Distortions induced by the K_{13} surfacelike elastic term in a thin nematic liquid-crystal film

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We have investigated some of the consequences of the inclusion of a nonzero (and fairly large) K_{13} term in the elastic free energy of a thin nematic liquid-crystal layer, where K_{13} is the splay-bend elastic constant. A sufficiently thin film is predicted to deform spontaneously in zero applied field, for large enough values of K_{13}. This deformation breaks the mirror symmetry of the film around its midplane and disappears at a critical value of the applied field which is a function of sample thickness. In the particular case where the boundaries favor parallel anchoring, the midplane of the spontaneously deformed layer will contain a nonsingular π wall. The existence of this anomalous distortion mode leads to dramatic changes in the topology of the Fréedericksz phase diagram: the onset of the Fréedericksz transition is predicted to occur at the critical field for infinitely strong anchoring, and the distorted state eventually becomes unstable with respect to the undistorted configuration as the strength of the applied field is further increased. For small K_{13} no spontaneously deformed state occurs and the critical field of the Fréedericksz transition is merely found to be shifted from its value for $K_{13}=0$. The possibility of experimentally observing some of these effects is also briefly discussed.

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I. INTRODUCTION

In the continuum theory of nematic liquid crystals, *small* departures from a uniform director texture $\mathbf{n}_0$ are described in terms of the bulk Frank elastic constants [1–3] K_{11},K_{22}, and K_{33}. These give the changes in the free energy to order $(\delta\mathbf{n})^2$ associated with splaylike, twistlike, and bendlike distortions, respectively. In addition to the usual Frank terms, there are two terms of the same order in $(\delta\mathbf{n})^2$ which can be expressed as divergences, and which introduce two further elastic constants, conventionally named K_{13} (splay-bend) and K_{24} (saddle-splay) [4]. These appear to have been introduced first by Oseen [1], were subsequently abolished by Frank [3], and were then reinstated by Nehring and Saupe [4], to whom we owe the standard nomenclature. The corresponding contributions to the integrated elastic free energy can be converted to surface integrals by the use of Gauss's theorem, and therefore these terms are often neglected in physical analyses, since they do not enter the Euler-Lagrange minimization equations; this point is discussed in more detail in [5]. There is, however, no fundamental reason why K_{13} and K_{24} should vanish or be negligible; indeed, several different microscopic calculations have yielded for either constant values of the same order of magnitude as the usual bulk constants [6–8]. Moreover, recent work suggests that K_{24} may give rise to some physical effects [9–12]. An intensive reexamination of the consequences of a nonvanishing K_{13} has been carried out in recent years by Hinov and Derzhanski [13–22], and by Barbero and co-workers [23–34].

We have embarked on a program aimed at clarifying the status of K_{13} in the elastic theory of nematics. In [5], one of us has presented a detailed analysis of the K_{13} and K_{24} surface terms and discussed the problem of minimizing a free energy containing such terms. In [8], we have evaluated the surface constants of a simple model nematogen using a microscopic theory, and shown that they are of the same order of magnitude as the usual bulk constants. We have also argued that the results thus obtained are essentially unambiguous. In this paper we work out some consequences of the presence of a K_{13} term in the nematic free energy. Some of our predictions are quite counter intuitive, or even exotic, and we make no claims as to their experimental realizability. Rather, we show that they follow from the widely used Landau theory of second-order transitions. At worst, our results can be interpreted as providing theoretical constraints on the magnitude of K_{13}, which, we hope, will stimulate further research.

This paper is organized as follows: in Sec. II A we discuss the paradox associated with the inclusion of the K_{13} term in the nematic free energy and briefly indicate how it can, in our view, be resolved. In Sec. II B we work out the Landau theory of field-induced transitions in a thin nematic layer and show how the standard results are affected by the inclusion of the K_{13} term; in particular, a spontaneously deformed (i.e., zero applied field) state is predicted to occur in sufficiently thin films, for values of K_{13}/K_{33} compatible with those obtained from our recent microscopic calculation [8]. This spontaneous deformation is *weakened*, and eventually destroyed, by the application of a magnetic field which would enforce the Fréedericksz transition [35]. Finally in Sec. III we give a critique of our results and make some concluding remarks.

