines one or more field strengths satisfying the equations, the lowest of which is the critical field. Thus this calculation tells us nothing about behavior above the critical field other than the initial form of the distortion just at the critical field.

In the case of low-molecular-weight liquid crystals the distorted state is uniform in the plane of the sample, i.e., $n_y = 0$, and f depends only on z. Varying the free energy with respect to $f(z)$ results in the differential equation

$$f_{zz} = (-\Delta\chi H^2 / K_1) f.$$

The solution satisfying the boundary conditions, i.e., $f = 0$ at $z = \pm d/2$, with minimum value of the field, H_c, is

$$f = A \cos(\pi z/d), \quad H_c = (\pi/d)(K_1/\Delta\chi)^{1/2}.$$

In order to calculate the critical field for a distortion which is periodic in the plane of the sample, one must

start from a general distortion function which is periodic. From the translational symmetry of the linearized equations one can show that sinusoidal solutions with different wave vector in y are independent of one another. Therefore, the most general solution which should be considered is of the form

$$n_z = f(z)\cos(qy), \quad n_y = g(z)\sin(qy),$$

for which the free energy (averaged over y) is

$$F = \tfrac{1}{4}\int_{-d/2}^{+d/2} dz\,[K_1(gq + f_z)^2 + K_2(g_z + qf)^2 - \Delta\chi H^2 f^2].$$

The differential equations obtained are

$$K_1(gq^2 + qf_z) - K_2(g_{zz} + qf_z) = 0,$$

$$-K_1(qg_z + f_{zz}) + K_2(qg_z + q^2 f) - \Delta\chi H^2 f = 0.$$

Following the usual procedures, we find a general solution of the form

$$f = A_1\cosh(q_1 z) + A_2\cos(q_2 z),$$

$$g = B_1\sinh(q_1 z) + B_2\sin(q_2 z),$$

in which q_1 and q_2 are determined from the differential equations. The boundary conditions require that

$$(B_1/A_1)(A_2/B_2)\tanh(q_1 d/2) = \tan(q_2 d/2).$$

This equation is solved numerically to find the minimum value of H for which a solution exists. The results for H_c and q are shown in Fig. 3. For K_1/K_2 less than about 3.3, there is no solution to these equations. At that point, however, q goes to zero, and the H_c obtained becomes equal to H_c(uniform splay), with the two curves meeting tangentially. This is a kind of second-order transition in which the striped solution in the limit of zero q becomes identical to the pure splay mode. A remarkable feature of this result is that the critical value of K_1/K_2 is only 3.3. This is not an enormous anisotropy. One might easily imagine that this ratio could occur in some ordinary nematic liquid crystals. However, the striped Fréedericksz transition of this kind has not been reported before. There are some electric field effects that produce stripes parallel to the director, but they occur with a negative dielectric anisotropy, and are therefore not a Fréedericksz transition.[3]

At the limit of K_2/K_1 becoming zero, i.e., infinite splay elastic constant, the only distortion possible is a pure twist mode, which is given by

$$n_z = fq\cos(qy), \quad n_y = -f_z\sin(qy).$$

The calculation for $K_2/K_1 = 0$ yields the following parameters for f, q, and H_c:

