Flexoelectric instability of liquid crystals

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The threshold field for flexoelectric instability in nematic liquid crystals, and the upper limit of the maximum tilt angle connected with this instability are rigorously evaluated. The nematic liquid crystal, with positive dielectric anisotropy, is assumed to be in the homeotropic configuration, without external field. The surface anchoring energy is considered infinitely strong on one wall and finite on the other. The stability of the distorted configuration is discussed from the energy point of view. The influence of the surface polarization on the threshold field is also reported. It is shown that the surface polarization changes not only the effective flexoelectric coefficient, in agreement with phenomenological theories, but also the effective anchoring energy, from the coupling with the flexoelectric effect.

I. INTRODUCTION

Uniform textures of nematic liquid crystals (monodomain single crystals) are produced by orienting a drop of bulk material in between two conveniently treated plates, which define usually a fixed orientation for the boundary molecules. This is the so-called strong-anchoring situation. Applying an electric field on such a texture results in a curvature volume distortion, at fixed-boundary orientation, as, for instance, in the Fredericksz transition. Long ago, Helfrich[1] had proposed a new kind of texture instability, in the case of weak anchoring, where the nematic orientation can change at the boundary, using the flexoelectric coupling between the nematic and the applied field, which results in polar surface effects. This instability was analyzed by Deuling,[2] who dealt with the dielectric case in the hypothesis of infinitely weak anchoring energy, and by Derzhanski, Petrov, and Mitov,[3] who dealt with the conductive case, in the hypothesis of small dielectric anisotropy ϵ_a and finite anchoring energy. More recently Monkade, Martinot-Lagarde, and Durand[4] have reported on the experimental observation of polar-surface instabilities, one of which has a similar behavior to the Helfrich flexoelectric instability. In Ref. 3 the theoretical analysis is performed by supposing ϵ_a to be small enough so that the electric field **E** inside the nematic does not depend substantially on the position. At the present time this restrictive hypothesis seems severe since polar instabilities have been observed in cyano-byphenil derivatives,[4] where $\epsilon_a \simeq 10$.

This paper presents a rigorous evaluation of the threshold field for flexoelectric instability and the upper limit of the maximum tilt angle connected with this instability, in the case of large ϵ_a and finite surface anchoring energy. In Sec. II the general equations governing the phenomenon are reported. In Sec. III the threshold field is deduced, whereas in Sec. IV the upper limit of the surface tilt angle is discussed. In Sec. V the threshold fields for some particular sets of the nematic material parameters are given. Energy considerations on the stability of the distorted configuration are reported in Sec. VI and in Sec. VII the case of negative dielectric anisotropy is rapidly analyzed. Finally in Sec. VIII the influence of the surface polarization on the threshold field is considered. It is assumed position dependent. The analysis shows that surface polarization introduces an effective flexoelectric coefficient and effective anchoring energy and that the variations of these quantities can be large.

II. GENERAL EQUATIONS

Let us consider a nematic slab of thickness d. The limiting plates are at $z=0$ and $z=d$, and the z axis is normal to them. In the absence of external field the nematic director **n** is parallel to the z axis (homeotropic alignment). We assume that (I) the dielectric anisotropy $\epsilon_a=\epsilon_{\parallel}-\epsilon_{\perp}$ of the nematic is positive and large, (II) the anchoring energy on the wall at $z=0$ is weak, whereas that on the wall at $z=d$ is strong (practically infinite), (III) the nematic-liquid-crystal Debye screening length is larger than the sample thickness. From hypothesis (III) it follows that the nematic material can be considered as an insulator. If an electric field **E** parallel to the z axis is applied to the sample, only a polar instability is possible, depending on the flexoelectric properties of the liquid crystals, since the nematic is dielectrically stable, given hypothesis (I).

Let $\theta(z)$ be the tilt angle formed by **n** with the z axis. A standard procedure[1,2,5–8] gives for the $\theta(z)$ bulk equation

$$K(\theta)\dot{\theta}^2-(1/8\pi)D^2/\epsilon_{33}(\theta)=B\ , \tag{1}$$

for the boundary conditions[8]

$$\begin{aligned}&-K(\theta_0)\dot{\theta}_0-(1/4\pi)D\,d\psi/d\theta_0+df_s/d\theta_0=0,\quad z=0\\&\theta_d=0,\quad \text{from hypothesis (II)}\end{aligned} \tag{2}$$

and for the voltage across the cell

$$V=D\lambda-\psi(\theta_0)\ . \tag{3}$$

In Eqs. (1), (2), and (3),

(i) B = integration constant;

(ii) $K(\theta)=K_{33}\{1-k\sin^2\theta+\frac{1}{4}k_f\sin^2 2\theta/[1-(\epsilon_a/\epsilon_{\parallel})\times\sin^2\theta]\}$ = effective elastic constant,[2,5–8] $k=1-(K_{11}/K_{33})$ = elastic anisotropy, and $k_f=4\pi e^2/(K_{33}\epsilon_{\parallel})$;