II. ELASTIC THEORY OF NEMATICS FOR $K_{13}\neq 0$

A. The Oldano-Barbero paradox

The Frank-Oseen elastic free energy can be written [1,2] as

$$F=\int_{\mathcal{V}} dv\, f_F+\int_{\mathcal{S}} dS(f_{13}+f_{24})\ , \tag{1}$$

where the integrals are taken over the volume $\mathcal{V}$ and the surface $\mathcal{S}$ of the nematic sample, the f_F term corresponds to the usual bulk Frank energy, and f_{13},f_{24} are surface terms associated with the constants K_{13} and K_{24}, respectively:

$$f_F=\tfrac{1}{2}K_{11}(\nabla\cdot\mathbf{n})^2+\tfrac{1}{2}K_{22}[\mathbf{n}\cdot(\nabla\times\mathbf{n})]^2 + \tfrac{1}{2}K_{33}[\mathbf{n}\times(\nabla\times\mathbf{n})]^2\ , \tag{2a}$$

$$f_{13}=K_{13}\boldsymbol{\nu}\cdot\mathbf{n}(\nabla\cdot\mathbf{n})\ , \tag{2b}$$

$$f_{24}=-(K_{22}+K_{24})\boldsymbol{\nu}\cdot[\mathbf{n}\nabla\cdot\mathbf{n}+\mathbf{n}\times(\nabla\times\mathbf{n})]\ , \tag{2c}$$

where $\boldsymbol{\nu}$ is a unit vector normal to the surface.

The terms involving K_{24}, and in particular K_{13} have presented previously unsuspected mathematical difficulties due to the fact that they contain derivatives of the nematic director, **n**. Standard variational analysis deals only with functionals, the surface parts of which do not contain any derivative-dependent terms. In this case minimizing a functional of the type given in Eq. (1) is equivalent to solving the bulk Euler-Lagrange equations; the boundary conditions on **n** are similarly obtained by minimization at the surface. (Note that it is always possible *formally* to derive Euler-Lagrange equations for *any* functional, although their solutions do not necessarily minimize the functional. We shall come back to this point later.) In this respect, Oldano and Barbero [26,29] have made the important point that the term f_{13} in Eq. (2b) leads to infinitely strong subsurface deformations. Pergamenshchik [5] has interpreted this result as a consequence of the fact that f_{13} is unbounded from below, the conventional minimization procedure thus involving finding a saddle point, rather than a minimum, of the functional given in Eq. (1). Clearly this casts considerable doubt on the validity of the conventional boundary conditions, as well as on the role, and even the existence, of the surface elastic constant K_{13}.

An interpretation of the f_{13} term must involve resolution of the Oldano-Barbero paradox. Hinov [18,19,22] has postulated that physical content should only be assigned to the relevant Euler-Lagrange equations, which nevertheless do not yield a minimum energy configuration, as mentioned above. On a different note, Barbero, Madhusudana, and Oldano [27] have argued that some fourth-order terms should be retained in the elastic free-energy expansion which would restrict the amplitude of deformations at the surface (or, equivalently, bound the free energy from below). The strong (but finite) subsurface deformations thus predicted by these authors are, however, rather difficult to accommodate in a continuum theory, in which smooth variations over mesoscopic length scales are assumed [5]. Moreover, the question arises as to *which* fourth-order terms should be retained; if all, that would mean including new divergencelike terms in the theory, with the result that the total free energy would again be unbounded from below. The same is true of the total contribution of *any* finite order [5]. Thus neither of the above ideas seems entirely satisfactory.

Recently, one of us has achieved a resolution of the Oldano-Barbero paradox by summing terms to all orders in the expansion of the elastic free energy. The details of this procedure are being published elsewhere [5]; here it suffices to say that the sum R_∞ of all higher-order terms acts as a regularization term which bounds the free energy from below and suppresses unphysically strong subsurface deformations. It is found that the equilibrium director configuration is given, to order $(\delta\mathbf{n})^2$, by the Euler-Lagrange equations associated with the functional of Eq. (1) (which are taken formally and do *not* result from any minimization procedure, since, as we have seen above, the functional in question has no minimum). Moreover, no information on R_∞ is required; hence no new constants need to be introduced into the theory to provide the missing lower bound. An important consequence is that the surface elastic constant K_{13} is a well-defined physical quantity, hence amenable, at least in principle, to experimental determination. In a previous paper [8], we have predicted, on the basis of a microscopic theory of nematic elasticity, that K_{13} should be of the same order of magnitude as the bulk constants K_{ii} ($i=1,2,3$). We thus seek an experimental situation in which K_{13} would play a prominent role. To this we turn in the next section.

