Theory of the Stripe Phase in Bend-Fréedericksz-Geometry Nematic Films

D. W. Allender and R. M. Hornreich
Department of Electronics, The Weizmann Institute of Science, 76100 Rehovot, Israel, and
The Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio 44242

and

D. L. Johnson
The Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio 44242
(Received 6 July 1987)

An outstanding problem in the physics of nematic films is the stripe phase which appears in the bend Fréedericksz geometry at temperatures slightly above that of the nematic to smectic-A phase transition in a sufficiently strong magnetic field. It is argued, by use of linear stability analysis, that in fact two transitions occur: the usual Fréedericksz transition to a uniformly distorted state, followed by a second transition to a stripe phase at a slightly higher field. Qualitative agreement is found between experimental results and theoretical predictions.

PACS numbers: 61.30.Gd, 64.70.Md

A periodic equilibrium configuration of the nematic director, giving rise to a stripe or ripple phase, has been experimentally observed in thin-film liquid crystals in an external field with appropriate boundary conditions.[1-3] We consider here the bend Fréedericksz geometry where, in the absence of a field, the director $\hat{\mathbf{n}}$ is uniformly aligned perpendicular to the plates forming the film boundaries. The field is applied in the film plane, i.e., perpendicular to $\hat{\mathbf{n}}$. In this geometry, stripes have been observed[2] slightly above T_{NA}, the nematic to smectic-A transition temperature. Thus the new phase occurs when the ratio of the splay to bend elastic constants is small.

Although various suggestions have been made,[1,4] a satisfactory explanation of the stripe phase in this geometry has not been found. In contrast, for the splay and twist Fréedericksz geometries, an explanation has been given.[3,5,6] There, when the elastic constants are sufficiently anisotropic, a transition from the uniform to the stripe phase replaces the usual Fréedericksz transition as it occurs at a lower threshold field. However, for the bend geometry, this model is *not* applicable; the uniform phase does not become unstable with respect to a striped structure. Thus a different explanation is required. By considering the Frank elastic free energy and using linear stability analysis, we find that the usual bend Fréedericksz transition always occurs but that, for certain elastic-constant ratios, the uniformly distorted Fréedericksz state is *unstable* against the formation of stripes. This second instability occurs in a field only marginally higher than that of the initial phase transition, except for a narrow diverging region (see Fig. 1). Rapid divergence of the bend elastic constant in the stripe regime[2] suggests a bend *expulsion* mechanism, as opposed to the splay *avoidance* which clearly prevails in the polymer problem.[3]

Consider the usual Frank free energy[7] in the dimensionless form

$$F=\tfrac{1}{2}\int d^3r\{M(2/\pi)^2(\nabla\cdot\hat{\mathbf{n}})^2+NM(2/\pi)^2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2+(2/\pi)^2(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2-h^2(\hat{\mathbf{n}}\cdot\hat{\mathbf{x}})^2\}. \quad (1)$$

Here $\hat{\mathbf{n}}(\mathbf{r})$ is the director, $M=K_1/K_3$, $N=K_2/K_1$, F is in units of $\pi^2K_3d/8$, lengths in units of $d/2$, and the field h in units of $(\pi/d)(K_3/\chi_a)^{1/2}$. K_1, K_2, and K_3 are the splay, twist, and bend elastic constants, respectively, d is the film thickness, and χ_a is the anisotropy of the magnetic or electric susceptibility which must be positive. The field is in the plane of the film along $\hat{\mathbf{x}}$.

For homeotropic boundary conditions, a suitable form satisfying $\hat{\mathbf{n}}^2=1$ is

$$\hat{\mathbf{n}}=\hat{\mathbf{x}}\sin\theta\cos\phi+\hat{\mathbf{y}}\sin\theta\sin\phi+\hat{\mathbf{z}}\cos\theta, \quad (2)$$

where $\hat{\mathbf{n}}$ is normal to the film plane at the boundaries. In the undistorted phase $\hat{\mathbf{n}}=\hat{\mathbf{z}}$ or $\theta=0$. In the uniformly (in the film plane) distorted state induced by the usual Fréedericksz transition, $\hat{\mathbf{n}}=\hat{\mathbf{x}}\sin\theta+\hat{\mathbf{z}}\cos\theta$ with $\theta=\theta(z)$. In general, both $\theta=\theta(\mathbf{r})$ and $\phi=\phi(\mathbf{r})$ are nonzero.