(iii) $\epsilon_{33}(\theta)=\epsilon_{\parallel}\cos\theta+\epsilon_{\perp}\sin^2\theta=z$, z component of the dielectric tensor;

(iv) $f_s=\frac{1}{2}w\sin^2\theta_0$ = anchoring energy. If we limit ourselves to consider $T\ll T_c$ this form of f_s is adequate.[9] But when $T\simeq T_c$ it is necessary to modify f_s introducing terms connected with order electricity.[9] In this paper we consider only the case $T\ll T_c$;[10]

(v) $\theta_0=\theta(z=0)$, $\theta_d=\theta(z=d)$, $\dot\theta=d\theta/dz$, $\dot\theta_0=(d\theta/dz)_0$;

(vi) $\lambda=\int_0^d dz/\epsilon_{33}(\theta)$;

(vii) $\psi(\theta_0)=-2\pi(e/\epsilon_a)\ln[1-(\epsilon_a/\epsilon_{\parallel})\sin^2\theta_0]$, where $e=e_1+e_3$ is the sum of the flexoelectric coefficients;[1]

(viii) D = z component of the dielectric displacement.

Equation (1) shows that, in our hypothesis, $\theta(z)$ is a decreasing function of z. In fact if $\theta(z)$ is not monotone a point z^* exists, at least, where it is maximum or minimum, and then $\dot\theta(z^*)=0$. Since $\theta(d)=0$ this point can only be a maximum. Let us suppose that $\theta(z)$ is not monotone. In this case by putting $\theta(z^*)=\theta_M$, from Eq. (1) we deduce that the integration constant is

$$B=-(1/4\pi)D^2/\epsilon_{33}(\theta_M)\ .$$

Consequently Eq. (1) becomes

$$K(\theta)\dot\theta^2=-\frac{(1/4\pi)\epsilon_a D^2(\sin^2\theta_M-\sin^2\theta)}{[\epsilon_{33}(\theta_M)\epsilon_{33}(\theta)]}\ ,$$

which is absurd since $K(\theta)>0$ and $\epsilon_{33}(\theta)>0$ for any θ in the range $(0,\pi/2)$. Hence $\theta(z)$ cannot have a maximum in $(0,d)$. $\theta(d)=0$ implies that $\theta(z)$ is a monotonically decreasing function, i.e., $\dot\theta(z)<0$, for any z. By taking into account this condition, from Eqs. (1), (2), (3), and (iv), (vii) we obtain

$$\int_0^{\theta_0}\{K(\theta)/[B+(1/4\pi)D^2/\epsilon_{33}(\theta)]\}^{1/2}d\theta=d\ , \tag{1'}$$

$$\{K(\theta_0)[B+(1/4\pi)D^2/\epsilon_{33}(\theta_0)]\}^{1/2}+[w-eD/\epsilon_{33}(\theta_0)]\sin\theta_0\cos\theta_0=0\ , \tag{2'}$$

$$V=D\int_0^{\theta_0}\left[\frac{K(\theta)}{B+(1/4\pi)D^2/\epsilon_{33}(\theta)}\right]^{1/2}\times\frac{d\theta}{\epsilon_{33}(\theta)}-\psi(\theta_0)\ . \tag{3'}$$

III. DETERMINATION OF THE THRESHOLD FIELD

Since $\theta_0\in(0,\pi/2)$, from Eq. (2′) we deduce that for any θ_0 the dielectric displacement D must be larger than $w\epsilon_{33}(\theta)/e$, and hence

$$D>D_1=\epsilon_{\parallel}v/L \quad\text{or}\quad E>E_1=v/L\ , \tag{4}$$

where $v=K_{33}/e$, $L=K_{33}/w$ is the extrapolation length and $E=D/\epsilon_{\parallel}$ is the electric field in the nematic medium when it is in homeotropic alignment. Equation (4) is obtained supposing $e>0$, as we will do in the following. In the case $e<0$ similar equations are obtained.

Eliminating B in Eqs. (1), (2), and (3) we obtain

$$\int_0^{\theta_0}f(D,\theta_0;\theta)d\theta=d \tag{1''}$$

and

$$V=D\int_0^{\theta_0}[f(D,\theta_0;\theta)/\epsilon_{33}]d\theta-\psi(\theta_0)\ , \tag{2''}$$

where

$$f(D,\theta_0;\theta)=\left[\frac{K(\theta)}{\dfrac{D^2}{4\pi}\left[\dfrac{1}{\epsilon_{33}(\theta)}-\dfrac{1}{\epsilon_{33}(\theta_0)}\right]+\left[\dfrac{eD}{\epsilon_{33}(\theta_0)}-w\right]^2\dfrac{\sin^2\theta_0\cos^2\theta_0}{K(\theta_0)}}\right]^{1/2}. \tag{5}$$