B. Field-induced transitions in a nematic layer for nonzero K_{13}

The most important manifestation of surface energy in nematics comes from the anchoring energy $w(\Theta_s)$, where Θ_s is the angle between the director at the interface and the easy axis on the surface. In what follows we shall assume the anchoring energy to be given by the simple Rapini-Papoular [36] form, viz.

$$w(\Theta_s)=\tfrac{1}{2}w\sin^2\Theta_s\ . \tag{3}$$

Unlike f_{13} and f_{24}, the anchoring energy depends on Θ_s, rather than on gradients thereof. Nevertheless, Lavrentovich and Pergamenshchik [10,12] have shown that the formation of striped domains in hybrid aligned nematic layers can be explained quite naturally if $K_{24}\neq 0$. Moreover, Allender, Crawford, and Doane [11] have found that textures in nematics confined to cylindrical regions cannot be consistently interpreted without invoking the existence of a nonzero K_{24}, if known values are used for the bulk elastic constants. Still a more dramatic exhibition of the surface terms would involve a qualitative, rather than a merely quantitative, effect. We now demonstrate the existence of such an effect in the case of K_{13}.

Consider a nematic layer of uniform thickness d sandwiched between two identical, weakly anchoring surfaces at $z=\pm d/2$ (we take the z axis to be perpendicular to the surfaces). Suppose that homeotropic anchoring [37] is favored at both surfaces with equal strength (the treatment is identical in the case of planar anchoring). The orientation of the director in the nematic layer is described by the *tilt angle* $\theta=\theta(z)$, which the director makes with the normal to the surfaces; we neglect azimuthal anchoring. In this geometry the director depends upon only one Cartesian coordinate, hence the contribution of the K_{24} term vanishes [9]. If a magnetic field of strength H is now applied in the x direction, the layer will remain undistorted if $H<H_{\text{th}}$; for $H\geq H_{\text{th}}$, the so-called *Fréedericksz transition* occurs: $\theta(z)\neq 0$, with a maximum at $z=0$ (in the midplane of the sample). The threshold field H_{th} is the root of the transcendental equation [36]

$$u=\frac{wd}{2K_{33}}\cot u \ , \quad 0\leq u\leq \pi/2 \ , \tag{4}$$

where $u=dq/2$, $q=(\chi_a H^2/K_{33})^{1/2}$, and $\chi_a>0$ is the anisotropic part of the magnetic susceptibility. Equation (4) is known as the *Rapini-Papoular equation* [36].

The free energy (per unit area) of the nematic layer including the K_{13} term is given by

$$F=\tfrac{1}{2}\int_{-d/2}^{d/2}dz[(K_{11}\sin^2\theta+K_{33}\cos^2\theta)\theta'^2-\chi_a(\mathbf{n}\cdot\mathbf{H})^2]+\tfrac{1}{2}w(\sin^2\theta_1+\sin^2\theta_2)-\tfrac{1}{2}K_{13}(\theta_2'\sin 2\theta_2-\theta_1'\sin 2\theta_1) \ , \tag{5}$$

where the primes denote differentiation with respect to z and the subscripts 2,1 correspond to quantities measured at the surfaces $z=\pm d/2$, respectively. As the transition is usually continuous, we may assume $\theta(z)$ to be small everywhere and solve the linearized Euler-Lagrange equation,

$$K_{33}\theta''+\chi_a H^2\theta=0 \ , \tag{6}$$

with the solution

$$\theta(z)=A\sin qz+N\cos qz \ . \tag{7}$$

We shall see later that the assumption of small θ is indeed justified *a posteriori*. In the standard treatment of the Fréedericksz transition, it is assumed that the layer has mirror symmetry around the plane $z=0$ and only the even (or symmetric) solution, $\theta_N(z)=N\cos qz$, is retained [33]. We shall show, however, that for sufficiently large K_{13} a *parity-breaking* mode $\theta_A(z)=A\sin qz$ can be excited which is odd (or antisymmetric) with respect to $z=0$ (see Figs. 1 and 2).

We now construct a Landau theory of the transition. To this end we expand Eq. (5) to order θ^4 to obtain

$$F\simeq F_2+F_4 \ , \tag{8a}$$

$$F_2=\tfrac{1}{2}\int_{-d/2}^{d/2}dz(K_{33}\theta'^2-\chi_a H^2\theta^2)+\tfrac{1}{2}w(\theta_1^2+\theta_2^2)-K_{13}(\theta_2\theta_2'-\theta_1\theta_1') \ , \tag{8b}$$

$$F_4=\tfrac{1}{2}\int_{-d/2}^{d/2}dz\left[(K_{11}-K_{33})\theta^2\theta'^2+\frac{1}{3}\chi_a H^2\theta^4\right]-\frac{1}{6}w(\theta_1^4+\theta_2^4)+\frac{2}{3}K_{13}(\theta_2^3\theta_2'-\theta_1^3\theta_1') \ . \tag{8c}$$

Equations (7) and (8b) can now be combined so as to reexpress F_2 in terms of A and N, yielding

$$F_2=c_{2,A}A^2+c_{2,N}N^2 \ , \tag{9}$$

where

$$c_{2,A}=q(\tfrac{1}{2}K_{33}-K_{13})\sin 2u+w\sin^2 u \ , \tag{10a}$$

$$c_{2,N}=-q(\tfrac{1}{2}K_{33}-K_{13})\sin 2u+w\cos^2 u \ , \tag{10b}$$

where, as before, $u=dq/2$. F_2 consists of the quadratic terms in the free-energy expansion in powers of A and N. These quantities are, in fact, order parameters in a Landau theory of the (continuous) Fréedericksz transition. Note that no cross terms (i.e., terms involving products of A and N) appear in F_2.