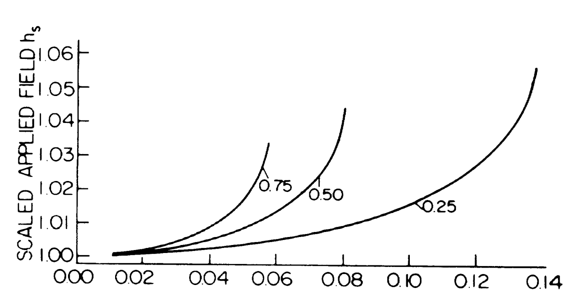

FIG. 1. Plots of the stripe threshold field, h_s, as a function of the ratio of elastic constants K_1/K_3 for three values of K_2/K_1: 0.75, 0.50, and 0.25. The corresponding end-point values of K_1/K_3 at which h_s diverges are 0.058, 0.080, and 0.138.

However, the Euler-Lagrange variational equations for θ and ϕ obtained from Eq. (1) are too complicated to solve exactly.

A simpler procedure uses linear stability analysis. Here, the stability of a configuration is checked with respect to small perturbations. This yields the stability limit for the phase being considered. For a continuous transition, this is identical to the actual phase boundary.

For the undistorted nematic, the equilibrium value of θ is zero, ϕ being irrelevant. In the bend geometry, we obtain to second order in these variables

$$F_A^{(2)}=\tfrac{1}{2}\int d^3r\{M(2/\pi)^2\theta_x^2+NM(2/\pi)^2\theta_y^2+(2/\pi)^2\theta_z^2-h^2\theta^2\}, \tag{3}$$

the subscripts denoting partial differentiation. $F_A^{(2)}$ is independent of ϕ in the bend geometry. This is *not* the case for the splay and twist geometries, where ϕ dependence leads to instability crossover.

The solution of the Euler-Lagrange equation obtained by minimization of $F_A^{(2)}$ with the boundary condition $\theta(z=\pm 1)=0$ is $\theta=\theta_0\cos(\pi z/2)$, with θ_0 arbitrary. At $h=1$, $F_A^{(2)}$ changes sign and this is the usual Fréedericksz transition for the bend geometry. It is *independent* of M and N. This is strongly supported by the results of Gooden *et al.*[2]

We now consider the local stability, for $h>1$, of the uniformly distorted state. Let

$$\theta(\mathbf{r})=W(z)+\Delta(\mathbf{r}),\quad \phi=\phi(\mathbf{r}), \tag{4}$$

where $W(z)$ is the exact solution of the *full* Euler-Lagrange equation.[8] We should thus substitute Eq. (4) into Eq. (1), keep terms to second order in Δ, ϕ, and their derivatives, and minimize the resulting expression. This results in a pair of linear, coupled, partial differential equations for Δ and ϕ. But, motivated by experiment, we used a different approach, assuming *a priori* that Δ and ϕ are periodic in y and independent of x. We set

$$\Delta(\mathbf{r})=\alpha f(z)\cos(qy),\quad \phi(\mathbf{r})=\beta g(z)\cos(qy+\psi), \tag{5}$$

where α,β are infinitesimal amplitudes, q is the (dimensionless) y-direction wave vector, and f, g, and ψ are determined by free-energy minimization. Since W is *not* small, it must therefore be kept in F to all orders.

We now expand F in α and β. The leading term, $F_B^{(0)}$, is just the free energy of the uniformly distorted Fréedericksz state and is[8]

$$F_B^{(0)}=\tfrac{1}{2}\int d^3r\{M(2/\pi)^2W_z^2\sin^2W+(2/\pi)^2W_z^2\cos^2W-h^2\sin^2W\}. \tag{6}$$

Since $\theta=W$, $\phi=0$ is an extremum of F, there is no contribution linear in α or β. The second-order terms are

$$F_B^{(2)}=\tfrac{1}{2}A[\alpha^2(A_1+q^2A_2)+\beta^2(B_1+q^2B_2)+2\alpha\beta qC], \tag{7}$$

where

$$\begin{aligned}
A_1&=\int_0^1 dz\{f^2\cos(2W)[(2/\pi)^2(M-1)W_z^2-h^2]+2(2/\pi)^2(M-1)ff_zW_z\sin(2W)+(2/\pi)^2f_z^2[M\sin^2W+\cos^2W]\},\\
A_2&=(2/\pi)^2\int_0^1 dz\,NMf^2,\quad B_1=\int_0^1 dz\{h^2g^2\sin^2W+(2/\pi)^2g_z^2\sin^2W[NM\sin^2W+\cos^2W]\},\\
B_2&=(2/\pi)^2\int_0^1 dz\,Mg^2\sin^2W,\quad C=\sin\psi(2/\pi)^2\int_0^1 dz\{\tfrac{1}{2}(M+1)fgW_z\sin(2W)+M\sin^2W[gf_z+Nfg_z]\},
\end{aligned} \tag{8}$$

and A is the dimensionless area of the sample in the film plane. To minimize $F_B^{(2)}$, we set $\psi=\pi/2$.