$f(D,\theta_0;\theta)$ depends only on $x_0^2=\sin^2\theta_0$ and $x^2=\sin^2\theta$. Hence we can rewrite it as

$$f(E,x_0;y)=\frac{1}{x_0}\left[\frac{K(x_0^2y^2)}{\left[\dfrac{eE}{1-(\epsilon_a/\epsilon_{\parallel})x_0^2}-w\right]^2\dfrac{1-x_0^2}{K(x_0^2)}-\dfrac{\epsilon_aE^2}{4\pi}\dfrac{1-y^2}{[1-(\epsilon_a/\epsilon_{\parallel})x_0^2][1-(\epsilon_a/\epsilon_{\parallel})x_0^2y^2]}}\right]^{1/2}, \tag{5'}$$

where $y=x/x_0(\le 1)$.

With Eq. (5′), Eq. (1″) becomes

$$d=x_0\int_0^1 f(E,x_0;y)(1-x_0^2y^2)^{-1/2}dy\ . \tag{6}$$

Equation (6) in the $x_0\to 0$ limit gives the threshold field. By taking into account that $\lim_{x_0\to 0}K(x_0^2y^2)=K_{33}$ we obtain

$$g(E;y)=\lim_{x_0\to 0}f(E,x_0;y)=K_{33}[(eE-w)^2-r^2E^2(1-y^2)]^{-1/2}\ , \tag{7}$$

where $r^2=\epsilon_aK_{33}/4\pi$.

By definition $y\le 1$; hence the function $g(E;y)$ will be real for any y only if

$$(eE-w)^2-r^2E^2>0\ , \tag{8}$$

which gives

$$E>E_2=(v/L)[1-(r/e)]^{-1}\ . \tag{9}$$

From Eq. (9) we deduce that e must be larger than r, i.e., $e^2>\epsilon_a K_{33}/4\pi$, as well known,[3,4] and furthermore that $E_2>E_1$.

In the considered $x_0\to 0$ limit, by taking into account Eq. (7), Eq. (6) gives

$$d=(K_{33}/2rE)\ln\{[(e+r)E-w]/[(e-r)E-w]\}\ . \tag{10}$$

Equation (10) defines another threshold field E_3. A simple analysis shows that $E_3>E_2$. Consequently the threshold field for the flexoelectric instability is given by Eq. (10). In any case if the anchoring energy is not very weak and the sample is not very thin[11] $E_3\simeq E_2$. In fact if we rewrite Eq. (10) as

$$(r/K_{33})Ed=\tfrac{1}{2}\ln\{[(e+r)E-w]/[(e-r)E-w]\}\ , \tag{11}$$

we can determine E_3 as the intersection point between the curve

$$h_1(E)=(r/K_{33})Ed \tag{12a}$$

and the curve

$$h_2(E)=\tfrac{1}{2}\ln\{[(e+r)E-w]/[(e-r)E-w]\}\ . \tag{12b}$$

The $h_2(E)$ curve has a vertical asymptote for $E=E_2$, and for $E>E_2$, it decreases monotonically. For $E\to\infty$, $h_2(E)$ approaches

$$\lim_{E\to\infty} h_2(E)=\tfrac{1}{2}\ln[(e+r)/(e-r)]\ .$$

Furthermore for $E=E_2$ we have

$$h_1(E_2)=(d/L)r/(e-r)\ ,$$

which is a large number, for a relatively strong anchoring and thick sample.[11] Hence, as already pointed out, in this particular case $E_3\simeq E_2$. However, E_3 is always greater than E_2.

IV. DETERMINATION OF THE UPPER LIMIT OF THE MAXIMUM TILT ANGLE CONNECTED WITH THE FLEXOELECTRIC INSTABILITY

For $E>E_3$, θ_0 is different from zero. In this case Eqs. (1″) and (3″) give E and θ_0 versus the applied voltage V when the voltage is the electric parameter used in the thermodynamics description.[2,8] On the other hand, if D is the electric parameter used in the description,[2,8] Eq. (1″) gives the surface tilt angle θ_0 versus the electric displacement D, and Eq. (3″) gives the voltage across the sample. In any case the tilt angle distribution is always given by

$$\int_{\theta(z)}^{\theta_0} f(D,\theta_0;\theta)d\theta=z\ . \tag{13}$$

Let D be the independent electric parameter. In this case Fig. 1 shows θ_0 versus the reduced electric displacement $E=D/\epsilon_{\parallel}$, obtained by numerical integration of Eq. (6).