The critical condition for a phase transition to occur is that the coefficient of one of the quadratic terms should vanish. The Fréedericksz transition obtains when $c_{2,N}$

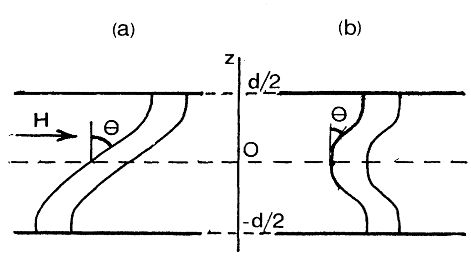

FIG. 1. Normal (a) and parity-breaking (b) distortion modes of a thin nematic layer between homeotropically aligning plates.

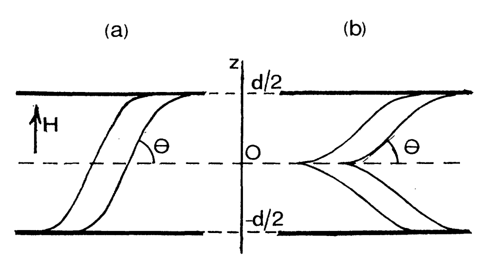

FIG. 2. Same as in Fig. 1, but for planar aligning plates. Note the nonsingular π wall in the midplane of the layer in (b).

goes negative; this implies

$$-\frac{u}{d}(K_{33}-2K_{13})\sin 2u + w\cos^2 u = 0 \Longrightarrow u = \frac{wd}{2(K_{33}-2K_{13})}\cot u \ . \quad (11)$$

If $K_{33} > 2K_{13}$, Eq. (11) is a generalization of the Rapini-Papoular equation, Eq. (4), to the case $K_{13} \neq 0$. In Fig. 3 we solve it graphically in the range $0 \le u \le \pi$; the reduced quantities $d^* = wd/K_{33}$, $q^* = qK_{33}/w$ have been used. Figure 4 illustrates the effect of $K_{13} \neq 0$ on the threshold field of the Fréedericksz transition: we have used the values of the elastic constants obtained from our microscopic theory for a fluid of Gay-Berne [38] particles of elongation $\kappa = 3$ and well depth ratio $\epsilon_e/\epsilon_s = 0.15$ [8,38]; in this theory, $K_{11} = K_{33}$ and $K_{13} > 0$.

If, however, $K_{33} < 2K_{13}$ (Fig. 5), the Fréedericksz transition can only occur at $u = \pi/2$ (the threshold field for infinitely strong anchoring). $c_{2,N}$ crosses zero again at a value of u given by Eq. (11), which now describes the *demise*, rather than the onset, of the normal distorted regime.

We now consider $c_{2,A}$. Clearly, if $K_{33} > 2K_{13}$ this term is positive for $0 \le u \le \pi/2$ and the system will undergo a Fréedericksz transition rather than deform anomalously. If $K_{33} < 2K_{13}$, the anomalous parity-breaking state will be realized if $c_{2,A} < 0$ for $0 \le u \le \pi/2$, i.e.,

$$w\sin^2 u - \frac{u}{d}(2K_{13}-K_{33})\sin 2u < 0 \ . \quad (12)$$

At very low fields ($u \ll 1$), this yields

$$wu^2 - \frac{2u^2}{d}(2K_{13}-K_{33}) < 0 \Longrightarrow d < \frac{4}{w}\left[K_{13} - \tfrac{1}{2}K_{33}\right] = d_c \ , \quad (13)$$

i.e., for given values of the elastic constants and anchoring strength, a spontaneously deformed state is realizable if $d < d_c$ (i.e., for sufficiently thin films), provided $K_{13} > K_{33}/2$. In Fig. 6 we plot $c_{2,A}$ as a function of u; the spontaneous deformation is suppressed if

$$w\sin^2 u - \frac{u}{d}(2K_{13}-K_{33})\sin 2u \Longrightarrow u = \frac{wd}{2(2K_{13}-K_{33})}\tan u \Longrightarrow u = \frac{d}{d_c}\tan u \ . \quad (14)$$