We now determine the minimum field in which $F_B^{(2)}$ vanishes with $\alpha,\beta\neq 0$. In principle, this field, which determines the stability limit, should be found by the solution of the coupled pair of Euler-Lagrange equations for f,g obtained by setting $\delta F_B^{(2)}=0$. While these equations are functions of a single variable only, they are nevertheless not amenable to analytic solution. We therefore use a different approach, which yields a field $h=h_s$ which is a rigorous *upper bound* on the stability limit.

Our procedure was to choose trial functions f,g consistent with the boundary conditions $f(\pm 1)=0$. Then, for fixed h, N, and T, the quantities A_i, B_i, and C were calculated numerically from Eq. (8). [This requires that $W(z)$ first be calculated[9] from Eq. (6).] Since $F_B^{(2)}$ is a quadratic form, it vanishes at a critical point for nonzero values of α,β when[10]

$$\begin{vmatrix} A_1+A_2q^2 & Cq \\ Cq & B_1+B_2q^2 \end{vmatrix}=0. \tag{9}$$

For Eq. (9) to have a solution with q^2 real, it is necessary (and sufficient) that

$$D=C^2-A_1B_2-A_2B_1-2(A_1A_2B_1B_2)^{1/2}>0. \tag{10}$$

The condition $D<0$ for $h=1$ causes the minimum value of h to occur at $D=0$. We therefore increased h in small increments for $h=1$ and varied our trial function so as to maximize D. This was repeated until we could attain $D=0$ with appropriate trial functions f,g.

After considering a number of possible trial functions, we found that

$$f=(1-z^a),\quad g=z^b,\quad 0\le z\le 1, \tag{11}$$

gave the best (minimum) value for the instability threshold field $h=h_s$. Thus our variational procedure reduced to changing a and b so as to attain $D=0$ at the lowest possible value of h. Optimum values were $a=1.6$ and $b=1.0$ at $M=0.1$ and $N=0.25$. In general, the resulting h_s was not sensitive to these parameters.

Our results are summarized in Figs. 1 and 2. In Fig. 1, we give the normalized stripe threshold field h_s as a function of $M=K_1/K_3$, for three values of $N=K_2/K_1$. For given K_2/K_1, we found that h_s *diverges* at a corresponding end-point value of K_1/K_3. In other words, the Fréedericksz bend state becomes unstable *only* when K_1/K_3 is less than this end-point value; it remains stable for any greater value of K_1/K_3. The end-point value decreases with increasing K_1/K_2.

Turning to Fig. 2, each point on the "theory" line corresponds to a value of K_2/K_1 and the associated end-point value of K_1/K_3. The regime in which a stripe phase is predicted to appear (above the appropriate threshold field) is so marked.

In order to compare our results with experiment, the elastic constants must be known. Using measurements by Gooden *et al.*[2] for octyloxycyanobiphenyl (8OCB) and scaling with the absolute measurements of Madhusudana and Pratibha,[11] we can parametrize the elastic constants (in dynes) by

$$\begin{aligned} K_1&=77.7\times10^{-7},\\ K_2&=2.8\times10^{-7}+2.07\times10^{-8}t^{-0.352},\\ K_3&=3.1\times10^{-7}+1.86\times10^{-8}t^{-0.709}, \end{aligned} \tag{12}$$

where $t=(T-T_{NA})/T_{NA}$, T is the absolute temperature, and $T_{NA}=339.93$ K. These expressions are valid for $10^{-5}\le t\le 2\times10^{-2}$. They yield the (M,N)-plane trajectory in Fig. 2 containing the points P and X. The former corresponds to $T-T_{NA}=0.06$ K and the latter to $T-T_{NA}=0.01$ K. As T approached T_{NA}, the elastic-constant ratios for 8OCB move along the trajectory with K_1/K_3 decreasing. Experimentally, stripes are observed when K_1/K_3 is less than 0.087 (i.e., point P).

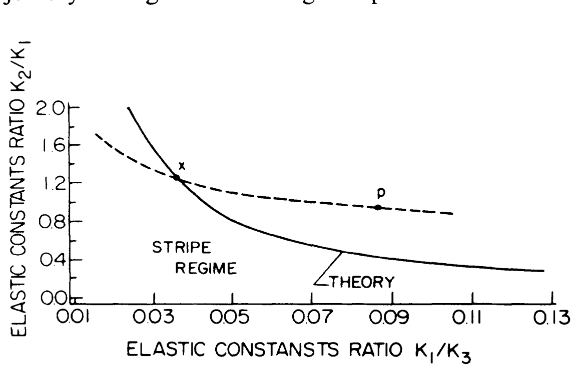

FIG. 2. Phase diagram showing the region where the stripe phase is predicted to exist. Also shown is a trajectory containing the points P and X (which does *not* separate different regimes of phase stability) which traces the experimentally observed elastic-constant ratios of the liquid-crystalline material 8OCB. Details are given in the text.