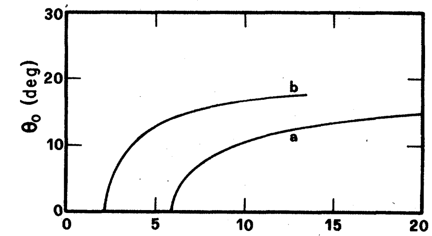

FIG. 1. Surface tilt angle θ_0 vs the reduced electric displacement $E=D/\epsilon_{\parallel}$. Curve a corresponds to $e=1.4\times10^{-3}$ dyn$^{1/2}$, whereas curve b to $e=2.8\times10^{-3}$ dyn$^{1/2}$. The other material parameters are reported in the text.

In the numerical calculation we have supposed that the nematic liquid crystal is 7CB and hence $K_{11}\simeq K_{33}\simeq 5\times10^{-7}$ dyn (Ref. 12) and $\epsilon_a=9.7$, $\epsilon_{\parallel}=15.7$,[13] with $d=10$ μm. The curve a corresponds to $w=5\times10^{-3}$ erg/cm^2, $e=1.4\times10^{-3}$ dyn$^{1/2}$, whereas the curve b corresponds to the same anchoring energy and $e=2.8\times10^{-3}$ dyn$^{1/2}$. This figure shows that $\theta_0(E)$ is a monotonically increasing function of E, which approaches a value $\theta_{0M}\neq\pi/2$ for $E\to\infty$. It is possible to show this by evaluating $d\theta_0/dE$, using Eqs. (6) and (5′) and taking into account the well-known theorems on the derivatives of functions defined by means of integrals. Here it is important only to evaluate the upper limit of $\theta_{0M}=\lim_{E\to\infty}\theta_0(E)$, which plays an essential role in the interpretation of recent measurements.[4] This limit is easy to obtain. In fact by imposing the condition of reality of $f(D,\theta_0;\theta)$ defined in (5), in the $D\to\infty$ limit [and hence $eD/\epsilon_{33}(\theta_0)\gg w$], we obtain

$$\frac{e^2}{\epsilon_{33}(\theta_{0M})}\frac{\sin^2\theta_{0M}\cos^2\theta_{0M}}{K(\theta_{0M})}>\frac{\epsilon_a(\sin^2\theta_{0M}-\sin^2\theta)}{4\pi\epsilon_{33}(\theta)}\ .$$

The function of θ on right-hand side is at its maximum for $\theta=0$. It follows that the previous inequality implies the following:

$$\frac{e^2\cos^2\theta_{0M}}{\epsilon_{33}(\theta_{0M})K(\theta_{0M})}>\frac{\epsilon_a}{4\pi\epsilon_{\parallel}}\ ,$$

giving the upper limit of the maximum surface tilt angle θ_{0M} for any set of material parameters. In particular if θ_{0M} is small the above-mentioned equation gives

$$\theta_{0M}<([1-(r/e)^2]/\{1+(\epsilon_a/\epsilon_{\parallel})[(e/r)^2-1]-k\})^{1/2}\ , \tag{13′}$$

obviously independent of the sample thickness d and anchoring energy w, since only the limit of large fields is considered. By assuming $e=1.4\times10^{-3}$ dyn$^{1/2}$, $K_{33}=5\times10^{-7}$ dyn (Ref. 12) and $\epsilon_a\simeq 9.7$ (Ref. 13) we obtain $\theta_{0M}<26°$, in agreement with the numerical calculation shown in Fig. 1, curve a.

With Eq. (13′) and the boundary condition (2) we can evaluate the order of magnitude of the surface gradient $\dot\theta_{0M}$ for large E. A simple calculation gives

$$\dot\theta_{0M}\simeq-(e/K_{33})E\theta_{0M}\ , \tag{13″}$$

i.e., it approaches $-\infty$ as $E\rightarrow\infty$. This fact implies that the birefringence of the sample, proportional to

$$\int_0^d \sin^2\theta(z)dz=\int_0^{\theta_0}(1/|\dot{\theta}|)\sin^2\theta\,d\theta\ ,$$

approaches zero as $E\rightarrow\infty$, or V is very large. This circumstance is due to the fact that ϵ_a is positive; hence for large E in the bulk $\theta(z)=0$, and the deformation is limited near the wall with weak anchoring. The layer where $\theta(z)$ is different from zero gets progressively thinner when E increases, giving zero birefringence in the considered limit.

V. THRESHOLD FIELD FOR SOME PARTICULAR SETS OF MATERIAL PARAMETERS

Let us consider now the threshold field for some particular cases.

(a) $\epsilon_a=0$. Equation (7) gives $E=v/L$, corresponding to a threshold voltage $V_2=v(d/L)$. Furthermore, Eq. (6) gives

$$E_3=v[(1/L)+(1/d)]\ ,$$

and hence[4]

$$V_3=v[1+(d/L)]\ . \tag{14}$$

V_3 is the threshold voltage for the examined instability.

(b) $\epsilon_a>0$, $w\rightarrow\infty$ (strong anchoring on both limiting walls). In this case Eq. (8) gives $E_2(w\rightarrow\infty)=\infty$. Consequently there is no flexoelectric instability.