If u is small nevertheless, we can expand about $u = 0$ to obtain the limiting behavior of the critical field H_c which destroys the spontaneously deformed state,

$$H_c \propto q_c \sim \frac{1}{d}\left[1 - \frac{d}{d_c}\right]^{1/2} , \quad (15)$$

where we have used

$$\tan u \simeq u + \frac{u^3}{3} , \quad (16a)$$

$$\frac{d_c}{d} = \left[1 - \frac{d_c - d}{d_c}\right]^{-1} \simeq 1 + \frac{d_c - d}{d_c} \ . \quad (16b)$$

We have thus arrived at the paradoxical result that a magnetic field applied along the x axis tends to align a nematic with *positive* magnetic anisotropy *perpendicular* to itself. This is a consequence of the fact that the

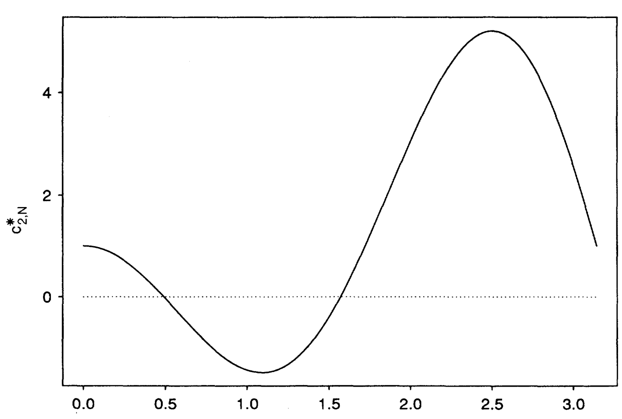

FIG. 3. $c^*_{2,N} = c_{2,N}/w$ vs u for $K_{33} > 2K_{13}$; the Fréedericksz transition obtains for $0 \le u \le \pi/2$.

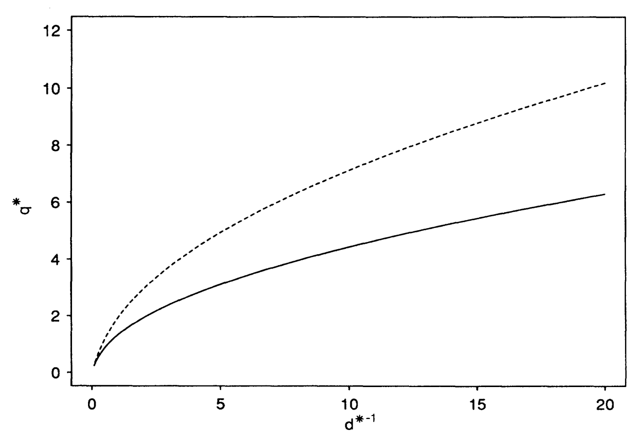

FIG. 4. Fréedericksz threshold field vs inverse thickness (in reduced units: see text) for a Gay-Berne model nematogen between homeotropically aligning plates. At $\rho^* = 0.65$, $T^* = 0.07$, microscopic theory [8] gives $(K_{13}/K)_{\rm micr} \simeq 0.31$. Solid line: $K_{13}/K = 0$; dashed line: $K_{13}/K = (K_{13}/K)_{\rm micr}$.

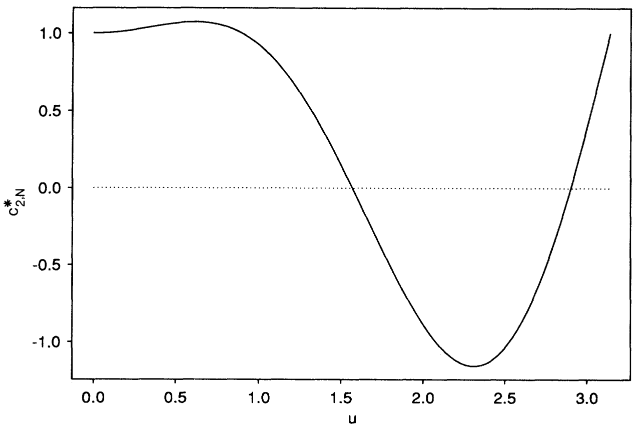

FIG. 5. $c^*_{2,N}=c_{2,N}/w$ vs u for $K_{33}<2K_{13}$; the onset of the Fréedericksz distorted state is now at $u=\pi/2$; the distortion is suppressed for $u \geq u^N_{\rm th} > \pi/2$.