$$A_1/A_2 = 0.018, \quad q_1 = 2.51\pi/d, \quad q_2 = 1.31\pi/d,$$

$$q = 1.51\pi/d, \quad H_c = 2.64(\pi/d)(K_2/\Delta\chi)^{1/2}.$$

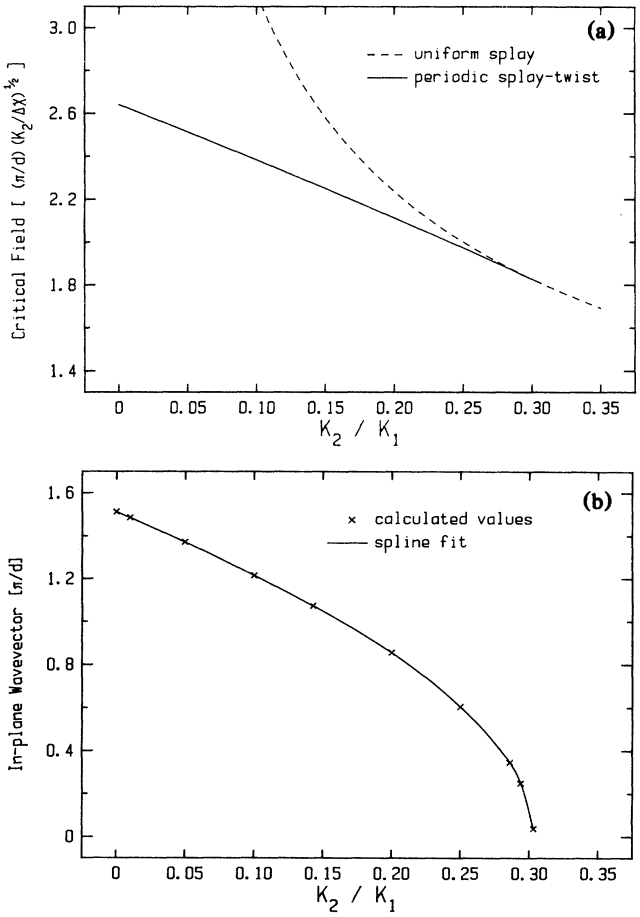

FIG. 3. Calculated values of (a) the critical field for the periodic splay-twist distortion, and (b) the in-plane wave vector.

Independent measurements of K_1/K_2 in the range of 10 to 30 have been made in this laboratory with use of light scattering methods in the same samples in which the periodic Fréedericksz transition has been observed.[4] Furthermore, with these same samples, Fréedericksz-transition measurements were made with the field in the plane of the sample, yielding values for $K_2/\Delta\chi$, and in a homeotropic section of the samples, yielding values for $K_3/\Delta\chi$ and K_1/K_3. These results were used to calculate the critical field and the wavelength for the periodic transition in the sample shown in Fig. 1. The predicted critical field of 4.25 kG is consistent with our experiment. The calculated wavelength is 52 μm, while that observed is 65 μm. The fact that the observed wavelength, produced by a field 1.3 times the critical value, is longer than the predicted wavelength at H_c should not be considered a serious disagreement since the theory makes no predictions for the behavior above the critical field. Prob-

ably the equilibrium wavelength should increase above H_c due to nonlinear effects. We do not view this phenomenon as a useful method for measuring K_1 and K_2. The static limit is very hard to approach, since near H_c response times become very long, while for fields a little above H_c a different phenomenon, involving obliquely oriented stripes generated by dynamic effects dominates the behavior of the system.[2]

Experimentally, the existence of this phenomenon means that for $K_1/K_2 > 3.3$, there is no longer a simple way of measuring K_1 by the Fréedericksz transition. Another field-alignment experiment involving the use of a magnetic field oriented at only a small angle with respect to the undisturbed director may be the next simplest method for determining K_1. It requires the measuring of the distortion amplitude as a function of field strength, rather than the simple determination of a critical field.

Theoretically, one could continue to study this phenomenon by determining the behavior above critical field, either by solving the full nonlinear problem or by numerical simulation methods. Our present analysis has found an instability that is almost surely the beginning of a continuous transition; the experimental evidence supports this interpretation. However, it is conceivable that a first-order transition to a state of finite distortion with a lower free energy could occur. In any case, one might expect that at high fields the periodic structure is replaced again by a uniform one, as the sample structure evolves to one consisting of a uniformly aligned central region with boundary layers at the surfaces. Even in these boundary levels, splay might be replaced by a periodic twist structure of some kind if the ratio K_1/K_2 is large enough.

In conclusion, we see that the geometric complexity of nematic liquid crystals still offers possibilities for the discovery of new phenomena.

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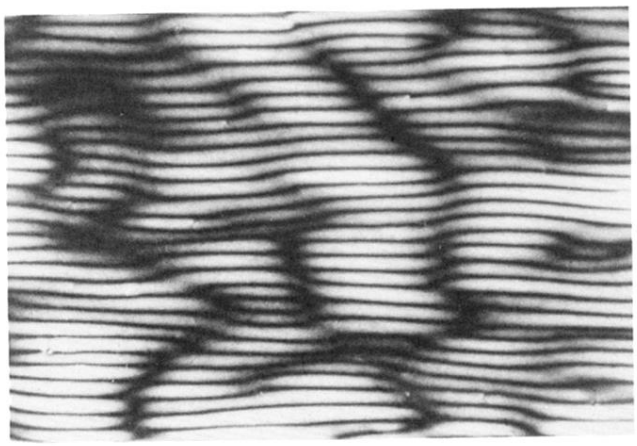

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