(c) $\epsilon_a>0$, $w=0$: there is no interaction between the nematic and the solid substrate. The boundary condition (2) is now the trasversality condition; the surface torque coming from the volume must be zero on the surface. In this situation Eq. (9) gives $E_2=0$, since at $w=0$ corresponds $L=\infty$. Then Eq. (11) becomes

$$E_3=(K_{33}/2rd)\ln[(e+r)/(e-r)]\ , \tag{15}$$

and the threshold voltage is found to be

$$V_3=(K_{33}/2r)\ln[(e+r)/(e-r)]\ . \tag{16}$$

If $e\gg r$ Eq. (16) gives

$$V_3=v \tag{17}$$

coincident with the threshold voltage given in Refs. 1 and 2. However, we would point out that Eq. (17) holds only if $e\gg r$, whereas Eq. (16) is valid for generic e and r. At the threshold, the ratio between the coherence length ξ, defined as $\xi=(4\pi K_{33}/\epsilon_a)^{1/2}E=(K_{33}/r)E$, and the sample thickness d, is found to be $\xi/d=2/\ln[(e+r)/(e-r)]$. By using for K_{33} and ϵ_a the above-mentioned values, and assuming $e=1.4\times10^{-3}$ dyn$^{1/2}$ we obtain $\xi/d\simeq2$.

VI. ENERGY CONSIDERATIONS ON THE STABILITY OF THE DISTORTED CONFIGURATION

Up to now we have determined the threshold field by considering Eq. (1″) in the limit $\theta_0\rightarrow0$. In this way we have no information on the stability of the distorted configuration. In order to obtain such information, we analyze the total free energy expanded in the power series of θ_0. If D is the independent electric parameter in the thermodynamics description, the total free energy is given by[2,6–8]

$$F=\int_0^d[\tfrac{1}{2}K(\theta)\dot{\theta}^2+(1/8\pi)D^2/\epsilon_{33}(\theta)]dz$$
$$-(1/4\pi)D\psi(\theta_0)+\tfrac{1}{2}w\sin^2\theta_0\ . \tag{18}$$

Equation (18), by using Eq. (1), becomes

$$F=\int_{\theta_0}^0K(\theta)\dot{\theta}\,d\theta-\tfrac{1}{2}Bd-(1/4\pi)D\psi(\theta_0)$$
$$+\tfrac{1}{2}w\sin^2\theta_0\ . \tag{19}$$

By taking into account Eq. (2) the latter three terms in Eq. (19), in the limit $\theta_0\rightarrow0$, give

$$-(1/8\pi)\epsilon_{\|}E^2d-\tfrac{1}{2}\{(eE-w)+(d/K_{33})$$
$$\times[(eE-w)^2-r^2E^2]\}\theta_0^2+O(\theta_0^4)\ . \tag{20}$$

The first term is independent of θ_0; we can then neglect it in the following stability considerations.

From Eqs. (1) and (2), in the limit of small angles, we have

$$\int_{\theta_0}^0K(\theta)\dot{\theta}\,d\theta=\theta_0^2\int_0^1[(eE-w)^2-r^2E^2(1-y^2)]^{1/2}dy$$
$$+O(\theta_0^4)\ , \tag{21}$$

where $y=\theta/\theta_0$, as in the previous case. Since (21) must be real we still obtain the condition (9). If this condition is satisfied, after a trivial integration we obtain

$$\int_{\theta_0}^0K(\theta)\dot{\theta}\,d\theta=\frac{1}{2}\left[(eE-w)+\frac{(eE-w)^2-r^2E^2}{2rE}\right.$$
$$\left.\times\ln\left[\frac{(e+r)E-w}{(e-r)E-w}\right]\right]\theta_0^2+O(\theta_0^4). \tag{22}$$

By putting (22) and (20) in (19) the total free-energy expansion up to the second order in θ_0 is found to be

$$F=\frac{(eE-w)^2-r^2E^2}{2rE}\left[\frac{1}{2}\ln\left[\frac{(e+r)E-w}{(e-r)E-w}\right]\right.$$
$$\left.-\frac{d}{K_{33}}rE\right]\theta_0^2+O(\theta_0^4)\ . \tag{23}$$

Equation (23) shows that for $E>E_3$, given by Eq. (10), the coefficient of θ_0^2 is negative; hence the distorted configuration is energetically stable. It follows that the flexoelectric instability is actual.

VII. NEGATIVE DIELECTRIC ANISOTROPY

Let us consider the case $\epsilon_a<0$, and hence $r^2<0$, corresponding to a nematic liquid crystal dielectrically unstable. Now $\theta(z)$ is no longer a monotone function.