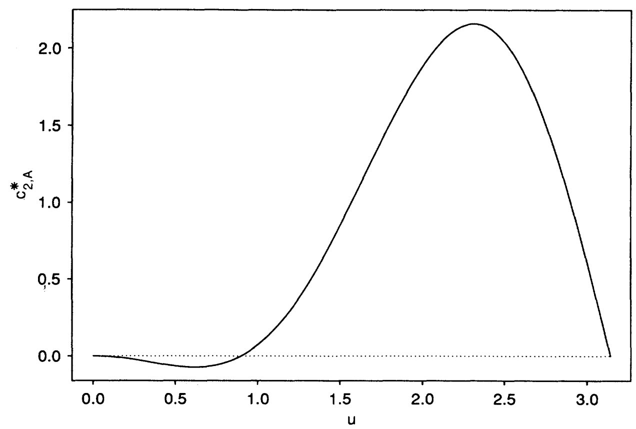

FIG. 6. $c^*_{2,A}=c_{2,A}/w$ vs u for $K_{33}<2K_{13}$; the anomalous parity-breaking distorted state is stable for $u \leq u^A_{\rm th} < \pi/2$.

relevant quantity describing the elastic response of the nematic is no longer K_{33} but an *effective* bend elastic constant $K^{\rm eff}_{13}=K_{33}-2K_{13}$, so for $K_{33}<2K_{13}$ the layer behaves as if it had a *negative* bend constant: energy has to be expended in order to produce an undeformed state. It would be interesting to investigate the dynamical mechanism by which this effect may be achieved.

Furthermore, it follows from the discussion of Eqs. (11) and (12) that the normal (Fréedericksz) and parity-breaking modes cannot be excited simultaneously, i.e., in the same range of u. Setting A and N alternately to zero in Eq. (7), we can compute the free energy of the normal and parity-breaking distorted states, respectively. The use of Eqs. (8) and (9) then yields, to fourth order,

$$F_N=c_{2,N}N^2+c_{4,N}N^4 \ , \tag{17a}$$

$$F_A=c_{2,A}A^2+c_{4,A}A^4 \ , \tag{17b}$$

where $c_{2,A}$ $c_{2,N}$ are given by Eqs. (10) and

$$c_{4,A}=\frac{q}{8}(K_{11}-K_{33})\left[u-\frac{\sin 4u}{4}\right]+\frac{q}{6}K_{33}\left[\frac{3}{4}u-\frac{\sin 2u}{2}+\frac{\sin 4u}{16}\right]+\frac{2}{3}qK_{13}\sin^2 u\,\sin 2u-\frac{1}{3}w\sin^4 u \ , \tag{18a}$$

$$c_{4,N}=\frac{q}{8}(K_{11}-K_{33})\left[u-\frac{\sin 4u}{4}\right]+\frac{q}{6}K_{33}\left[\frac{3}{4}u+\frac{\sin 2u}{2}+\frac{\sin 4u}{16}\right]-\frac{2}{3}qK_{13}\cos^2 u\,\sin 2u-\frac{1}{3}w\cos^4 u \ . \tag{18b}$$

Figure 7 shows the Fréedericksz phase diagram in the case $K_{13}>K_{33}/2$; we have again used values of K_{33} and K_{13} from our microscopic theory [8], for the same elongation and well depth ratio as in Fig. 4, but at a different temperature. What happens when the field is increased beyond that which destroys the normal distorted state is open to question. In principle, there is nothing to stop us from solving Eqs. (11) and (14) at still higher fields, thus obtaining a sequence of alternate normal deformed–undeformed ($d>d_c$) or anomalous deformed–undeformed–normal deformed ($d<d_c$) domains, as the field is increased. If such an exotic effect could be observed, it would provide substantial evidence in support of the existence of a K_{13} term.

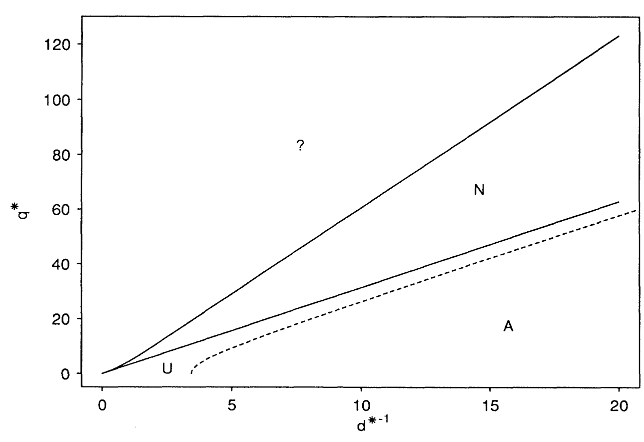

FIG. 7. Fréedericksz phase diagram of a Gay-Berne model nematogen between homeotropically aligning plates. At $\rho^*=0.65$, $T^*=0.085$, microscopic theory [8] gives $(K_{13}/K)_{\rm micr}\simeq 0.57$. A, anomalous deformed regime; U, undeformed regime; N, normal (Fréedericksz) regime. See text for discussion.