Although our calculations predict that stripes should appear only at point X and not at point P on the trajectory, it is important that both theory and experiment[2] exhibit an end-point value of t above which stripes cannot occur. The rapid increase of h_s at this end-point value is approached is also in agreement.[2] We do not believe that the discrepancy is serious since the experimental trajectory for 8OCB nearly parallels the theoretical stripe-regime boundary. Thus small changes in the values of the elastic constants or better trial functions could result in a large shift in the end-point value of t.

A further point of comparison is the wave vector q for the stripe phase at threshold. From Eq. (9), we find that when $D=0$,

$$q^2=(C^2-A_1B_2-A_2B_1)/(2A_2B_2). \tag{13}$$

Typical values of $\lambda=\pi d/q$ are a few tenths of the film thickness d. The same order of magnitude is observed experimentally.[1] Notice that λ never becomes infinite (i.e., the uniform, Fréedericksz, and stripe phases never meet at a common point).

The effect of a small deviation of the magnetic field direction from the film plane was also investigated. This results in a slight shift of the h_s vs K_1/K_3 curves shown in Fig. 1 to the left and upward.

Although it is encouraging that our analysis explains the observed periodic director configurations in the bend Fréedericksz geometry, several avenues for future analysis are apparent. These include determining (1) whether the phase transition to the stripe phase is indeed continuous, occurring at the stability limit, or whether it occurs at a lower field via a first-order transition; (2) whether more complex instability modes exist under suitable conditions; (3) the mechanism, e.g., bend and/or splay expulsion, for stripe onset;[12] and (4) more accurate trial functions f and g. Experimentally, accurate measurements of the elastic constants for different liquid crystals as well as determinations of the stripe periodicity are necessary for a more quantitative evaluation of our model.

In summary, the behavior of a thin nematic film in the Fréedericksz bend geometry has been examined as a function of applied field strength and anisotropy of the elastic constants. The usual Fréedericksz transition is found always to occur. However, there is a further instability, resulting in the formation of a stripe configuration, in a higher field when the elastic constants are sufficiently anisotropic. Qualitative agreement with experiment is good, but quantitative comparison requires additional data.

One of us (D.W.A.) acknowledges the receipt of a

Meyerhoff Visiting Professorship at the Weizmann Institute. We are grateful to Ms. A. Sauvage for programming assistance. We also acknowledge National Science Foundation support under Solid State Chemistry Grants No. DMR87-03524 and No. DMR82-44461.

[1]P. Cladis and S. Torza, J. Appl. Phys. **46**, 584 (1975).

[2]C. Gooden, R. Mahmood, D. Brisbin, A. Baldwin, D. L. Johnson, and M. E. Neubert, Phys. Rev. Lett. **54**, 1035 (1985).

[3]Franklin Lonberg and Robert B. Meyer, Phys. Rev. Lett. **55**, 718 (1985).

[4]K. C. Chu and W. L. McMillan, Phys. Rev. A **15**, 337 (1977).

[5]C. Oldano, Phys. Rev. Lett. **56**, 1098 (1986).

[6]U. D. Kini, J. Phys. (Paris) **47**, 693 (1986).

[7]See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[8]A. Saupe, Z. Naturforsch **15a**, 815 (1960).

[9]While $W(z)$ is known exactly, it is expressed (see Ref. 8) as an inverse elliptic integral of the third kind. This is inconvenient for numerical calculations. We therefore approximated W by $W' = r(1-z^p)$, with r and p treated as variational parameters which were fixed by minimization of $F_B^{(0)}$ [see Eq. (6)]. This approximation was everywhere within 2% of the exact result. As a check, a three-parameter approximation, $W'' = r(1-z^p)^s$, was also tested. Using W'' instead of W' has a negligible effect, so that W' was used to obtain the results reported here.

[10]The alternate possibility that one of the main diagonal terms in Eq. (9) vanishes is not relevant here.

[11]N. V. Madhusudana and R. Pratibha, Mol. Cryst. Liq. Cryst. **89**, 249 (1982).

[12]Note that the stripe boundary in Fig. 2 may have a horizontal asymptote at a very small value of K_2/K_1, implying that the stripes may occur in the regime where $K_1 \gg K_2, K_3$. In that regime splay expulsion is a likely mechanism. This is in contrast to the experimental regime (Ref. 2) ($K_1/K_3 \ll 1$, $K_2/K_1 \geq 1$) where bend expulsion is more likely. Only calculations will resolve this and certainly more experiments are in order.