The function $g(E;y)$ for the present situation is

$$g(E,y)=K_{33}[(eE-w)^2+|r^2|E^2(1-y^2)]^{-1/2}\ , \tag{7'}$$

which is real for any E, since $y \in (0,1)$. By taking into account Eq. (7′), Eq. (6) in the $x_0 \to 0$ limit gives

$$|r^2|E^2/[(eE-w)^2+|r^2|E^2]=\sin^2(|r^2|^{1/2}Ed/K_{33}) , \quad (10')$$

which defines the threshold field.

Equation (10′) in the $w \to \infty$ limit gets Fredericksz's threshold field for usual dielectric instability, whereas for $e=0$ and w finite it becomes Rapini-Papoular's expression.[14]

VIII. INFLUENCE OF THE SURFACE POLARIZATION ON THE FLEXOELECTRIC INSTABILITY

In Sec. III we determined the threshold field in a general way and in Sec. VI the analysis of the stability of the distorted configuration was made by means of a Landau's expansion of the total free energy in terms of the surface tilt angle. As is well known it is possible to obtain the same results by linearizing the total free energy (18) in θ^2, and analyzing the Euler-Lagrange equation connected with this approximated form of F. Of course, this method does not give information on θ_0. Following this procedure we write (18) as

$$F=\int_0^d [\tfrac{1}{2}K_{33}\dot{\theta}^2+(1/8\pi)\epsilon_a E^2\theta^2+eE\theta\dot{\theta}]dz + \tfrac{1}{2}w\theta_0^2+O(\theta^4) . \quad (24)$$

The function $\theta(z)$ which minimizes (24) is a solution of the differential equation

$$\ddot{\theta}(z)-(\epsilon_a E^2/4\pi K_{33})\theta(z)=0 , \quad (25)$$

in the bulk, and on the boundaries $\theta(z)$ must satisfy the conditions

$$-K_{33}\dot{\theta}_0+(w-eE)\theta_0=0 \quad \text{at } z=0$$

and (26)

$$\theta_d=0 \quad \text{at } z=d .$$

The solution of (25) is of the kind $\theta(z)=a\cosh(qz)+b\sinh(qz)$, where $q=(\epsilon_a/4\pi K_{33})^{1/2}E$. Substituting the above form of $\theta(z)$ in the boundary conditions (26) we obtain that $\theta(z)$ is not identically zero (i.e., a and b do not vanish) only if the equation

$$[(eE-w)/K_{33}]\tanh(qd)=q \quad (27)$$

holds. Equation (27) defines the threshold field and is equivalent to Eq. (10). As pointed out, this linearized analysis cannot give information on θ_0. For this reason we analyzed the problem in a different way. But if we wish to study only the influence of some other effect on the threshold field for flexoelectric instability, the linearized analysis is sufficient. In the following we use this method to determine the influence of the surface polarization P_s on E_3.

As known[15,16] a surface polarization P_s can occur if the two ends of the nematic molecules have different chemical affinity with limiting surface. In this case the surface gives a preferential order to the nematic molecules since $\mathbf{n}$ and $-\mathbf{n}$ are not equivalent. The physical origin of this polarization is well examined in.[15,16] A surface polarization can exist even if the two ends of the nematic molecules have the same chemical affinity with the surface, but the surface imposes an order parameter different from the bulk.[9] This is due to the fact that the nematics are quadrupolar ferroelectric materials. The connected polarization is called order polarization. In the following we suppose that the surface order parameter is the same as the bulk one and hence the order polarization is identically zero. This hypothesis holds good probably very far from T_c.

As pointed out in Refs. 15 and 16 the surface polarization plays an essential role only if the nematic is in the homeotropic alignment. The functional form proposed for $|\mathbf{P}_s|$ (Refs. 15 and 16) is of the kind $|\mathbf{P}_s(\theta,z)|=p\delta(z)$, where $\delta(z)$ is Dirac's function and p a constant depending on the chemical affinity between the ends of the molecules and the surface. This model introduces a large discontinuity in $|\mathbf{P}_s|$ and some problems in the evaluation of the contribution of the self-energy to the total free energy. For this reason it is better, as in Ref. 4, to suppose that

$$\mathbf{P}_s(\theta,z)=p(z)\cos\theta(z)\mathbf{n} , \quad (28)$$

where $p(z)$ is different from 0 only near the limiting wall at $z=0$, on a range l of some molecular lengths. When $\mathbf{P}_s$ is present, the total polarization independent of the electric field is $\mathbf{P}=\mathbf{P}_f+\mathbf{P}_s$ where $\mathbf{P}_f$ is the flexoelectric polarization.[1] Taking into account (28) the total free energy up to the second order in θ is now

$$\int_0^d \{\tfrac{1}{2}K_{33}\dot{\theta}^2+e(E-4\pi p/\epsilon_{\parallel})\theta\dot{\theta} + [(1/8\pi)\epsilon_a E^2-pE[(\epsilon_a/\epsilon_{\parallel})-\tfrac{1}{2}] + (2\pi p^2/\epsilon_{\parallel})[(\epsilon_a/\epsilon_{\parallel})-1]\theta^2\}dz + \tfrac{1}{2}w\theta_0^2+O(\theta^4)+\text{const} . \quad (29)$$