In order to characterize the transitions we need to define a suitable order parameter. Since we are neglecting twist deformations, we assume that the director always lies in a single plane, which we take to be the xOz plane. If we write the (uniaxial) nematic order-parameter tensor in the usual form [37],

$$\mathsf{Q}(z)=\tfrac{1}{2}Q(3\mathbf{nn}-\mathsf{I}) \ , \tag{19}$$

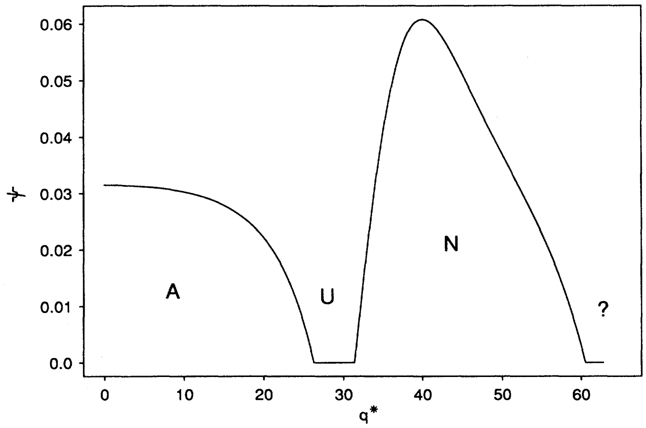

FIG. 8. Order parameter ψ vs q^* for $d^*=0.1$ in Fig. 6. A, anomalous deformed regime; U, undeformed regime; N, normal (Fréedericksz) deformed regime.

where Q is the scalar nematic order parameter and I is the unit tensor, then a suitable order parameter will be

$$\psi=\langle Q_{xx}-Q_{yy}\rangle=\frac{1}{d}\int_{-d/2}^{d/2} dz\frac{3}{2}\sin^2\theta(z) , \tag{20}$$

where perfect orientational order along $\mathbf{n}$ (i.e., $Q=1$) has been assumed. The amplitudes of the normal and parity-breaking modes, N and A, are found by minimizing the free energy, Eqs. (17), with respect to N and A, respectively. We obtain

$$N=-\frac{c_{2,N}}{2c_{4,N}} , \quad A=-\frac{c_{2,A}}{2c_{4,A}} . \tag{21}$$

In Fig. 8 we plot ψ as a function of magnetic field for $d^*=0.1$, which lies in the range where anomalous transitions are allowed. If we take $K_{33}\sim 2\times 10^{-6}$ dyn and $w\simeq 2\times 10^{-3}$ erg/cm^2, then $\xi=K_{33}/w\sim 10^{-3}$ cm and $d=\xi d^*\sim 10^{-4}$ cm. On the other hand, $\psi\sim\langle\theta^2\rangle\sim 0.06$, hence $\theta\sim 10^0$, which should be observable.