Minimizing (29) we obtain the Euler-Lagrange equation

$$K_{33}\ddot{\theta}-\{(1/4\pi)\epsilon_a E^2-2pE[(\epsilon_a/\epsilon_{\parallel})-\tfrac{1}{2}] + 4\pi(p^2/\epsilon_{\parallel})[(\epsilon_a/\epsilon_{\parallel})-1]+4\pi e\dot{p}/\epsilon_{\parallel}\}\theta=0 \quad (30)$$

with the boundary conditions

$$-K_{33}\dot{\theta}_0+[w-e(E-4\pi p_0/\epsilon_{\parallel})]\theta_0=0 \quad \text{at } z=0 ,$$

and (31)

$$\theta_d=0 \quad \text{at } z=d ,$$

where $p_0=p(0)$. Let us consider now the order of magnitude of P_s. If $N=10^{21}\ \text{cm}^{-3}$ is the molecular density and $\mu=1$ debye is the electric molecular dipole, $P_{smx}=N\mu \simeq 10^3$ statcoulomb/cm^2. Of course, $P_s \ll P_{smx}$, since the polar order near the surface is far from complete. If $P_s \simeq 1-10$ statcoulomb/cm^2 (Ref. 17) and it drops to zero over a distance of the order $l \simeq 70$ Å (Ref. 15) for any z in the range $(0,l)$, Eq. (30) can be approximated as

$$\ddot{\theta}_1(z)-(4\pi e\dot{p}/K_{33}\epsilon_{\parallel})\theta_1(z)=0, \quad z\in(0,l) \tag{30'}$$

where $\dot{p}\simeq -p_0/l$, with the boundary condition

$$-K_{33}\dot{\theta}_1(0)+[w-e(E-4\pi p_0/\epsilon_{\parallel})]\theta_1(0)=0 \quad \text{at } z=0 \, . \tag{31'}$$

For any z in the range (l,d) we have $p(z)=\dot{p}(z)=0$ and Eq. (30) becomes

$$\ddot{\theta}_2(z)-(\epsilon_a E^2/4\pi K_{33})\theta_2(z)=0, \quad z\in(l,d) \tag{30''}$$

with the boundary condition

$$\theta_2(d)=0, \quad \text{at } z=d \, . \tag{31''}$$

Hence we can solve the problems (30'), (31') and (30''), (31'') separately, and impose the matching conditions. In Eq. (30) the coefficient of $\theta(z)$ is a continuous function. This implies that $\theta(z)$ and $\dot{\theta}(z)$ are continuous functions, i.e.,

$$\theta_1(l)=\theta_2(l) \quad \text{and} \quad \dot{\theta}_1(l)=\dot{\theta}_2(l) \, . \tag{32}$$

Let us suppose $p_0<0$. The solution of Eqs. (30') and (30'') with the boundary conditions (31'), (31''), and (32) gives the threshold field

$$q_2 d=\tfrac{1}{2}\ln\left[\frac{[(R/q_2)+1]-[(q_1/q_2)+(R/q_1)]\tanh(q_1 l)}{[(R/q_2)-1]-[(q_1/q_2)-(R/q_1)]\tanh(q_1 l)}\right], \tag{33}$$

where

$$q_1=(4\pi e\dot{p}/K_{33}\epsilon_{\parallel})^{1/2}, \quad q_2=(\epsilon_a/4\pi K_{33})^{1/2}E \tag{34}$$

and

$$R=[e(E-4\pi p_0/\epsilon_{\parallel})-w]/K_{33} \, . \tag{35}$$

We observe that for $p_0\to 0$, $q_1\to 0$ and Eq. (33) gives Eq. (27). Supposing $p_0\simeq 1-10$ statvolt/cm^2 and $l\simeq 10^{-6}$ cm the term $q_1 l$ is found to be of the order of $10^{-1}-3\times 10^{-2}$. Hence, $\tanh(q_1 l)\simeq q_1 l$. With this approximation Eq. (33) becomes

$$(\epsilon_a/4\pi K_{33})^{1/2}Ed =\tfrac{1}{2}\ln\{[(e+r^*)E-w^*]/[(e-r^*)E-w^*]\} \, , \tag{36}$$

where

$$r^*=r+(\epsilon_a/\epsilon_{\parallel})(p_0 l/r) \tag{37}$$

and

$$w^*=w+(8\pi e/\epsilon_{\parallel})p_0 \, . \tag{38}$$

In (36) we have neglected terms of the kind rl/L and $(rel/K_{33})E^2$ since near the threshold they are much smaller than the others. Equation (38) shows that if $p_0<0$, $w^*<w$, i.e., the effective anchoring energy is smaller than that in the absence of surface polarization. Furthermore from Eq. (37) $r^*<r$. The condition $e>r$ obtained from Eq. (9) now becomes $e+(\epsilon_a/\epsilon_{\parallel})(p_0 l/r)>r$. In our conditions the presence of the surface polarization is equivalent to a flexoelectric coefficient $e^*=e+(\epsilon_a/\epsilon_{\parallel})(|p_0|l/r)$ larger than e, as already pointed out phenomenologically in Refs. 3, 4, and 5. The correction on e introduced by P_s, with the above-mentioned values of p_0 and l is of the order of 10^{-4} dyn$^{1/2}$, in agreement with the estimation reported in Ref. 3. We would point out that this correction is of the same order as e.

From the above discussion it follows that the value of the threshold field, given by Eq. (36), is smaller than that obtained with $P_s=0$. A similar analysis is possible for $p_0>0$ and shows that $w^*>w$ and $r^*>r$, or $e^*<e$. In this case the threshold field is larger than that obtained with $P_s=0$.

In conclusion, contrary to the model of Refs. 3 and 4, the existence of surface polarization is not simply equivalent to a flexoelectric renormalization (here the change $r\to r^*$). There is also a change in the anchoring energy $(w\to w^*)$ from the coupling between flexo and surface polarization.

IX. CONCLUSIONS

In this paper the flexoelectric instability in nematic liquid crystal has been reconsidered. The threshold field has been calculated exactly. We obtain relations which contain as particular cases other relations found in literature and valid only for some particular sets of material parameters. Furthermore, the maximum tilt angle is evaluated. Its value depends, obviously on the flexoelectric coefficients, dielectric anisotropy, and splay elastic constant. For reasonable values of these parameters the maximum surface tilt angle is found to be relatively small for large ϵ_a. Hence the flexoelectric transition is optically a "ghost" transition, as experimentally observed.[4] In the last part of the paper we have considered the influence of the surface polarization, assumed position dependent, on the threshold field of the examined instability. Our analysis shows that the presence of this polarization introduces large variations on the flexoelectric coefficient, as already predicted, and on the surface energy, from the coupling between flexo and surface polarization. The obvious conclusion is that surface polarization can mask the flexoelectric effect and that the presence of the flexoelectric effect and surface polarization introduces some problems on the w determination.

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[11]If the sample thickness d is larger than Debye-screening length the nematic cannot be considered as an insulator. For the cyano-biphenil compounds the Debye length can be of the order of 10 μm, which represents the limit for large d. By supposing $w=10^{-2}$ erg/cm^2 and $K_{33}=5\times10^{-7}$ dyn the extrapolation lengths L is 0.5 μm. Furthermore, if $\epsilon_a=9.7$ and $e=1.4\times10^{-3}$ dyn$^{1/2}$ we have $r=6.2\times10^{-4}$ dyn$^{1/2}$ and consequently $E_2=12.8$ statvolt/cm, whereas the true threshold field is found to be $E_3=13.1$ statvolt/cm. Only for very weak anchoring energy and very thin samples is E_2 different from E_3.

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[17]The value $p_0 \simeq 1$ statvolt/cm^2 is reasonable. In fact the polarization coming from the polar order near the wall is $\mathbf{P}_s = mP_{smx}\cos\theta\,\mathbf{n}$, where $m=[n(+)-n(-)]/N$ is the polar-order parameter when $n(+)$ represents the nematic density of molecules with $\mathbf{n}$ parallel to the z axis and $n(-)$ the density of molecules with $\mathbf{n}$ antiparallel to the z axis. From symmetry considerations $\mathbf{P}_s$ is parallel to the nematic director, but the average surface polarization is parallel to the z axis. In order to obtain an order of magnitude of $p_0 = mP_{smx}$, let us consider the situation analyzed by R. N. Thurston, J. Cheng, R. B. Meyer, and G. D. Boyd, J. Appl. Phys. **56**, 263 (1984). In this paper the value $Q_s = 10^{-5}$ C/cm^2 of the adsorbed charge density of negative sign is estimated for a typical liquid crystal. Q_s gives origin to a localized surface electric field $E_s \simeq 20$ statvolt/cm parallel to the z axis. Let us suppose the surface polarization due only to the adsorbed charges. In this case the polar order m is given by Langevin's formula for bistable systems: $m=[U(+)-U(-)]/KT$, where $U(\pm) = \pm E_s\mu$ is the interaction energy between the nematic dipole and the surface electric field, and $1/KT$ Boltzman's factors. With abovementioned values for E_s and μ, $U(+) - U(-) \simeq 3\times10^{-5}$ eV, giving $m \simeq 10^{-3}$ and hence $p_0 \simeq 1$ statvolt/cm^2, as assumed. Of course, the polar order could come even by different effects, whose analysis is more complicated and requires detailed models.