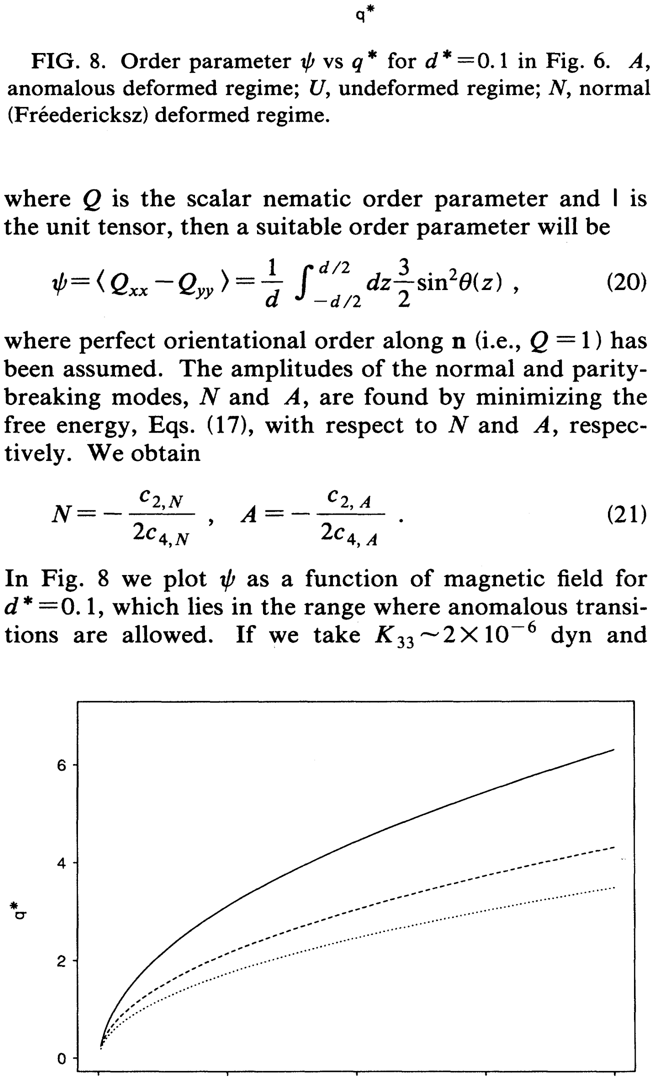

FIG. 9. Fréedericksz threshold field vs inverse thickness (in reduced units; see text) for a Gay-Berne model nematogen between parallel aligning plates, at the same temperature and density as in Fig. 6: $(K_{13}/K)_{\rm micr}\simeq 0.57$. Solid line: $K_{13}/K=0$; dashed line: $K_{13}/K=(K_{13}/K)_{\rm micr}$; dotted line: $K_{13}/K=2(K_{13}/K)_{\rm micr}$ (compare with Fig. 3).

All the above results pertain to a homeotropically aligned film. The planar case can be treated in exactly the same way by writing Eq. (5) in terms of $\bar{\theta}=\pi/2-\theta$, and it is easily shown that all relevant expressions can be obtained from the corresponding homeotropic ones by making the substitutions $K_{33}\rightarrow K_{11}$, $K_{13}\rightarrow -K_{13}$. Hence the parity-breaking mode is now allowed only if $K_{13}<0$ and $|K_{13}|>K_{11}/2$; this same mode now leads to the appearance of a nonsingular π wall in the midplane of the sample. In Fig. 9 we illustrate the effect of $K_{13}\neq 0$ on the threshold field of the Fréedericksz transition in a planar geometry; the same microscopic theory [8] has been used for the elastic constants, and the reduced quantities are now $d^*=wd/K_{11}$, $q^*=qK_{11}/w$. Note that $K_{13}>0$ raises the critical field of a homeotropically aligned layer while lowering that of a parallel aligned one (compare Figs. 4 and 9).

III. DISCUSSION AND CONCLUSIONS

We have developed a simple Landau theory of field-induced transitions in a thin nematic layer including the K_{13} term in the Frank elastic energy. We have shown that a *small* $K_{13}>0$ shifts the critical field of the Fréedericksz transition by renormalizing the relevant bulk elastic constant. The shift is upwards in the case of a homeotropically aligned layer, and downwards for a parallel aligned one. However, if $K_{13}>0$ and $K_{13}>K_{33}/2$ (homeotropic geometry) or $K_{13}<0$ and $|K_{13}|>K_{11}/2$ (planar geometry), a spontaneously (i.e., zero field) deformed state is predicted to occur in addition to the usual Fréedericksz deformed state, in sufficiently thin layers (this phenomenon bears some resemblance to that encountered, as early as 1979, by Hinov and Derzhanski, in the context of a nonlinearized theory of the electric-field-induced Fréedericksz transition [17,39]). The existence of this anomalous distorted regime also affects the Fréedericksz transition, leading to a rather exotic phase diagram where the applied field alternately enhances and inhibits distortions.

In this paper we have restricted ourselves to the one-dimensional problem. A more rigorous analysis would have to take into account the possibility of out-of-plane (twistlike) distortions; if these are energetically favored, the whole picture we have described might change substantially. This work is in progress.

Clearly much work still needs to be done before these issues are fully understood. Nonetheless, by working out in some detail the consequences of such a term using a simple theory of phase transitions, we feel that we have made a case for further investigations, both on the theoretical and on the experimental fronts. At present, there is no consensus over whether the K_{13} term in the free energy exists at all, and if so, whether it can be calculated unambiguously from a microscopic theory [40]. A density-functional theory of nematic elasticity could help clarify this point, which is a consequence of the fact that the usual description in terms of the Frank elastic constants does not take into account the detailed microscopic structure of nematics. Such an approach would also allow a detailed investigation of the dependence of K_{13} and K_{14} upon the features of the intermolecular potentials. On a different level, it would be interesting to know how the dynamic behavior of nematics is affected by the existence of a K_{13} term and the associated energy minimization problems. Experimentally, we believe the most promising method for observing any of the effects predicted in this paper would be the wedge-cell technique [41,42], in which the thickness of the layer can be varied continuously.

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